Rui Pedro Fernandes Barbosa

Graduated in Environmental Engineering

Master on Bioenergy

Study on the valorization routes of ashes from thermoelectric power plants working under mono- and co-combustion regimes

Thesis submitted to obtain the Doctoral degree in Energy and Bioenergy

Supervisor: Nuno Lapa, Assistant Professor, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa

Co-Supervisor: Helena Lopes, Assistant Researcher, Laboratório Nacional de Energia e Geologia

Jury/Júri:

Chairman/ Presidente: Professor/Prof. Doutor António da Nóbrega de Sousa da Câmara

Examiners/ Arguentes:
Professor/Prof. Doutor João António Labrincha Batista
Professor/Prof. Doutora Margarida Maria João de Quina

Members/ Vogais:
Professor/Prof. Doutora Benilde Simões Mendes
Professor/Prof. Doutora Susete Martins Dias
Professor/Prof. Doutor Nuno Carlos Lapa dos Santos Nunes
Professor/Prof. Doutora Maria Helena Santos Duarte Lopes

FACULDADE DE
CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

September 2013

The author,

Rui Pedro Fernandes Barbosa

Direitos de cópia

O autor,

Rui Pedro Fernandes Barbosa

The Look of Love

ACKNOWLEDGMENTS

Along the development and preparation of the present thesis I had the support of several persons to which I would like to deeply acknowledge.

Firstly, I would like to refer my supervisor and friend, Professor Nuno Lapa. Along these years I have worked very closely with Professor Nuno Lapa. These fourteen years of professional relationship allowed to develop my knowledge in the fields of valorization of residues/materials and bioenergy. Thank you, Nuno.

To Dr. Helena Lopes, my co-supervisor, for the important comments and guidance along the thesis development.

To Professor Benilde Mendes and Professor Santos Oliveira for giving me the opportunity to study in the Doctoral Programme of Energy and Bioenergy and for making available the laboratory and experimental conditions for the development of the present thesis.

To Professor João Morais for the important technical discussions along this project and also for the anti-stress talks, during lunch, related with a common hobbie, cooking!

To Professor Ana Luisa, for the support in atomic absorption spectrometry methods.

To Mota-Engil and their technicians Augusto Camala, José Farinha, and Carlos Vieira, for the availability shown for performing the compressive strength tests to concrete formulations.

To all colleagues that gave support along these years, namely Diogo, André, Jorge, Annika, Maria, Susana, Cláudio, Emanuel, Liliana, Mário, Emanuel, and Inês.

To Rita Braga and Rosa Pinto for the availability to solve several laboratory issues.

To Lurdes Carvalho for the management of the administrative issues related with the PhD thesis.

To European Commisson for the funding of the European Project “COPOWER – Synergy effects of co-processing biomass with coal and non-toxic wastes for heat and power generation”, through the 6th Framework programme. This funding allowed developing the first part of the theses.

To Foundation for Science and Technology (Fundação para a Ciência e a Tecnologia) of the Ministry of Education and Science (Ministério da Educação e Ciência) of Portugal for having funded the PhD grant SFRH/BD/62372/2009.

AGRADECIMENTOS

Ao longo do desenvolvimento e preparação da presente tese tive o apoio de várias pessoas às quais gostaria de agradecer profundamente.

Em primeiro lugar, eu gostaria de referir o meu orientador científico e amigo, Professor Nuno Lapa. Ao longo destes anos, trabalhei muito proximamente com o Professor Nuno Lapa. Estes catorze anos de relação profissional permitiram desenvolver o meu conhecimento na area da valorização de materiais e bioenergia. Thank you, Nuno.

À Doutora Helena Lopes, minha co-orientadora científica, pelos importantes comentários e linha orientadora ao longo do desenvolvimento da tese.

À Professora Benilde Mendes e Professor Santos Oliveira por me terem proporcionado a oportunidade de frequentar o Programa Doutoral em Energia e Bioenergia e por me terem proporcionado as condições laboratoriais e experimentais necessárias ao desenvolvimento da tese.

Ao Professor João Morais pelas importantes discussões técnicas ao longo deste projecto e pelas conversas anti-stress, ao almoço, de um hobbie comum, a cozinha!

À Professor Ana Luisa, pelo apoio técnico associado ao equipamento de absorção atómica.

À Mota-Engil e seus técnicos Augusto Camala, José Farinha e Carlos Vieira, pela disponibilidade demonstrada para a elaboração dos ensaios de compressão às formulações de betão.

A todos os colegas, que deram apoio, das mais variadas formas, ao longo destes anos, nomeadamente o Diogo, André, Jorge, Annika, Maria, Susana, Cláudio, Emanuel, Liliana, Mário, Emanuel, e Inês.

À Rita Braga e Rosa Pinto pela disponibilidade em resolver um conjunto de questões e problemas típicos de laboratório.

À Lurdes Carvalho pela gestão das questões administrativas associadas à tese de Doutoramento.

À Comissão Europeia pelo financiamento do projecto Europeu “COPOWER – Synergy effects of co-processing biomass with coal and non-toxic wastes for heat and power generation”, através do 6º Programa-Quadro. Este financiamento permitiu desenvolver a primeira parte da tese.

À Fundação para a Ciência e Tecnologia do Minstério da Educação e Ciência de Portugal, pelo financiamento da bolsa de Doutoramento ref. SFRH/BD/62372/2009.

Abstract

The main objective of this thesis was to study new valorization routes of ashes produced in combustion and co-combustion processes. Three main valorization pathways were analyzed: (i) production of cement mortars, (ii) production of concretes, and (iii) use as chemical agents to remove contaminants from wastewaters.

Firstly, the ashes produced during the mono-combustion of coal, co-combustion of coal and meat and bone meal (MBM), and mono-combustion of MBM were characterized. The aim of this study was to understand the ashes properties in extreme levels of substitution of coal by a residue with a high contamination of specific metals. The substitution of coal by MBM produced ashes with higher content of heavy metals.

Secondly, the ashes coming from an industrial power plant working under mono-combustion (coal) and co-combustion conditions (coal+sewage sludge+MBM) were studied. The use of co-fuels did not promote significant changes in the chemical and ecotoxicological properties of ashes. Fly ashes were successfully stabilized/solidified in cement mortar, and bottom and circulating ashes were successfully used as raw materials in concrete.

The third step involved the characterization and valorization of biomass ashes resulting from the combustion of forestry residues. The highest concentrations of metals/metalloids were found in the lowest particle size fractions of ashes. Biomass ashes successfully substituted cement and natural aggregates in concretes, without compromising their mechanical, chemical, and ecotoxicological properties.

Finally, the biomass ashes were tested as chemical agents to remove contaminants from wastewaters. The removal of P, mainly phosphates, and Pb from wastewaters was assayed. Biomass ashes presented a high capacity to remove phosphates. As fly ashes were more efficient in removing phosphates, they were further used to remove Pb from wastewaters. Again, they presented a high efficiency in Pb removal.

New potential valorization routes for these ashes are now opened, contributing to improve their valorization rates.

Keywords: Ashes; Concrete; Ecotoxicology; Eluates; Valorization; Wastewater treatment.

Resumo

O objectivo principal desta tese foi o de se estudar novas vias de valorização de cinzas produzidas em processos de combustão/co-combustão. Foram analisadas três vias principais de valorização: (i) produção de argamassas de cimento, (ii) produção de betão, e (iii) uso como agentes de remoção de contaminantes de águas residuais.

Numa primeira fase, foram analisadas as cinzas produzidas durante a mono-combustão de carvão, co-combustão de carvão e farinha de carne e ossos (FCO) e mono-combustão de FCO. O objectivo deste ensaio consistia em avaliar as propriedades das cinzas produzidas em condições de substituição extremas por um resíduo contendo um elevado teor de metais específicos. A substituição de carvão por FCO produziu cinzas com um teor elevado de metais pesados.

Numa segunda fase, foram estudadas as cinzas produzidas numa central termoeléctrica a operar em condições de mono-combustão (carvão) e co-combustão (carvão + lamas residuais urbanas + FCO). O uso destes co-combustíveis não promoveu alterações significativas nas propriedades químicas e ecotoxicológicas das cinzas. As cinzas volantes foram estabilizadas/solidificadas, com sucesso, em argamassas de cimento e as cinzas de fundo e de recirculação foram incorporadas, com sucesso, em betões.

A terceira etapa envolveu a caracterização e valorização de cinzas de biomassa resultantes da combustão de resíduos florestais. As concentrações mais elevadas de metais/metalóides foram registadas nas fracções de cinzas com menores dimensões. Estas cinzas substituíram com sucesso cimento e agregados naturais em betão, sem comprometer as suas propriedades mecânicas, químicas e ecotoxicológicas.

Por último, avaliou-se a possibilidade de se usar as cinzas de biomassa como agentes de remoção de contaminantes de águas residuais. Foi avaliada a remoção de P, essencialmente fosfatos, e Pb. As cinzas de biomassa apresentaram uma elevada capacidade para remover fosfatos. Dado que as cinzas volantes foram mais eficientes a remover fosfatos, foram usadas posteriormente para remover Pb. Uma vez mais, apresentaram uma elevada eficiência de remoção de Pb dos meios líquidos.

Foram encontradas novas vias de valorização destas cinzas, contribuindo-se para aumentar a taxa de valorização destes subprodutos.

Palavras-chave: Cinzas; Betão; Ecotoxicologia; Eluatos; Valorização; Tratamento de águas residuais.

Contents

INDEX OF FIGURES

INDEX OF TABLES

LIST OF ABBREVIATIONS, ACRONYMS AND SYMBOLS

AAS – atomic absorption spectrometry

APHA/AWWA/WEF - American Public Health Association/American Water Works Association/Water Environment Federation

ar – as received

b - Langmuir's constant

BFBC - bubbling fluidized bed combustor

BMD - building materials decree

BOD_5 - biochemical oxygen demand, after 5 days of incubation

BSE - bovine spongiform encephalopaty

C_e – (from Langmuir's equation) equilibrium concentration of the chemical species adsorbed

C_e – (from Freundlich's equation) equilibrium concentration of the chemical species adsorbed

CEMWE - Criterion and Evaluation Methods for Waste Ecotoxicity

CHP - cogeneration of heat and power

CLT - column leaching test

COD - chemical oxygen demand

Copower – Acronym of a European project called "COPOWER – Synergy effects of co-processing biomass with coal and non-toxic wastes for heat and power generation"

db –dry basis

df - degrees of freedom

DOC - dissolved organic carbon

ds - dry solids

E_{64d} - emission after 64 days of leaching, in the diffusion leaching test (NEN 7345, 1995)

EC - European Commission

EC_{xx} - Effective Concentration that promotes effect on xx% of the population sudied

EDTA – diaminoethanetetraacetic acid

EEC – European Economic Community

EGR – code of fly ashes produced in Duisburg power plant

EU - European Union

f_{bev} - correction for the moistening conditions of exposure. This factor is 1 for conditions of permanent moistening conditions and is 0.1 for conditions of limited moistening conditions;

FBK – code circulating ashes produced in Duisburg power plant

FBR - fluidized bed reactor

FCO - rarinha de carne e ossos

f_{ext} - extrapolation factor from 64 days to 1 or 100 years. This factor is 2.4 for sulfates and chlorides and 15 for the remaining parameters

F_{iso} - correction factor for the isolation conditions. This factor is 1 without insulation conditions and is 0.1 with insulation conditions

f_{temp} - correction factor of the temperature, from the laboratory and environment

GHG - greenhouse gases

GNIP - Grupo Nacional para a Integração de Processos

I_c - calculated emission factors based on Dutch Building Materials Decree

ICREPQ'11 - International Conference on Renewable Energies and Power Quality of 2011

i-e - inhabitant equivalent

ILE - Industrial Liquid Effluents

I_{max} - maximum emission factors based on Dutch Building Materials Decree

IPPC - Integrated Pollution Prevention and Control

ISO – International Standardization Organization

IWWTP - industrial wastewater treatment plant

L/A –Liquid to Area (ratio)

L/V - liquid to volume (ratio)

LHV - Lower Heating Value

L/S - liquid to solid (ratio)

LNEG - Laboratório Nacional de Energia e Geologia

LNEG-UEZ - Laboratório Nacional de Energia e Geologia da Unidade de Emissões Zero

MBM - meat and bone meal

MSW - municipal solid waste

NEL - Normalized Ecotoxicity Levels

n - (from Freundlich's equation) empirical constant

p - Probability of F-critical to be higher or lower than F-ratio depending on the value of F-ratio to be higher or lower than 1, respectively

P - (from Freundlich's equation) empirical constant

PPWW - pulp and paper mill wastewater

PPWWTP - paper mill wastewater treatment plant

Q - (from Langmuir's equation) maximum amount of the chemical species adsorbed per unit mass of the adsorbent

QL - quantification limits

R^2 - determination coefficients

RDF - Refuse Derived Fuel

RT - relative toxicity

s/s - stabilized/solidified

SD – standard deviation

SS - sewage sludge

SWW - synthetic wastewater

TDS - total dissolved solids

TE - toxicity equivalent

TL - toxicity level

TSS - total suspended solids

TU - toxicity units; TU = 100%/EC_{XX}

UEZ - Unidade de Emissões Zero

UK - United Kingdom

USEPA- United States Environmental Protection Agency

WBK – code of bottom ashes produced in Duisburg power plant

ww – weight/weight

WWTP - wastewater treatment plants

Y_e - (from Langmuir's equation) mass of the chemical species adsorbed by unit mass of the adsorbent

Y_e – (from Freundlich's equation) mass of the chemical species adsorbed by unit mass of the adsorbent

1 Introduction

1.1 Thermal valorization of coal, SS, MBM, and forestry residues in power plants

During recent decades, developed and developing countries have been facing substantial challenges related to energy. One of these challenges is to find new cleaner and renewable sources of energy. The main goals of the Integrated Pollution Prevention and Control (IPPC) Directive (European Parliament and Council Directive 2008/1/EC) are the sustainable management of natural resources, the efficient use of energy, and the reduction of the CO_2 emissions. Despite some progress in the energy efficiency use, the overall consumption of energy is generally increasing. Associated with the increase of energy consumption is the increase in fossil CO_2 emissions. Therefore, two issues that need to be solved are the decrease of the high levels of energy demand and the decrease of fossil CO_2 emissions.

In what concerns the production of energy in thermoelectric power plants, coal has been widely used and still is the primary fuel. In some countries and power plants, coal was replaced by natural gas, which has fewer environmental negative effects (Mao et al., 2005; Venkatesh et al., 2012; McCubbina et al., 2013). Despite this fact, natural gas is a fossil fuel; therefore, its use also produces fossil CO_2 emissions. Thus, it is not a solution for coal replacement in a long-term perspective.

According to the Directive 2009/28/EC of the European Parliament and of the Council, each Member State shall ensure that the share of energy from renewable sources, in gross final consumption of energy in 2020, is at least its national overall target for the share of energy from renewable sources in that year, as defined in the Directive 2009/28/EC. Such mandatory national overall targets will allow the European Union (EU) to accomplish a target of at least a 20% share of energy from renewable sources in terms of the community’s gross final consumption of energy in 2020.

Finding and studying alternative fuels has become an imperative issue in the international agenda. What properties should the alternative fuels have? The best solution for power production must have several characteristics. It must be profitable, with low environmental impact and it must be sustainable. Fossil fuels are profitable, but are not sustainable and have significant environmental effects. The replacement of fossil fuels by renewable sources of energy allows the improvement of the environmental performance and sustainability of electricity and heat production (Pantoleontos et al., 2009; Morais et al., 2011). The environmental performance can be improved through, for example, the reduction of greenhouse gas (GHG) emissions attained by the reduction of the amount of coal extracted, transported and used in the thermoelectric power plant (Prochnow et al., 2009; Rourke et al., 2009; Morais et al., 2011).

Experience has shown that the geographic and/or seasonal availability of alternative fuels, such as biomass and bio-residues from seasonal activities, can be an obstacle for their extensive use for energy production (Richers et al., 2002). The use of non-hazardous wastes may be an alternative to biomass, if they are economically unattractive for recycling or if placing them in landfills proves to be too costly (Khan et al., 2009). The use of such wastes for energy production is promising if they do not promote negative effects on the combustion system, on the ash quality, or on the exhaust gas quality. Therefore, it is necessary to achieve satisfactory synergy between coal and alternative fuels, because their co-firing is a subject of great interest for the sustainability of energy production and reduction of GHG emissions (Lopes et al., 2003; Arias et al., 2008).

With respect to the properties and valorization routes of coal ashes, there are several works that focused on this subject. For example, Ahmaruzzaman (2010) has prepared a review paper regarding the routes of coal fly ashes valorization. According to this author, coal fly ashes can be used in cement and concrete products, as structural filler and cover material, in roadways and pavement construction, as an additive to construction materials as a light weight aggregate, as infiltration barriers, and underground void filling. The properties and valorization routes of coal ashes seem to be already well studied.

Nevertheless, the use other fuels in combustion processes will promote changes in the composition of ashes, as observed by Vassilev et al. (2013). Figure 1.1 shows the composition of coal and biomass ashes.

Based on Figure 1.1, it is possible to conclude that there are differences in the composition of coal and biomass ashes mainly in phases “Si–Al–Fe–Na–Ti” (mostly in glass, silicates and oxyhydroxides), “Ca–Mg–Mn” (commonly in carbonates, oxyhydroxides, glass, silicates and some phosphates and sulphates), and “K–P–S–Cl“ (normally in phosphates, sulfates, chlorides, glass and some silicates and carbonates). These differences may lead to different routes of valorization for these materials.

Based on this analysis, now and in the near future, a challenge in the management of ashes other than those produced by coal combustion is expected. These challenges are essentially associated with the quantity and quality of this type of ash.

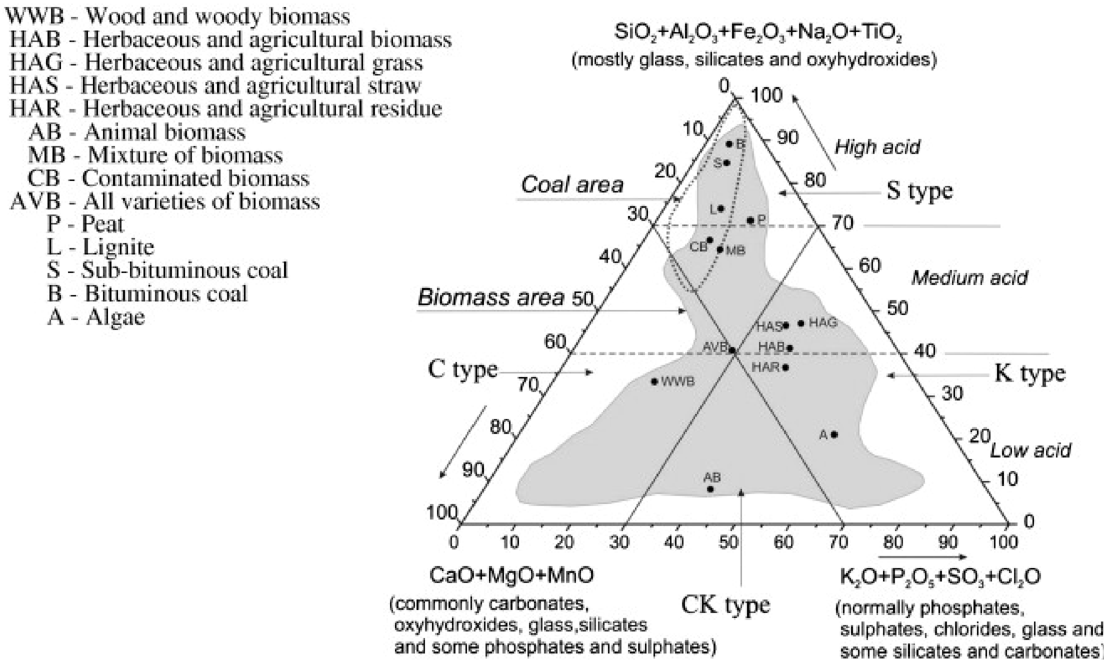


Figure 1.1- Composition of coal and biomass ashes (Vassilev et al., 2013)

Some types of non-fossil fuels have been tested in recent years in laboratory assays, in pilot-scale units, and in industrial power plants. The main non-fossil fuels that have been tested are sewage sludge (SS) from urban wastewater treatment plants, meat and bone meal (MBM), and forestry residues. Several studies were devoted to the possibility of using these non-fossil fuels in power plants and assessing the effects in combustors and in the exhaust gas properties (Heikkinen et al., 2008; Arias et al., 2008; Khan et al., 2009; Kookos et al., 2011).

Several studies have been performed related to the utilization of combustion residues. For example, in Sweden, solid biofuels are the major fraction of fuels used, while coal and fuel oil have much less utilization. In this country, 1.3 million tons of combustion residues were produced in 2006. Since 2002, the combustion plants implemented R&D programs aimed at demonstrating uses for combustion residues (ashes) and providing an improved understanding of combustion residues for the purpose of resolving regulatory questions. Several projects related to combustion residues were developed in Sweden, such as, for example, leaching tests for the evaluation of the environmental effects of combustion residues. The lack of experience with residues in real applications limits the prediction of the material behavior in real environments (Bjusrtröm et al., 2012).

In a recent paper, Modolo et al. (2013) have successfully used bottom ashes produced during the combustion of forest biomass residues, namely eucalyptus bark, in a Portuguese bubbling fluidized bed combustor. The bottom ashes have replaced conventional sand that is used as coarse aggregate in industrial rendering-mortars. The major problem identified by these authors was the level of leaching of chlorides, which was solved by a simple washing process.

According with Sarabèr and Haasnoot (2012), the application of ashes in The Netherlands is based on their physical properties, nutrient concentration, or free lime content. These authors have identified a negative aspect, which is the (high) price of biomass ashes when compared with the price of municipal solid waste incinerator ashes. The most important applications of biomass ashes in The Netherlands are asphalt filler and fertilizer. However, these authors defend that the use of ashes as asphalt filler may only be possible if sound and secured. The application of ashes as fertilizer in agriculture depends on the capacity of reducing the concentration of some critical trace elements and/or if the concentration of CaO will increase.

1.1.1 Sewage sludge

According to the European Commission (2013), the production of SS in Europe has increased from 5.5 million tons in 1992 to 9 million tons in 2005. This increase was related to the implementation of the Urban Wastewater Treatment Directive (Council of the European Communities Directive 91/271/EEC). Table 1.1 shows the absolute sewage sludge production per year, the specific sewage sludge production per inhabitant equivalent (i-e), and the specific sewage sludge production per inhabitant equivalent attended by wastewater treatment (i-ea) in the EU-27.

According to Table 1.1, the countries that contribute more to the production of SS in EU-27 are Germany, United Kingdom, Spain, France, and Italy. These five countries represent more than 50% of the SS production in EU-27. The high amounts of SS produced in wastewater treatment plants pose a problem related with management and final destination. In the past, SS was mainly disposed of in landfills. This strategy is no longer possible, since the European Landfill Directive limits the deposition of biodegradable material in landfills.

In the context of the “sludge directive” (Council of the European Communities Directive 86/278/EEC), the application of SS in agricultural land generally is considered in the EU as a good environmental option, due to the high content of N, P and K (fertilizer) and organic matter (conditioner). Through this directive, the EU encourages the deposition of SS in agriculture lands provided no negative effects on soil, fauna, water, and humans may occur.

Table 1.1 - Sewage sludge production and specific sewage sludge production for total population and population served by wastewater treatment plants in EU-27 countries (DS: dry solids; i-e: inhabitant equivalent; i-ea.: population equivalent attended by wastewater treatment) (Source: Kelessidis and Stasinakis (2012) citing data from http://epp.eurostat.ec.europa.eu)

Country	Year	Sewage sludge production (10^3 t DS/year)	Specific sewage sludge production (kg/(i-e.year)	Specific sewage sludge production (kg/(i-ea.year)
Germany	2005	2170	26.3	27.7
United Kingdom	2005	1771	29.5	32.0
Spain	2005	1121	26.0	28.6
France	2004	1059	17.0	21.3
Italy	2005	1053	18.1	19.2
Sweden	2005	210	23.3	27.1
Portugal	2007	189	18.0	26.1
Finland	2005	148	28.2	34.8

However, a number of factors are making land-spreading of SS increasingly difficult. For example, the transportation distances between wastewater treatment plants and suitable agricultural lands generally are increasing. As a consequence, there is an increasing cost associated with this management option (Donatello and Cheeseman, 2013). Aside from this negative economic aspect, there are other negative effects. In a review paper, Fonts et al. (2012) presented some negative aspects of SS use, which are associated with the content of heavy metals and some persistent organic contaminants. Presently, many countries are defining more restrictive limits on pollutants/contaminants present in SS than are defined in the "sludge directive." These more restrictive limits are because of public concerns about pathogen transfer to crops and the accumulation of heavy metals in agricultural soils. For example, in the United Kingdom (UK), a voluntary disposition known as the ‘‘safe sludge matrix’’ was introduced. This disposition only permits limited application of pre-treated SS (with very low risk of biological contamination) under specific conditions, namely secure harvesting intervals (Donatello and Cheeseman, 2013). According to Fonts et al. (2012), there is another problem with the deposition of SS in agricultural land. This deposition only occurs once or twice a year while the production of SS is more or less constant during the year. Therefore, it is necessary to store the SS for long periods of time, which represents a negative social influence.

Another possible route for the treatment and valorization of SS is the use as a fuel for energy production through combustion or co-combustion. This contributes for the chemical and biological stabilizations of SS and allows reducing the fossil fuels for power production (Davis 1995; ISWA, 1995; Werther and Ogada, 1999). According to Leckner et al. (2004), the high content of organic matter in SS is an excellent property, which allows its use in co-combustion processes for the production of energy. Nevertheless, the moisture content (about 30% w/w in mechanical dehydrated SS) can be a problem. Therefore, the co-combustion of SS with other fuels with less moisture content and high lower heating value (LHV) can be viewed as an adequate procedure to overcome the heat loss related with its high moisture content (Lin and Ma, 2012). In addition, SS can be converted into a refuse-derived fuel (RDF), which is easier to be handled, due to its homogeneity and low moisture content (Wzorek, 2012). Table 1.2 shows some of the treatment methods applied to SS in some European countries.

Table 1.2 - Sludge treatment methods applied in some EU countries (+: rare method; ++: common used; +++: most common used) (European Commission, 2006a; Kelessidis and Stanisakis, 2012, citing European Commission, 2001; Eco Logic and Institute for European Environmental Policy, 2009; Milieu Ltd., WRc and Risk & Policy Analysts Ltd (RPA), 2010; Spinosa, 2011)

Country	Stabilization				Conditioning				Others		
	Aerobic	Anaerobic	Lime	Composting	Lime	Other inorganics (NH$_3$, iron, salts)	Thermal	Thermal drying	Solar Drying	Pasteurization	Long term storage
Germany		++	++	+			++	+++			
United Kingdom	++	+++	++	++				++			++
Spain	++	+++	++	+				++			++
France	++	++	++	++	++			++	++		
Italy	++	+++	++	++	++	++	++	+		+	
Sweden	++	++	++	++		++	++	++			
Portugal	++	++						++			
Finland	++	+++	+	+++							

Regarding sludge stabilization, anaerobic and aerobic digestion seem to be the most common methods used in EU-27; anaerobic digestion is applied in 24 of 27 countries (89%), and aerobic digestion is used in 20 of 27 countries (74%) (Kelessidis and Stanisakis, 2012). Anaerobic digestion is currently used in Spain, UK, and Italy, while the technology of aerobic digestion is commonly used in UK, Spain, France, Italy, Sweden, Portugal, and Finland. Among EU-27, the thermal treatment of sewage sludge is only performed in Germany, Italy, and Sweden.

Table 1.3 shows the amount of SS for which the final treatment/valorization is incineration, in the same countries considered in the previous tables (Table 1.1 and Table 1.2).

Table 1.3 - Amount of SS for which the final treatment/valorization technique is incineration, in some EU countries (millions of kilograms; n.a.: not available) (http://epp.eurostat.ec.europa.eu/portal/page/portal/statistics)

Country	Year					
	2004	2005	2006	2007	2008	2009
Germany	1966	2170	2049	2056	2054	n.a.
United Kingdom	1721	1771	1792	1817	1815	1706
Spain	1092	1121	1065	1153	1156	1205
France	1059	n.a.	n.a.	n.a.	n.a.	n.a.
Italy	n.a.	1053	n.a.	n.a.	n.a.	n.a.
Sweden	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Portugal	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Finland	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

According to the information shown in Table 1.3, between 2004 and 2009, the amount of SS submitted to incineration has slightly increased in Germany, UK, and Spain. In the remaining countries, there is no information in this period or there is information related to a few years.

The increase of the amount of SS submitted to incineration increases the amount of ashes produced in this process. According to Cyr et al. (2007), the production of ashes ranges between 300 and 400 kg per ton of dried SS. As the incineration of SS is a well-established technology, it is foreseen as an increment in the production of ashes from the combustion of SS in the near future. Therefore, the countries that use this type of final treatment/valorization of SS will need to adopt an adequate management system for the increasing amounts of ashes produced.

The concentration of the major elements in SS depends on the sludge treatment processes, level of industrial activity in the catchment basin, and whether the sewerage system is combined (collecting together urban wastewaters and storm-waters) (Donatello and Cheeseman, 2013). If the wastewater treatment plants include tertiary systems, probably the precipitation salts used to remove P, which are usually $FeCl_3$ or $Al_2(SO_4)_3$, will increase the Fe or Al content in SS and consequently in ashes.

According to Cyr et al. (2007), the major constituents of ashes produced by SS combustion are Si, Al, Ca, Fe and P. Crystalline forms of these elements are quartz (SiO_2), whitlockite ($Ca_3(PO_4)_2$) and hematite (Fe_2O_3). Aluminum typically is present in feldspar and amorphous glassy phases (Mahieux et al., 2010). The content of the amorphous glassy phase may fluctuate considerably between SS ashes. These compounds are the major constituents of the raw material that produces cements; therefore, these properties are important when considering ashes as a potential pozzolanic additive in blended cements.

Minor elements present in ashes from SS are much more variable and are dependent on the degree and nature of industrial activity in the catchment basin of the wastewater treatment plant.

Metals such as Hg, Cd, Sb, As, and Pb are expected to be volatilized during combustion (Elled et al., 2007). Nevertheless, van de Velden et al. (2008) found that 20% of Hg, 93% of As and almost 100% of Cd and Pb were retained in the ashes produced during the combustion of SS. These findings support the theory that volatile trace metals condense on the surfaces of the ashes as temperatures fall during flue gas heat recovery.

Cyr et al. (2007) have assessed several studies related with the use of ashes from the combustion of SS in cement-based materials as cement or sand substitutes. The main conclusions regarding the properties and the changes in the production of cement-based materials were the reduction in the workability of fresh mortars and the increase in the setting time of cements. The majority of these studies have concluded that there is a decrease of the compressive strength values of mortars and concretes when ashes from SS are used as a cement or sand substitute.

1.1.2 Meat and bone meal

MBM is the common name for mammalian protein derived from the whole or part, excluding blood, of any dead mammal by the process of rendering. The production of MBM in Europe differs from country to country. This production depends on the dimension of the population of each country and on the eating habits regarding mammalian proteins. For example, in France, the production of MBM is higher than 850000 t/year (Chaala and Roy, 2003), while in Germany, there is an estimated production of 378000 t/year. In Switzerland, the production is close to 45000 t/year (Conesa et al., 2003). In Denmark, the production is 100000 t/year (Paisley and Hostrup-Pedersen, 2005), and in Spain the production is 400000 t/year. Globally, more than 3.5 million t per year of MBM are produced in the EU (Coutand et al., 2008).

Table 1.4 shows the amounts of mammalian raw material processed, and MBM and fat produced, in 2012, in Portugal. The definitions of the tissues/materials belonging to categories 1, 2, and 3 are extensive. Shorter definitions can be as follows: a) category 1 includes the tissues/materials with high probability of containing the disease Bovine Spongiform Encephalopathy (BSE) or that present a high risk of infectivity if contains the vector of the BSE disease; b) category 2 includes the tissues/materials with medium probability of containing the disease of BSE or that present a medium risk of infectivity if contains the vector of BSE disease; c) category 3 includes the tissues/materials with low or very low risk of containing the BSE prion or that have low probability of infectivity if they contain the vector of BSE disease.

Table 1.4 - Amount of mammalian raw material processed, MBM and fat produced, in 2012, in Portugal, as a function of the categories of risk of Bovine Spongiform Encephalopathy (BSE) defined in regulation number 1069/2009 of the European Parliament and Council (personal contact with the former Direcção de Serviços de Planeamento; n.e.: not extracted)

Category of the sub-products	Amount of raw material processed (t)	Amount of derived products	
		MBM (t)	Fat (t)
Category 1	75464	15985	3910
Category 2	7550	2245	n.e.
Category 3	85175	24970	23129

According to regulation number 142/2011 of the European Commission, the sub-products that fall in categories 1 and 2 must be submitted to an autoclaving process while the sub-products that fall in category 3 can be submitted to autoclaving or incineration. In Portugal, and according to the information of the former Direcção de Serviços de Planeamento, approximately 168 kt of mammalian raw material were processed in 2012, which led to approximately 43 kt of MBM. From this amount of MBM, approximately 25 kt could be incinerated, according to regulation number 142/2011 of the European Commission.

Incineration effectively is a possible treatment route for MBM (Heikkinen et al., 2008; Kookos et al., 2011). The relatively high LHV of MBM is a characteristic of this material, which makes it interesting for combustion (Kookos et al., 2011). Nevertheless, the use of MBM for energy is promising if it combines well with other fuels during the thermal conversion process for energy production and does not have negative effects on the combustion system, ashes quality, or exhaust gas emissions (Lopes et al., 2003; Tortosa Masiá et al., 2007).

The ashes produced during the co-combustion of coal with MBM should be studied carefully. There are some studies that have concluded that the substitution of coal by MBM can produce ashes with higher content of contaminants, such as heavy metals (Cyr and Ludmann, 2006; Skodras et al., 2007; Fryda et al., 2007; Senneca et al., 2008; Coutand et al., 2009; Coutand et al., 2011). The properties of the ashes are particularly important, since differences in these properties may require different management strategies for the ashes.

1.1.3 Forestry residues

To achieve higher levels of production of energy from renewable sources, Europe has been studying several types of biomass fuels and also new or adapted technologies for thermal conversion. Forestry residues are one of those sources to produce heat and electricity that have been applied on industrial and domestic scales.

Cogeneration of heat and power (CHP) has been developed intensively over the past few years and is used by wood-processing facilities (European Commission, 2006b; Obernberger and Thek, 2008). In power plants without cogeneration systems, the thermodynamic cycle promotes the rejection of a large percentage of heat to the atmosphere. In these power plants, the heat rejection occurs in condensers where up to 70% of the heat in steam is emitted to the atmosphere. In CHP processes, the heat is not wasted and is instead used in the vicinity of the power plant. The power capacity of a CHP process can range from a few kilowatts to several megawatts along with the simultaneous production of heat ranging from less than a hundred kW_{th} to several MW_{th} (Abbasi and Abbasi, 2010).

In northern Italy, many small power plants use wood chips or waste wood as fuel. The total amount of wood chips and waste wood consumed is approximately 300000 t/y. The amount of fly and bottom ashes is approximately 30000 t/y (Maschio et al., 2011).

In Portugal, there are dedicated forestry biomass power plants. According to Patrão (2010), in 2010 there were five facilities that consumed 810000 t/y of forestry residues. This value represents approximately 10% of the total forestry biomass available in Portugal (Centro da Biomassa para a Energia, 2007). Aside from the dedicated power plants, there are forestry biomass combustion facilities associated with the pulp and paper industrial sector. In these facilities, the forestry residues are also submitted to thermochemical conversion to steam through combustion.

In Portugal, the total production of paper and board has increased 7.1% between 2010 and 2011, mainly due to the increase of the production of paper for printing, writing, sanitary, and domestic uses. As a consequence, the production of solid residues from pulp and paper industries has increased during the decade from 2001-2011 (Figure 1.2).

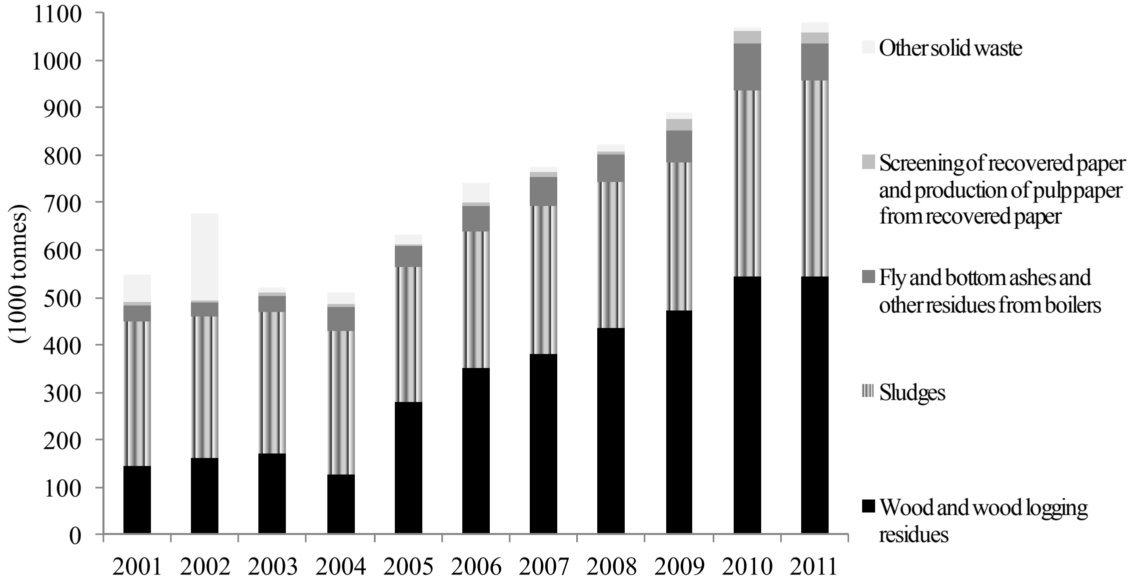


Figure 1.2 - Production of solid wastes in the Portuguese pulp and paper sector, in the period 2001-2011 (CELPA, 2012)

Figure 1.2 shows that from 2004 until now an increase in the production of solid wastes by the Portuguese pulp and paper sector was registered. This fact is related to the increase in the production rate of this industrial sector during the 2001-2011 decade. The production of ashes and other residues from boilers has also increased in this decade.

Figure 1.3 shows the final destination of solid wastes produced in the Portuguese pulp and paper sector, in the decade from 2001-2011.

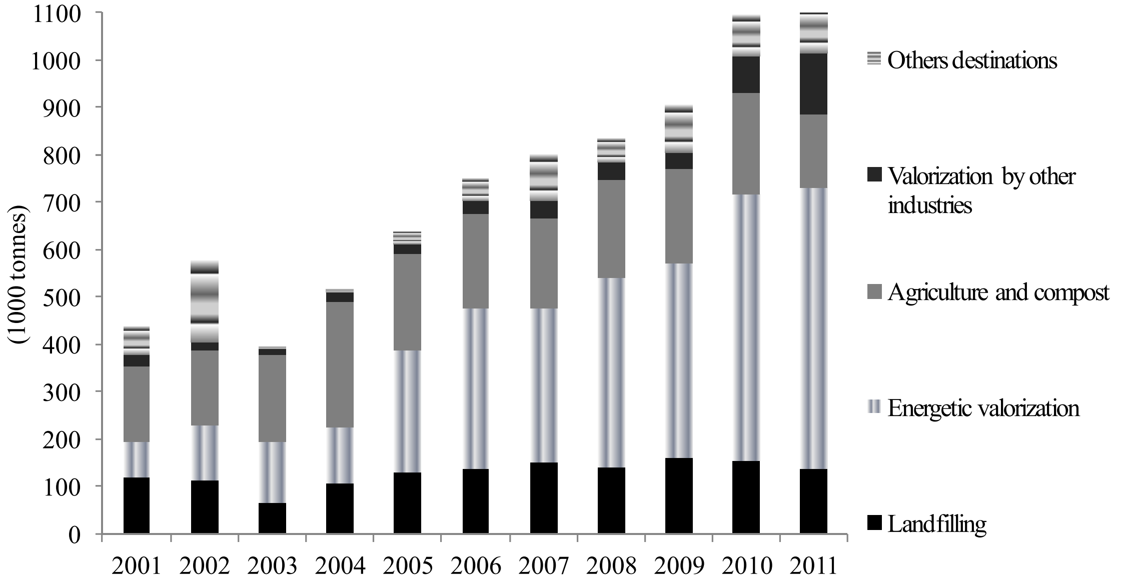


Figure 1.3 - Final destination of solid wastes produced in the Portuguese industries of the pulp and paper sector, in the period 2001-2011 (CELPA, 2012)

The option for energetic valorization of wastes and for the valorization by other industries has increased since 2004 (Figure 1.3). The landfill and agricultural use options have generally decreased due to legislation constraints. The increase of the energetic valorization route indicates that the pulp and paper industrial sector is increasing the combustion of forest residues. This is performed by co-generation for the production of electricity. As a consequence, the pulp and paper industrial sector has increased the production of forestry biomass ashes (Figure 1.2).

1.2 Management of ashes from combustion and co-combustion processes

Generally, the ashes produced in the thermal conversion of renewable fuels present different physical and chemical characteristics from those produced by coal. This is an important aspect for the management of ashes produced in the co-combustion processes (van der Sloot et al., 2001; Lapa et al., 2002; Lopes et al., 2005; Lapa et al., 2007; Papadimitriou et al., 2008). According to Cossu et al. (2012), the use of biomass ashes has a lack of practical experience. This may be the reason for the existence of limitations in technical and regulatory procedures, as well as in logistics for the use of biomass ashes. Thus, it is imperative to identify and develop valorization routes based on the intense study of the properties of biomass ashes (van Eijk et al., 2012).

With the increase of the combustion of alternative fuels, such as bio-wastes, some studies have focused on the properties of ashes resulting from their combustion (Lopes et al., 2003; Lopes et al., 2005; Cyr and Ludmann, 2006; Elled et al., 2007; Lapa et al., 2007; Coutand et al., 2008; Barbosa et al., 2009; Johnson et al., 2010). For example, some studies have revealed that the ashes produced during the co-combustion of coal with MBM should be analyzed carefully, since the substitution of coal by MBM can produce ashes with higher contaminant content, such as heavy metals (Cyr et al., 2006; Fryda et al., 2007; Skodras et al., 2007; Senneca et al., 2008; Coutand et al., 2009; Coutand et al., 2011). The properties of the ashes are particularly important, since differences in these properties may require different management strategies of the ashes produced.

As a consequence of the studies on the properties of ashes produced in the combustion and co-combustion of bio-wastes, some studies focused on the management routes of these ashes (Travar et al., 2009; Mandre et al., 2010; Kalembkiewicz and Chmielarz, 2012). Travar et al. (2009) have demonstrated that the ashes from RDF and composed mainly of paper, cardboard, plastic, wood, railway ties, wood chips, and municipal solid waste (MSW), showed a potential to be used in landfill cover constructions. Mandre et al. (2010) have concluded that the application of biofuel ashes (i.e., wood and peat ashes) had a significant effect on the nutrient composition of peat substrate and mineral nutrition of *Betula pendula* seedlings. They have also observed an enhanced radial and height growth, which suggests that fertilization of nutrient-poor peat soils with biofuel ashes is a possible solution for this type of material. Kalembkiewicz and Chmielarz (2012) have identified in a review paper that ashes from the co-combustion can be used in agriculture due to the pH, bulk density, contents of heavy and alkali metals, but also for the production of synthetic materials (zeolites) depending on the mineralogical composition and the content of aluminum and silicon. Other routes for the management of ashes, such as construction of roads, and the polymer industry, are also possible, but these authors state that the different characteristics of ashes that are produced by the combustion of different types of biomass should be considered.

1.2.1 Recycling of ashes as fertilizers in forest soils

Bjusrtröm et al. (2012) argued that the recycling of wood ashes to forest soils is the best management practice for this type of ashes. This is because sustainability in the use of solid wood biofuels requires that forestry is sustainable in terms of the nutrient return. The mineral nutrients removed in an intensive harvest must be returned to the forest soil, for example, in the form of ashes. The addition of ashes to soil is particularly important as intensive forestry promotes the acidification of forest soil and the addition of ashes restores its buffer capacity.

In Austria, the fertilization of forests and grassland with cyclone and grate ashes from wood combustion is allowed, but it is strictly controlled by the authorities. Filter ashes and sludge from flue gases condensation are sent to landfills. In Denmark, the ashes produced by the combustion of woodchips often are used as fertilizers in the forest area from which the wood was harvested. The ashes from straw-fired thermal power plants are essentially used as fertilizer in agriculture. In Germany, the use of biomass ashes as a fertilizer and soil conditioner in agriculture and forestry is dependent on the regulation for fertilizers. The ashes retained in the furnace (i.e., bottom ashes or grate ashes) and produced from the mono-combustion of non-treated biomass can be used for the production of fertilizers and soil conditioners. Nevertheless, the fly ashes cannot be used for such applications. The utilization of herbaceous biomass ashes as fertilizer, or for any other agricultural purpose, must respect the heavy metal concentration limits of the German Biowaste Ordinance (Spliethoff, 2010).

Despite all of these practices in using biomass ashes in forest soils, this option is not enough to guarantee the complete recycling of these by-products. Currently, the forest areas devoted to the ashes disposal are less than the forest areas from which the forest biomass was collected. Therefore, the mass of nutrients allocated per unit area of forest soils is very high, limiting the amount of biomass ashes that can be incorporated in these soils.

1.2.2 Use of ashes as raw materials for civil engineering materials

According to Bjusrtröm et al. (2012), the use of combustion residues in the construction sector may produce functionally equivalent materials, or even better, than those obtained from natural materials (e.g., natural aggregates, natural pozzolanic materials). However, waste materials are considered as handicapped when their use is considered for the production of civil engineering materials, as their properties differ from those of conventional natural materials.

Approximately 80% of the total amount of 1.3 million tons of ashes produced in Sweden, in 2006, were used as construction materials in the closure of landfills (i.e., as filling materials and for capping). However, this solution will not be available in the near future, as many current active landfills will be closed within the next few years. Therefore, this specific type of application is limited in the near future (Bjusrtröm et al., 2012).

Currently, new applications for woody biomass ashes are being developed. These new applications are for the civil engineering sector, through the production of cement clinker, bricks, and binding materials for soil stabilization and landscape management. The biomass ashes are being used as well as raw materials for the production of synthetic aggregates, fertilizers or liming agents (van Eijk et al., 2012). However, according to van Eijk et al. (2012), only a limited amount of biomass ashes are used and a large part is still disposed of in landfills in many countries.

The bottom ashes produced by the co-firing of coal and biomass (for up to 20% w/w of biomass) have been applied successfully in road construction and as concrete aggregates, replacing natural stone (van Eijk et al., 2012). Some studies have assessed the possibility of using fly ashes from coal-biomass co-firing processes for cement production. For example, a recent study (Tkaczewska et al., 2012) has evaluated the possibility of using fly ashes produced by the co-combustion of bituminous coal and wood biomass (willow shrubs) in the cement production of the type CEM II/A-V 42.5R. Fly ashes from the second and the third section in electrostatic precipitator systems were analyzed. These authors have evaluated the physical properties, the chemical composition, and pozzolanic activity of the ashes, heat of hydration, and compressive strength of fly ashes cements. Results showed that fly ashes from the second and the third section can be used to obtain cement type CEM II/A-V 42.5.

As was previously mentioned, there are still barriers related with the availability and quality of biomass ashes and ashes from blends of coal and biomass, when they are intended to be used in cement and concrete industries (Baxter, 2005; Pels et al., 2005; Wang and Baxter, 2007; Zheng et al., 2007; Umamaheswaran, 2008; van Loo and Koppejan, 2008; Rajamma et al., 2009; Wang et al., 2012). Some standards, such as EN 197-1 (2011) and EN 450-1 (2012), which are related to the use of ashes for cement preparation, or as concrete additives do not allow, or at least establish limitations for, the use of ashes other than coal ashes. For example, the standard EN 450-1 (2012) allows the use of fly ashes from co-combustion of coal and biomass in concrete manufacturing, but it introduces the requirement for a minimum content of coal in fuel mixture of 60% by mass (or 50% if wood residues recently produced are used as co-fuel), and a maximum content of ashes, produced according to the previous description, of 30%. According to EN 450-1 (2012), biological solid materials, urban sewage sludge, pulp and paper sewage sludge, petroleum coke, meat and bone meal, gaseous and liquid fuels with very low content of ashes can be used as co-fuels. These restrictions on the use of co-combustion ashes, such as those from herbaceous and forestry biomass, are related with the alkali and chloride contents, and occasionally sulfates and loss on ignition.

Several tests have been performed regarding the use of coal ashes (Aydın et al., 2007; Ha et al., 2007; Singhal et al., 2008) and ashes from blends of fuels (i.e., coal and forestry/herbaceous biomass) in concrete production and cement-based mortars (Wieck-Hansen et al., 2000; Baxter, 2005; Wang and Baxter, 2007; Zheng et al., 2007; Miller and Miller; 2007; Wang et al., 2008a; Rajamma et al., 2009; Ban and Ramli, 2011). The main conclusions were that the ashes resulting from blends of fuels do not promote significant changes in the bulk cement chemistry. The materials produced in such conditions have equal or even better performances than those produced with coal ashes. According to the recent studies of Melchers and Li (2009) and Pack et al. (2010), it is possible to use concrete containing biomass ashes for coastal protection and embankment reinforcement of inland water flow systems. Moreover, the use of concrete in the shore can reduce the eroding action of waves and also promote the development of high quality waves for surf practice.

1.2.3 Use of ashes as chemical agents to remove pollutants from wastewaters

1.2.3.1 Removal of heavy metals

The classical wastewater treatment processes for the removal of metals comprises their precipitation through the conversion of soluble metal salts into insoluble salts (Jankowski et al., 2006; Kumpiene et al., 2008). The precipitate formed can then be removed from the treated wastewater by sedimentation and/or filtration. Depending on the type of process used, the sludge produced can be submitted to metal recovery (Meunier et al., 2002; Drogui et al., 2005). The classical precipitation systems use ferric-chloride, ferric-sulfate, and aluminum sulfate as coagulation reagents. Nevertheless, due to the high costs of these chemical reagents, many efforts have been made to search for lower cost coagulation reagents.

There are several studies (Rao et al., 2002; Cho et al., 2005; Jankowski et al., 2006; Alinnor, 2007; Malakootian et al., 2008; Al-Zboon et al., 2011; Gonzalez et al., 2011a) related to wastewater treatment using different types of fly ashes. None of these studies was focused both on the removal of lead (Pb) from wastewaters produced in industries of lead-acid batteries and on the use of forestry biomass fly ashes as a coagulation agent. The majority of these works were focused on the use of coal fly ashes for the purpose of removing metals from synthetic aqueous solutions, but not real wastewaters.

Coal fly ashes have a high potential in the treatment of wastewater because of its chemical properties. Coal fly ashes have a high content of alumina, silica, ferric oxide, calcium oxide, magnesium oxide, and carbon, which may participate in the removal of several elements from wastewaters (Jankowski et al., 2006; Kumpiene et al., 2008). Aside from these aspects, the physical properties of coal fly ashes, such as porosity, particle size distribution, and surface area also show adequate values for the adsorption of metals from aqueous solutions. Coal fly ashes also have an alkaline nature, which is good when there is the need of neutralizing acidic wastewaters and precipitate metals under alkaline conditions (Bayat, 2002a; Bayat, 2002b).

Al Zboon et al. (2011) have produced a geopolymer from coal fly ashes and used it for the removal of Pb^{2+} from a synthetic solution. These authors have tested the effects of various parameters such as geopolymer dosage, initial concentration of Pb^{2+}, exposure time, pH, and temperature. Despite the good results that were obtained, the assays were not performed on real wastewater.

Alinnor (2007) has evaluated the removal characteristics of Pb^{2+} and Cu^{2+} from aqueous solution through coal fly ashes. Several conditions were tested, namely contact time, pH and temperature. The removal of these metals has generally increased with the increase of pH values. Concerning temperature, the highest removal rate of those metals was achieved at 40ºC. According to this author, the main mechanisms involved in the removal of Pb^{2+} and Cu^{2+} from solution were adsorption at the surface of the coal fly ashes and precipitation.

Malakootian et al. (2008) have evaluated the removal of heavy metals (Pb and Co) from an effluent produced by a paint industry. The effects dealing with pH and dosages of wood ashes were tested. The highest Pb removal efficiency was of 96.1% at pH 2 with a contact time of 3 h and 100 g wood ashes/L. The highest Co removal efficiency was of 99.0 % at pH 2 with a contact time of 3 h and 100 g wood ashes/L.

1.2.3.2 Removal of phosphorus (P)

The European Union (EU) established the concentrations of 1 mg P/L (more than 100000 i-e and 2 mg P/L (10000-100000 i-e) as the limit-values of Phosphorus (P) in the treated effluents of urban wastewater treatment plants (WWTP) (Directive 98/15/EC). A concentration of 1 mg P/L is high enough to cause eutrophication problems. Therefore, despite the actual limit-values, some European countries have decided to define even more restrictive concentrations (0.5 to 0.8 mg P/L) (Hussain et al., 2011).

In this context, several treatment processes to remove P from wastewaters have been studied (for example, Ugurlu and Salman 1998; Douglas et al., 2004; Parsons and Berry, 2004). In the field of chemical processes, Caravelli et al. (2010) have studied the removal of P by ferric chloride in the presence of activated sludge. Results showed that the presence of activated sludge did not affect the orthophosphate precipitation. However, addition of ferric chloride caused a drop of pH to values not compatible with the normal activity of activated sludges. The addition of $NaHCO_3$ made the removal of P more expensive.

Several works related with the high P-adsorption capability have been done (Douglas et al., 2004; Lu et al., 2009; Xiong et al., 2011). For example, Xiong et al. (2011) have studied the phosphate removal capability of freshwater mussel shells converted into powder. The authors have concluded that a thermal treatment of 700ºC, for 20 min, would be necessary to enhance the phosphate removal capability of the mussel shell powders from 25% to 55%, at a pH value of 5.5. Despite the interesting P-removal efficiencies, the thermal treatment would increase the cost of the final adsorption product.

Biomass ashes are very interesting inorganic materials, because they have high pH values and high concentrations of active Ca, Al, and Fe that can participate in P removal (Singh et al., 2011). Aside from this aspect, these ashes contain heavy metals in trace or undetectable concentrations, which will not compromise the chemical quality or the toxicity level of the treated effluent (Olanders and Steenari, 1995; Mellbo et al., 2007; Reimann et al., 2008; Ahmaruzzaman, 2010). In this context, the use of forestry biomass ashes to remove P from wastewaters becomes a very thought-provoking issue.

1.3 Main goals and novel aspects of the thesis

The main goal of the present PhD thesis was to find new valorization routes for the ashes produced in the co-combustion of coal and alternative fuels, namely MBM and SS, and the ashes from the combustion of forestry residues. Studies related to the production of mortars through stabilization/solidification, production of new formulations of concretes, and removal of pollutants from synthetic and industrial wastewaters through the use of ashes were the new routes assessed in this PhD thesis for the valorization of these by-products.

The main novel aspects of the present PhD thesis were the following:

- To study both chemical and ecotoxicological properties of ashes produced during the co-combustion of coal, SS, and MBM;
- To develop mortars and concretes with the ashes produced during the co-combustion of coal, SS, and MBM and to study their mechanical, chemical, and ecotoxicological properties;
- To study the chemical and ecotoxicological properties of size fractionated biomass (forestry) ashes;
- To develop concretes with biomass ashes and to study their mechanical, chemical and ecotoxicological properties after three different cure periods (i.e., 28, 60, and 90 days);
- To test the chemical and ecotoxicological properties of concretes produced with biomass ashes under marine water and freshwater conditions;
- To characterize the properties of biomass ashes as removal agents of pollutants from wastewaters, which is a very new issue in the reuse of this type of ashes.

1.4 Structure and content of the thesis

Aside from the present introductory chapter, this thesis is constituted by three main chapters and the list of bibliographic references. Chapter 2 was devoted to the study of ashes produced during the co-combustion of coal, MBM, and SS, while Chapter 3 was dedicated to the study of ashes produced in the combustion of biomass residues. Chapter 4 comprises the main conclusions of all the work performed in the present thesis and future work.

The structure, content, and work developed in this PhD thesis, are as follows:

Chapter 1 – Introduction. This chapter indicates the reasons for which the study of ashes coming from co-combustion processes is important and it why has become an issue of current interest among the scientific community. Some aspects dealing with the co-firing of coal and several non-fossil fuels, and the properties and valorization routes of ashes produced during co-combustion and mono-combustion processes are discussed.

Chapter 2 - Contribution for the study and valorization of the ashes produced by the co-combustion of coal and MBM and coal, SS and MBM.

This part of the PhD thesis was developed under the European project entitled Copower (Contract number SES6-CT-2004-503806). Chapter 2 presents the studies on the ashes produced in the pilot-scale combustor of Laboratório Nacional de Energia e Geologia (LNEG) and in Duisburg power plant (Duisburg, Germany).

First, the ashes produced during the co-combustion of coal and MBM in the pilot scale combustor of LNEG, in the former Unidade de Emissões Zero (UEZ), were characterized fully. The combustion tests performed in LNEG-UEZ essentially were devoted to the assessment of the properties of ashes produced in extreme conditions of substitution of coal by MBM.

Second, the work was focused on the assessment of the properties of ashes produced in the Duisburg power plant (Duisburg, Germany). Based on the characterization of ashes, a strategy for their management was established: the ashes containing a higher amount of metals were submitted to a stabilization/solidification process for the development of inert mortars; the ashes with lower concentrations of metals were used as substitutes of raw materials usually applied in concretes. Therefore, fly ashes were stabilized/solidified, while bottom and circulation ashes were used for the preparation of new formulations of concretes.

These studies contributed to the study of new management options of ashes produced by the co-combustion of coal and alternative fuels, namely SS and MBM.

Chapter 2 is divided into two sub-chapters:

Sub-Chapter 2.1. In this chapter, the characterization of ashes produced in the combustion of coal, co-combustion of coal and MBM, and combustion of MBM, in a pilot-scale fluidized bed reactor is presented. This sub-chapter is based on the following paper and oral communication:

Barbosa, R., Lapa, N., Lopes, H., Mendes, B., 2012. Chemical and ecotoxicological properties of ashes produced in the co-combustion of coal and meat and bone meal in a fluidized bed reactor. *Fuel Processing Technology* 96, 48–55.

Barbosa, R., Lapa, N., Lopes, H., Gulyurtlu, I., Mendes, B., 2011. Quality of Ashes Produced in the Co-Combustion of Coal and MBM in a Fluidized Bed Reactor. *International Conference on Renewable Energies and Power Quality (ICREPQ'11)*, Las Palmas de Gran Canaria, Spain, 13-15 April.

Sub-Chapter 2.2. In this chapter, the study on the stabilization/solidification and valorization of ashes produced in a large-scale power plant is presented. This sub-chapter is based on the following paper and oral communication:

Barbosa, R., Lapa, N., Lopes, H., Gulyurtlu, I., Mendes, B., 2011. Stabilization/solidification of fly ashes and concrete production from bottom and circulating ashes produced in a power plant working under mono and co-combustion conditions. *Waste Management* 31, 2009–2019.

Barbosa, R., Lapa, N., Lopes, H, Mendes, B., 2010. Study of the valorization of ashes produced in a thermoelectric power plant, working under co-combustion of coal and biomass, and in a pulp and paper industry. *International workshop on Energy Optimization in Industry and Reduction of CO_2 emissions*, Lisboa, Portugal, 3rd November.

Chapter 3 - Study on the valorization of ashes produced in the combustion of forestry residues in a pulp and paper industry.

The second part of this PhD thesis was dedicated to the reuse of biomass ashes produced in power plants that produce electricity by burning forestry residues. This part of the work was developed with biomass ashes produced in a fluidized-bed combustor of a pulp and paper industry.

The change in the type of ashes assessed was because of the following reasons: a) biomass ashes are produced in high amounts in Portugal, Europe and worldwide; b) the traditional valorization routes are not enough to solve the management problems dealing with these ashes; c) these ashes have low concentrations of heavy metals and low levels of ecotoxicity when compared with the ashes produced in mono-combustion of coal and co-combustion of coal and residues. As their use in forestry soils is becoming more restrictive and their production is increasing, new reuse routes are needed. Finding alternative uses for this by-product was the main goal of the second part of the thesis. Two new routes were investigated: incorporating forestry biomass ashes in concretes and using them as removal agents of pollutants from industrial wastewaters. This chapter is divided into the following four sub-chapters:

Sub-Chapter 3.1. In this sub-chapter, the chemical and ecotoxicological properties of size fractionated bottom and fly ashes produced in the combustion of forestry residues in a pulp and paper industry is presented. The main goal of this task was to identify size fractions, which could pose negative effects to the chemical and ecotoxicological properties of biomass ashes that were used in the subsequent tasks. This sub-chapter is based on the following paper and oral communication in a peer reviewed workshop:

Barbosa, R., Dias, D., Lapa, N., Lopes, H., Mendes, B., 2013. Chemical and ecotoxicological properties of size fractionated biomass ashes. *Fuel Processing Technology* 109, 124-132.

Barbosa, R., Lapa, N., Lopes, H, Mendes, B., 2010. Study of the valorization of ashes produced in a thermoelectric power plant, working under co-combustion of coal and biomass, and in a pulp and paper industry. *International workshop on Energy Optimization in Industry and Reduction of CO_2 emissions*, Lisboa, Portugal, 3rd November.

Sub-Chapter 3.2. In this sub-chapter, the study on the valorization of forestry ashes as raw material for the production of concrete is presented. Bottom and fly ashes were used as partial substitutes of cement and natural aggregates for the production of concretes. After 90 days of cure, some concrete formulations were selected. The selected concrete formulations were submitted to leaching tests that simulate marine and freshwater environments. This sub-chapter is based on the following paper and oral communication in a peer reviewed conference:

Barbosa, R., Lapa, N., Dias, D., Mendes, B., 2013. Concretes containing biomass ashes: mechanical, chemical and ecotoxic performances. *Construction and Building Materials* 48, 457-463.

Barbosa, R., Lapa, N., Dias, D., Mendes, B., 2012. Using Biomass Ashes in Concretes Exposed to Salted Water and Freshwater: Mechanical and Chemical Properties. *International Conference on Civil Engineering and Materials 2012—ICCEM12*, Paris, France, 7th-8th July.

Sub-Chapter 3.3. In this sub-chapter, a study on the valorization of forestry biomass ashes as a low-cost removal agent of P from industrial wastewaters is presented. Bottom and fly ashes were used as coagulation-flocculation agents for the removal of phosphorus from a synthetic wastewater and from an effluent produced in a pulp and paper mill. This sub-chapter is based on the following paper:

Barbosa, R., Lapa, N., Lopes, H., Morujo, A., Mendes, B., Removal of phosphorus from wastewaters by biomass ashes. Water Science and Technology (approved for publication).

Sub-Chapter 3.4. In this sub-chapter the study on the valorization of forestry biomass ashes as a low-cost removal agent of Pb from industrial wastewaters is presented. Bottom and fly ashes were used as coagulation-flocculation agents for the removal of lead (Pb^{2+}) from a synthetic wastewater, and from two industrial wastewaters of a plant producing lead-acid batteries. This sub-chapter is based on the following paper:

Barbosa, R., Lapa, N., Lopes, H., Günther, A., Dias, D., Mendes, B., 2013. Biomass fly ashes as low-cost chemical agents for Pb removal from synthetic and industrial wastewaters. Journal of Colloid and Interface Science (Submitted; Under review).

Chapter 4 – General conclusions and future work. An overview of the main conclusions from the work performed in the PhD are presented in this chapter.

2 Contribution for the study and valorization of the ashes produced by the co-combustion of coal and MBM and coal, SS and MBM

2.1 Chemical and ecotoxicological properties of ashes produced in the co-combustion of coal and meat and bone meal in a fluidized bed reactor

Based on the following paper and oral communication:
Rui Barbosa, Nuno Lapa, Helena Lopes, Benilde Mendes (2012), Chemical and ecotoxicological properties of ashes produced in the co-combustion of coal and meat and bone meal in a fluidized bed reactor. Fuel Processing Technology 96, 48–55
doi:10.1016/j.fuproc.2011.12.013
IF (2012): 2.819; 5-year IF: 3.493
Fuel Processing Technology is indexed on Scopus, SCImago and WoS

R. Barbosa, N. Lapa, H. Lopes, I. Gulyurtlu, B. Mendes (2011) Quality of ashes produced in the co-combustion of coal and MBM in a fluidized bed reactor. International Conference on Renewable Energies and Power Quality (ICREPQ'11), 13-15 April, Las Palmas de Gran Canaria, Spain

Abstract

The co-combustion of coal and MBM is a possible energetic valorization route for this residue. Nevertheless, the properties of ashes produced have to be studied. To evaluate these properties, three combustion tests were performed in a fluidized bed reactor: 1) coal combustion; 2) coal+MBM (85%+15%) co-combustion; 3) MBM combustion. The characterization of ashes was focused on the following aspects: (1) Determination of bulk content of Cr, Zn, Ni, Cu, Pb, Cd, Hg, As, Ba, Mo, Sb, Se, Ca, Na, Mg, Fe, Al and K; (2) Leaching properties of ashes based on the European Standard EN12457-2 (2002). The eluates were characterized for some of the metals referred above and for Cr VI, CN^-,pH, Cl^-, F^-, SO_4^{2-}, Dissolved Organic Carbon and Total Dissolved Solids. The eluates were also characterized for ecotoxicological levels by using the following bio-indicators: bacterium *V. fischeri*, microalgae *P. subcapitata* and microcrustacean *D. magna*. The ashes produced in the combustion of coal and co-combustion of coal+MBM have not shown evidences of ecotoxicity, while the ashes produced in the combustion of MBM were classified as ecotoxic. An assessment of the relationship between the chemical and the ecotoxicological properties of the ashes was performed. pH seemed to be the chemical parameter that most influences the ecotoxicological level of ashes.

Keywords: ashes; chemical properties; coal; combustion; ecotoxicological properties; meat and bone meal.

2.1.1 Introduction

The replacement of fossil fuels by renewable sources of energy can contribute to improve the environmental performance and sustainability of the electricity and vapor production (Pantoleontos et al., 2009; Morais et al., 2011). The experience has shown that the availability of alternative fuels can be an obstacle for its extensive use for energy production. The use of non-hazardous wastes may be an alternative to biomass, if they are economically unattractive for recycling or if they have a high cost for landfilling (Khan et al., 2009). Co-firing non-hazardous wastes with coal is, therefore, a subject of great interest for the sustainability of energy production and for the reduction of the emissions of fossil greenhouse gases (Arias et al., 2008).

One possible solution for MBM treatment is incineration (Heikkinen et al., 2008; Kookos et al., 2011). The relatively high LHV of MBM is a characteristic of this material which allows classifying it as interesting for combustion (Kookos et al., 2011). Nevertheless, the use of MBM for energy is promising if it combines well with other fuels during the conversion process for energy and does not have negative effect on the combustion system, ashes quality and gaseous emissions (Lopes et al., 2003; Tortosa Masiá et al., 2007).

The thermal valorization of organic residues with considerable quantities of mineral matter content may lead to the production of ashes with different properties. The ashes produced during the co-combustion of coal with MBM should be carefully studied, since the substitution of coal by MBM can produce ashes with high content of contaminants, such as heavy metals (Cyr et al., 2006; Fryda et al., 2007; Skodras et al., 2007; Senneca et al., 2008; Coutand et al., 2009; Coutand et al., 2011). The properties of the ashes are particularly important, since differences in these properties may require different management strategies of the ashes produced by the facility that performs the thermal valorization of MBM.

The main objectives of the work was to assess the chemical and ecotoxicological properties of the ashes produced during the combustion of coal with those produced during the co-combustion of coal and MBM and to classify these ashes according to their ecotoxicity. One additional goal is to assess the relationship between the chemical and the ecotoxicological properties of the ashes.

2.1.2 Materials and Methods

2.1.2.1 Fluidized bed reactor, fuels and combustion conditions

The combustion and co-combustion tests were performed, by UEZ team, in a pilot-scale bubbling fluidized bed reactor (FBR) of LNEG/UEZ (Figure 2.1). This equipment includes the reactor and the auxiliary systems: fuel feed-in system; air fans for primary and secondary air injection and for exhaustion of gases, two heat exchangers and two cyclones for fly ashes removal. The reactor has an internal square section with 0.3m×0.3m and of 5m height. The internal chamber is of refractory steel (AISI 310). The bottom of the reactor is settled over a wind box chamber with 0.3m×0.3m and with 0.2m height. The primary air is injected through the wind box and is distributed at the bottom of the reactor through an air distribution plate. The fuel feed-in pipe is located 500 mm above the air distribution plate. The secondary air is injected 1100 mm above the air distribution plate. The heat exchangers are located close to the bed of the reactor and at the top of the combustor chamber. The bottom ashes are collected through the wind box and the fly ashes are collected in the bottom of two sequential cyclones.

Figure 2.1 - Pilot-scale bubbling fluidized bed reactor where has occurred the combustion assays (LNEG/UEZ)

The average temperatures in the first and second cyclones were of 300 and 150 °C, respectively. The flue gases are exhausted through a fan located in the bottom of a vertical stack. Silica sand was used as the fluidization agent in the bed. Further details of this FBR are shown in Gulyurtlu and Monteiro (1991) and Gulyurtlu et al. (2005). Three combustion tests were performed: 1) combustion of coal; 2) co-combustion of coal (85%) and MBM (15%); 3) combustion of MBM.

Each combustion test produced three types of ashes: bottom ashes and two cyclone ashes (1st and 2nd cyclone ashes). The fossil fuel used was a bituminous coal from the open pit mine of El Cerrejón, in Colombia. MBM was produced in slaughter houses of Germany.

2.1.2.2 Bulk characterization of fuels and ashes

The biomass was submitted to the following characterization: C, H, and N (CEN/TS 15104, 2005), Cl, and S (CEN/TS 15289, 2006), moisture content (CEN/TS 14774, 2009), LHV (CEN/TS 14918, 2005), ashes (CEN/TS 14775, 2004), volatile matter (CEN/TS 15148, 2005), fixed carbon (calculated by difference). The coal was submitted to the following characterization: C, H, and N (ASTM D5373, 2008), S (ASTM D3177-02, 2007), Cl (ASTM D4208-02, 2007), moisture content (ASTM D3173, 2008), ashes (ASTM D3174, 2004), volatile matter (ASTM D3175, 2007).

The quantification of Cr, Zn, Ni, Cu, Pb, Cd, Ba, Mo, Sb, Se, As and Hg was performed over samples submitted to an acidic digestion according to the USEPA Method 3051A (2007) (HNO_3/HCl). The quantification of Mg, Al, Fe, Ca, Na and K was performed over samples submitted to an acidic digestion according to the European Standard EN 13656 (2002) (HF/HNO_3/HCl). The digestions were performed in microwave oven (Milestone Ethos 1600) using closed vessels and with controlled temperature (175±5ºC, 10 min). The quantification of metals was achieved through AAS (Thermo AAS, M series): As (air-acetylene flame; EN ISO 11969, 1996), Hg (AAS cold vapour; ISO 5666/1, 1983), Cd, Cu, Ni, Pb, Zn (AAS air acetylene flame; ISO 8288, 1986), Cr (AAS nitrous oxide-acetylene flame; ISO 9174, 2009), Cr VI (NF T90-043, 1988), Se (AAS air acetylene flame; ISO 9965, 1993), Sb, Mg, Fe (AAS, air-acetylene flame; APHA/AWWA/WEF, 2005), Na (AAS air acetylene flame - ISO 9964-1, 1993), K (AAS air acetylene - ISO 9964-2, 1993), Ca (AAS nitrous oxide flame - ISO 7980, 2010), Al, Ba, Mo (AAS nitrous oxide-acetylene flame; APHA/AWWA/WEF, 2005). Phosphorous content was determined through a UV/Vis by using the spectrophotometric method of ascorbic acid.

2.1.2.3 Leaching test, and chemical and ecotoxicological characterizations of eluates

The ashes were submitted to the leaching test described in the European Standard EN12457-2 (2002). The eluates were characterized for As (AAS air-acetylene flame; EN ISO 11969, 1996), Hg (AAS cold vapour; ISO 5666/1, 1983), Cd, Cu, Ni, Pb, Zn (AAS air acetylene flame; ISO 8288, 1986), Cr (AAS nitrous oxide-acetylene flame; ISO 9174, 2009), Cr VI (colorimetric method; NF T90-043, 1988), Se (AAS air-acetylene flame; ISO 9965, 1993), Mg, Sb (AAS air-acetylene flame, method 3111; APHA/AWWA/WEF, 2005), Ca (AAS nitrous oxide flame; ISO 7980, 2010), Na (AAS air-acetylene flame; ISO 9964-1, 1993), K (AAS air acetylene flame; ISO 9964-2, 1993), Mo, Ba (AAS nitrous oxide-acetylene flame, method 3111; APHA/AWWA/WEF, 2005), pH (electrometric, method 4500; APHA/AWWA/WEF, 2005), DOC (Dissolved Organic Carbon) (Combustion and detection by Infra-Red; ASTM D7573, 2009), free CN^- (colorimetric method; APHA/AWWA/WEF, 2005), SO_4^{2-} (Turbidimetric, method 4500 E; APHA/AWWA/WEF, 2005), F^- (SPADNS, method 4500 D; APHA/AWWA/WEF, 2005), TDS (gravimetric method; APHA/AWWA/WEF, 2005), Cl^- (Mohr's method; ISO 9297, 1989), phenol compounds (colorimetric method; ISO 6439, 1990).

The eluates were also characterized for the following ecotoxicological parameters: a) Luminescence inhibition of the bacteria *Vibrio fischeri* (performed in a miniaturized system of Microtox® according with ISO 11348-3, 2007); b) Mobility inhibition of the crustacean *Daphnia magna* (performed in a miniaturized kit of Microbiotests® according with ISO 6341, 1996); and c) growing inhibition of the algae *Pseudokirchneriella subcapitata* (performed in a miniaturized kit of Microbiotests® according with ISO 8692, 2004). The evaluation of the ecotoxic properties (property H14 of Council Directive 91/689/EEC, of the Council of the European Communities) of bottom and fly ashes was based on the Criterion and Evaluation Methods for Waste Ecotoxicity (CEMWE) (French Ministry of Environment). The original CEMWE methodology was adapted according to the discussion previously shown in Lapa et al. (2007).

2.1.2.4 Chemical Index

All materials were ranked according to a chemical index based on the chemical composition of eluates and the limit values defined in CEMWE. This chemical index was based on the following steps:

(a) Calculation of the toxicity equivalent (TE): The TE was calculated by the conversion of the CEMWE limit value, of each parameter, from mg/L to µmol/L. Then, it was calculated the ratio between the parameter with the highest toxicity, i.e., the parameter with the lowest limit value (expressed as µmol/L), and the limit value (expressed as µmol/L) of each chemical parameter.

(b) Calculation of the relative toxicity (RT): RT for each chemical parameter was obtained through the product of TE by the concentration determined in the eluates.

(c) Calculation of the toxicity level (TL): TL was calculated for each sample as the sum of all RT calculated for each chemical parameter. The unit of Toxicity Level is μmol/L.

In this work, since in the leaching assays most of the results are lower than the quantification limits (QL), two values of TL are shown for each sample. The lowest one, named as "Lowest Toxicity Level", was calculated assuming a concentration value of zero when the concentration was below the QL. The highest value of TL, named as "Highest Toxicity Level", was calculated assuming the value of QL, for each parameter, when the concentration was below the QL.

2.1.2.5 Ecotoxicological Index

In order to assess the Ecotoxicological Level of each sample, three Normalized Ecotoxicity Levels (NEL) were defined. These NEL were defined taking into account the following values: 1) average values of Toxicity Units (TU) obtained in *D. magna*, *V. fischeri* and *P. subcapitata* assays; 2) average values of the TU obtained in *D. magna* and *P. subcapitata* assays; 3) TU obtained in *V. fischeri* assay. The TU were calculated according to Eq. 2.1.

$$TU = \frac{Effective\ Concentration\,(\%)}{100\%} \qquad \text{Eq. 2.1}$$

To define NEL, three threshold limits were considered: a) the lowest TU that was determined; b) the limit value of the ecotoxicological parameter indicated in CEMWE; and c) the highest TU that was determined.

The conditions for the definition of the NEL were the following:

a) The NEL values range from 0 to 100;
b) NEL was scored as 0, for TU lower than the lowest TU that was determined;
c) For TU between the lowest TU that was determined and the CEMWE limit value, the NEL ranged between 0 and 50 and it was assumed a linear relation between TU and NEL;
d) For TU equal to CEMWE limit value it was attributed the score of 50;
e) For TU between the CEMWE limit and the highest TU that could be determined, the NEL ranged between 50 and 100, and it was assumed a linear relation between TU and NEL;
f) For TU higher than the highest TU that was determined, the score of 100 was attributed to NEL.

Figure 2.2 shows an example of conversion of TU to NEL, for *V. fischeri*.

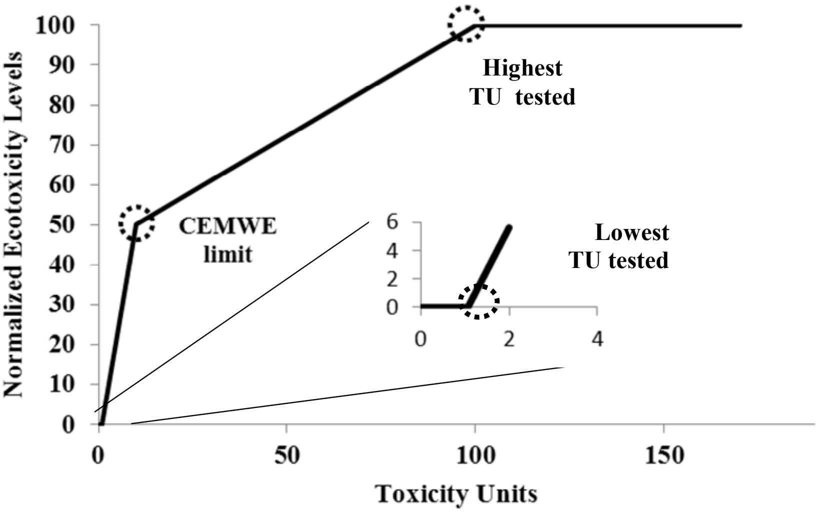


Figure 2.2 - Methodology for the definition of the NEL based on the TU obtained during the ecotoxicological characterization of the eluates

2.1.3 Results and discussion

2.1.3.1 Bulk characterization of fuels

Table 2.1 shows the proximate analysis of fuels used in the combustion and co-combustion tests. The coal used on the combustion tests was a bituminous coal. This type of coal presents a high LHV, which is in agreement with that found by Wagland et al. (2011), of 26.5 GJ/t. The LHV of MBM was similar to those observed by Senneca (2008) (14.47 GJ/t) and Gulyurtlu et al. (2005) (13.06 GJ/t), but lower than that found by Beck et al. (2004) (15.7 GJ/t), Conesa et al. (2005) (17 GJ/t) and Cummins et al. (2006) (18.19 GJ/t).

Table 2.1 - Proximate analysis of the fuels used in the combustion and co-combustion tests (LHV: Low Heating Value; ar: as received; db: dry basis)

Fuels	Water content (% wt ar)	LHV (GJ/t ar)	Ashes (% wt db)	Volatile Matter (% wt db)	Fixed Carbon (% wt db)
Bituminous coal	13.0	24.79	12.6	37.0	50.4
MBM	2.9	13.10	28.8	63.1	8.1

Table 2.2 shows the average bulk content and elemental composition of coal and MBM.

The concentration of Cr in coal was higher than those concentrations found by López-Antón et al. (2008) (19.9 mg/kg), Lopes et al. (2003) (12.2 mg/kg), Miller et al. (2004) (24.0 mg/kg) and Ward et al. (2011) (11.0 mg/kg). Miller et al. (2004) and Reddy et al. (2005) have found concentrations of Cr and Zn similar to those found in the present work. Nevertheless, these authors have found higher levels of As (1.83 mg/kg and 41.9 mg/kg), Cu (25.0 and 43.0 mg/kg), Pb (34.0 and 29.4 mg/kg) and Se (2.4 and 12.1 mg/kg). Lopes et al. (2003) and Ward et al. (2011) have found similar levels of As and Cu to those determined in this work. The concentrations of Mg, Al, Fe, Ca, K, Na and P found in coal were higher than those determined by Gulyurtlu et al. (2005). The differences in the composition of coal are probably associated with the differences in the geological conditions in the different places from where the coal samples were extracted.

Table 2.2 - Average bulk content and elemental composition of coal and MBM (± SD; n=2; n: number of replicates; SD: standard deviation; db: dry basis; n.a.: not applicable)

Parameter	Unit	Coal	MBM
C	% db (m/m)	66.4 (±5.0)	39.2 (±4.1)
H	% db (m/m)	4.7 (±0.4)	4.8 (±0.4)
N	% db (m/m)	1.4 (±0.1)	8.5 (±1.0)
S	% db (m/m)	0.96 (±0.01)	0.43 (±0.04)
Cl	% db (m/m)	0.07 (±0.001)	0.29 (±0.03)
Ca	% db (m/m)	0.23 (±0.02)	13.4 (±1.1)
K	% db (m/m)	0.24 (±0.02)	0.26 (±0.03)
Na	% db (m/m)	0.08 (±0.01)	0.63 (±0.07)
P	% db (m/m)	0.004 (±0.0003)	5.0 (±0.51)
Fe	% db (m/m)	0.64 (±0.04)	0.020 (±0.003)
Al	% db (m/m)	1.29 (±0.10)	0.080 (±0.001)
Mg	% db (m/m)	0.0040 (±0.0003)	5.0 (±0.5)
Ba	mg/kg db	<3.6 (n.a.)	452 (±36)
Sb	mg/kg db	<0.07 (n.a.)	0.13 (±0.01)
Mo	mg/kg db	<22.4 (n.a.)	117 (±16)
Se	mg/kg db	<0.21 (n.a.)	0.30 (±0.02)
As	mg/kg db	<0.73 (n.a.)	<0.65 (n.a.)
Hg	mg/kg db	<0.27 (n.a.)	<0.24 (n.a.)
Cd	mg/kg db	<7.3 (n.a.)	<6.5 (n.a.)
Pb	mg/kg db	<22.8 (n.a.)	<20.4 (n.a.)
Cu	mg/kg db	<9.4 (n.a.)	9.9 (±1.2)
Ni	mg/kg db	<14.4 (n.a.)	<14.0 (n.a.)
Zn	mg/kg db	36.8 (±4.9)	94.3 (±17.1)
Cr	mg/kg db	33.5 (±4.1)	<10.2 (n.a.)

Generally, MBM has shown the highest concentrations of the heavy metals. MBM has presented high levels of Ba and Mo, which can be explained by the fact that these elements are rapidly transported in blood plasma and accumulated in bones, through ingestion or airborne exposition (World Health Organization, 2003; World Health Organization, 2004). The concentrations of K, Fe, Mg and Na in MBM determined in the present work were similar to those found by Dybowska et al. (2009). MBM has presented, namely, the highest concentrations of Ca and P. This fact may explain the high levels of some metals in the ashes produced during the combustion test. The concentrations of As, Hg, Cd, Pb and Ni were below the QL.

2.1.3.2 Bulk characterization of ashes

Table 2.3 shows the bulk composition of ashes (bottom ashes; 1st cyclone ashes; 2nd cyclone ashes). Generally, the metal content was higher in fly ashes. The substitution of coal by MBM has promoted, globally, a higher concentration of metals in ashes. The concentrations of Cr, Ni and As were similar in bottom ashes. The 2nd cyclone ashes, especially those produced in the combustion of MBM, have presented the highest concentration of Cr, Zn, Ni, Cu and Pb, which can be attributed to the lower particle size of the ashes that usually present enrichment in heavy metals due to volatilization/condensation phenomena, especially in the presence of high levels of Cl (Lopes et al., 2009; van de Velden et al., 2008; Barbosa et al., 2009).

Ba and Mo were also found in high concentrations in the ashes from the combustion tests in which MBM was used as fuel. This behavior is probably associated with the high concentrations of these elements in MBM. The 1st and 2nd cyclone ashes, produced in the combustion of coal and co-combustion test, have retained As and Se in higher levels than those observed in the same type of ashes produced in the combustion of MBM, although the levels were insignificant in the fuels. The same behavior was observed for Cr and Cd. The relative high concentration of Cd in ashes may be explained by the following two reasons: 1) the enrichment factor in the ashes; and 2) the immobilization of Cd in ashes as $Ca_{10}{-}xCd_x(PO_4)_6(OH)_2$ or as $CdCO_3$ (otavite) as it was observed by Coutand et al. (2009). According to Dybowska et al. (2009), the apatite present in the ashes may remove Cd, Pb, Zn and Cu, through the chemical precipitation of these metals with phosphates as Pb hydroxylapatite, Zn phosphate (hopeite), Cd phosphate and Cu phosphate (libenthenite).

Table 2.3 - Bulk composition of bottom ashes, 1st cyclone ashes and 2nd cyclone ashes (mg/kg db ± SD, n=2; Coal: Combustion of coal; Coal+MBM: Co-combustion of coal and MBM; MBM: Combustion of MBM)

Parameter	Bottom ashes			1st cyclone ashes			2nd cyclone ashes		
	Coal	Coal+MBM	MBM	Coal	Coal+MBM	MBM	Coal	Coal+MBM	MBM
K	4016(±201)	8070(±225)	5705(±261)	14082(±1801)	14442(±1980)	9583(±1002)	14735(±1901)	17890(±1801)	27016(±3201)
Na	3129(±299)	7731(±701)	8121(±645)	6778(±701)	8585(±981)	15544(±1604)	6733(±701)	9300(±1202)	23236(±3001)
Ca	48056(±501)	18078(±223)	129617(±1301)	15880(±168)	51336(±6877)	238378(±29021)	9185(±1011)	16463(±1601)	210427(±22065)
Cr	172(±21)	162(±11)	133(±11)	313(±29)	308(±45)	572(±65)	59.0(±6.8)	292(±33)	4800(±505)
Zn	18.3(±2.1)	28.6(±2.8)	128(±11)	148(±19)	178(±19)	233(±29)	167(±19)	234(±38)	1495(±131)
Ni	69.6(±5.8)	30.3(±2.9)	43.5(±4.1)	298(±35)	173(±22)	202(±32)	156(±21)	158(±14)	3828(±3901)
Cu	<8.4	<10.4	<9.3	47.8(±4.1)	49.9(±6.1)	81.1(±12.9)	68.7(±8.2)	73.4(±7.9)	470(±49)
Pb	<17.4	<18.9	<17.6	<26.2	<22.5	81.1(±3.8)	44.7(±5.2)	35.6(±4.1)	470(±33)
Cd	19.5(±1.8)	22.5(±2.1)	<0.70	<9.1	<18.6	177(±21)	19.8(±1.9)	19.7(±2.2)	5.7(±0.5)
Ba	<10.4	133(±12)	3110(±401)	1238(±150)	1608(±225)	485(±55)	1086(±121)	1428(±131)	1782(±188)
Mo	<34.8	<37.7	<35.2	<37.8	73.3(±8.9)	140(±19)	90.3(±10.1)	102(±11)	508(±68)
Sb	<0.10	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11
Se	<0.70	<0.75	<0.70	32(±3)	1.9(±0.2)	<0.73	9.7(±1.2)	12.9(±1.2)	<0.73
Hg	<0.42	<0.45	<0.42	<0.45	<0.61	<0.44	<0.44	<0.75	0.9(±0.1)
As	1.4(±0.1)	0.89(±0.09)	<0.70	3.5(±0.9)	3.4(±0.3)	<0.73	6.0(±0.9)	6.2(±0.9)	4.8(±0.6)

2.1.3.3 Leaching behavior of ashes

2.1.3.3.1 Chemical characterization of the eluates

Table 2.4 shows the release of chemical species from the ashes under the leaching test conditions described in sub-chapter 2.1.2.3.

Table 2.4 - Chemical characterization of the eluates produced by bottom ashes, 1st cyclone ashes and 2nd cyclone ashes (pH: Sorensen ± SD; other species: mg/kg db ± SD)

Parameter	Bottom ashes			1st cyclone ashes			2nd cyclone ashes		
	Coal	Coal+MBM	MBM	Coal	Coal+MBM	MBM	Coal	Coal+MBM	MBM
pH	11.5 (±0.1)	9.7 (±0.1)	8.0 (±0.1)	10.5 (±0.1)	9.6 (±0.1)	7.4 (±0.1)	11.3 (±0.1)	10.8 (±0.1)	7.3 (±0.1)
SO_4^{-2}	1580 (±201)	2897 (±309)	1863 (±119)	18925 (±1900)	18734 (±2109)	1786 (±209)	13531 (±1208)	10320 (±998)	1338 (±189)
DOC	54.2 (±6.5)	77.4 (±8.0)	<0.99	4.2 (±0.5)	129 (±13)	12.8 (±1.3)	<1.0	98.9 (±9.1)	72.3 (±8.1)
TDS	4652 (±551)	4775 (±501)	11685 (±1099)	26401 (±2909)	31519 (±4211)	23056 (±2208)	23955 (±2588)	35098 (±4043)	120056 (±15206)
CN^-	<0.13	<0.13	<0.13	0.30 (±0.3)	0.47 (±0.05)	0.21 (±0.01)	<0.13	<0.13	0.25 (±0.3)
Cl^-	98.5 (±9.2)	<25.0	993 (±101)	179 (±19)	206 (±22)	1559 (±166)	103 (±11)	156 (±16)	302 (±33)
F^-	95.7 (±9.1)	1.5 (±0.2)	79 (±8)	135 (±14)	108 (±12)	52.3 (±5.8)	110 (±12)	95.4 (±8.2)	641 (±78)
K	52 (±4)	153 (±16)	2986 (±359)	650 (±75)	610 (±78)	3852 (±299)	341 (±38)	1033 (±99)	2430 (±258)
Na	127 (±19)	244 (±29)	2310 (±302)	781 (±79)	958 (±110)	3782 (±404)	658 (±78)	2302 (±189)	22739 (±2354)
Ca	757 (±88)	799 (±99)	113 (±12)	1939 (±202)	2880 (±301)	1610 (±198)	2953 (±301)	1234 (±120)	6621 (±689)
Cr	<0.49	<0.50	2.0 (±0.3)	<0.51	<0.51	4.6 (±0.5)	<0.51	<0.52	3.3 (±0.4)
CrVI	<0.49	<0.50	1.6 (±0.2)	<0.51	<0.51	1.8 (±0.2)	<0.51	<0.52	1.7 (±0.2)
Ni	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	17.2 (±1.9)
Ba	<1.6	6.0 (±0.6)	<1.6	4.5 (±0.6)	<1.6	6.5 (±0.7)	<1.6	2.7 (±0.3)	4.1 (±0.4)
Mo	6.9 (±0.7)	6.1 (±0.6)	<0.97	33.3 (±4.0)	18.2 (±1.9)	46.1 (±3.1)	71.3 (±9.9)	79.7 (±8.0)	35.5 (±4.9)
Se	0.19 (±0.02)	<0.009	0.50 (±0.05)	29.7 (±3.2)	0.10 (±0.01)	0.09 (±0.01)	0.82 (±0.7)	9.6 (±0.9)	0.28(±0.03)
Hg	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05 (±0.01)	<0.01	<0.01
As	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.12 (±0.01)	<0.03	0.17(±0.02)

The concentrations of Sb, Zn, Ni, Cu, Pb, Cd and phenolic compounds were below the QL values. pH values of the eluates produced by bottom ashes were between 8.0 and 11.5, which can be attributed to the high level of alkaline oxides in the bottom ashes. pH values of eluates produced by the 1st cyclone ashes were slightly lower (7.4 and 10.5) than those of bottom ashes. pH levels of eluates from the 2nd cyclone ashes were similar to those from the 1st cyclone ashes (7.3 to 11.3). The decrease of pH levels from the eluates of bottom to fly ashes are probably related to the presence of acidic condensates from the flue gases (Otsuka, 2008; Jiao et al., 2011).

The concentration of Cr VI was below the QL, except in the eluates produced by the ashes from the combustion of MBM. The concentrations of alkali (Na and K) and Cl^- were, generally, higher in the eluates produced by ashes of the co-combustion test and in the combustion of MBM, which can be due to the high concentration of this element in MBM (Gulyurtlu et al., 2007). The concentrations of F^- and SO_4^{2-} were higher in the ashes resulting from the combustion tests in which coal was used as fuel. Generally, Cl^-, F^-, SO_4^{2-} were found in higher concentration in fly ashes, which may be associated with the accumulation of soluble particles with high content of these species and to the presence of acidic condensates (Barbosa et al., 2009).

The combustion tests in which MBM was used as fuel have produced ashes with higher concentration of Total Dissolved Solids (TDS), specially the fly ashes retained in the 2nd cyclone. Relative high concentration of As was also found in the eluate of the 2nd cyclone ashes of the combustion of MBM. This behavior was also observed by McDonnell et al. (2010), and can be associated to the higher contents of soluble species in these particles (Barbosa et al., 2009).

Figure 2.3 shows the Lowest and Highest Toxicity Levels of eluates.

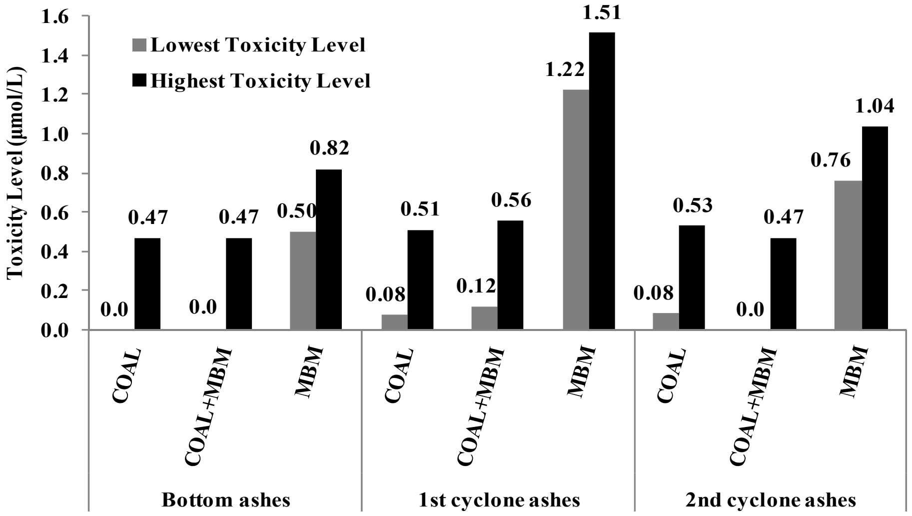


Figure 2.3 - Lowest and Highest Toxicity Levels based on the ecotoxicological characterization of the eluates and the limits defined in CEMWE

Ashes produced in the combustion of MBM have presented the highest TL. Among these ashes, the increasing order of toxicity is as follows: bottom ashes < 2nd cyclone ashes < 1st cyclone ashes. The TL values in the eluates of the ashes produced during the combustion of MBM are related with the leachability of Cr and Cr VI. The ashes produced during the combustion of coal and co-combustion of coal and MBM have presented similar TL values.

2.1.3.3.2 Ecotoxicological characterization of eluates

Table 2.5 shows the TU limits defined by CEMWE and those obtained in the eluates of ashes. The eluates have presented low ecotoxicological levels which were even below the limit values defined in CEMWE. Based on CEMWE, all ashes were classified as non-ecotoxic.

Table 2.5- TU limits defined in CEMWE and TU of the eluates of bottom ashes, 1st cyclone ashes and 2nd cyclone ashes

Parameter	CEMWE limit	Bottom ashes			1st cyclone ashes			2nd cyclone ashes		
		Coal	Coal + MBM	MBM	Coal	Coal + MBM	MBM	Coal	Coal + MBM	MBM
D. magna	10	1.95	<1.05	<1.05	<1.05	<1.05	1.57	<1.05	<1.05	3.39
V. fischeri	10	4.59	<1.01	2.58	<1.01	<1.01	2.35	<1.01	<1.01	<1.01
P. subcapitata	1000	4.63	1.91	<1.05	<1.05	<1.05	<1.05	28.6	1.31	2.53

The bottom ashes produced during the combustion of coal have presented higher ecotoxicity levels probably due to the high pH levels (Barbosa, 2005; Barbosa et al., 2009; Lopes et al., 1999) or the synergic effect of pH and solubility of heavy metals. The 2nd cyclone ashes have produced eluates with the highest ecotoxicological levels, especially those produced in the combustion of coal. The *P. subcapitata* was particular sensitive to the eluate produced by the 2nd cyclone ashes from the combustion of coal.

Figure 2.4 shows the NEL. Generally, the ashes produced during the combustion of MBM have presented NEL values higher than the other ashes, except for the bottom ashes produced in the combustion assays with coal.

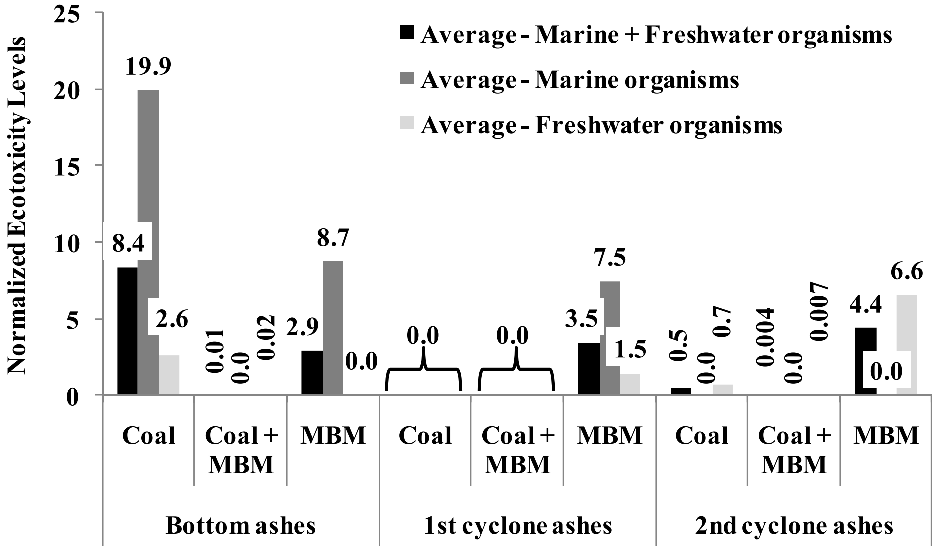


Figure 2.4 - NEL of the eluates of bottom ashes, 1st cyclone ashes and 2nd cyclone ashes

2.1.3.4 Assessment of factors that affect the biological response of the biological indicators

It is difficult to indicate a definitive explanation for the biological responses shown in Table 2.5, since the eluates of ashes are a very complex matrix. Nevertheless, it is proposed in this work a methodology to identify which parameters have significantly conditioned the biological responses of the biological indicators. An analysis of possible relationships between the chemical and ecotoxicological characterizations was performed. The assessment was developed through the application of dispersion graphs to a set of parameters. It was decided to consider the NEL values for the three bio-indicators tested as a whole (*D. magna, V. fischeri* and *P. subcapitata*), the NEL values for freshwater organisms (*D. magna* and *P. subcapitata*), and the NEL values of the marine organism (*V. fischeri*). These last two were considered as independent approaches from the former. The main reason for this methodology is related with the possibility of occurring different biological responses by those two groups of organisms. For example, the organisms belonging to a marine environment can be more resistant to higher concentrations of Cl^-, and SO_4^{2-} than those belonging to freshwater environment (Kang et al., 2011).

Figure 2.5 to Figure 2.7 show the relationship between the pH and the NEL values of the three bio-indicators, the NEL values based on the results of the marine bio-indicator and the NEL values based on the results of the freshwater bio-indicators, respectively. The results seem to indicate a relationship between the pH of the eluates and the biological responses: pH levels close to the interval 8 to 10 have promoted low NEL values, while pH levels above or below this interval have promoted an increase of this ecotoxicological parameter.

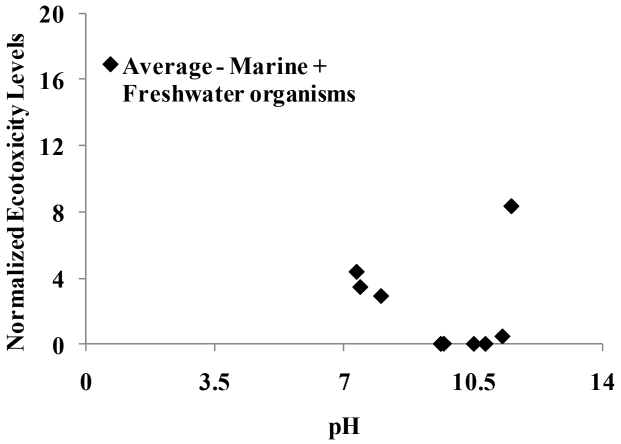


Figure 2.5 - Relationship between pH and NEL based on the average of the Ecotoxicity Levels of the three bio-indicators

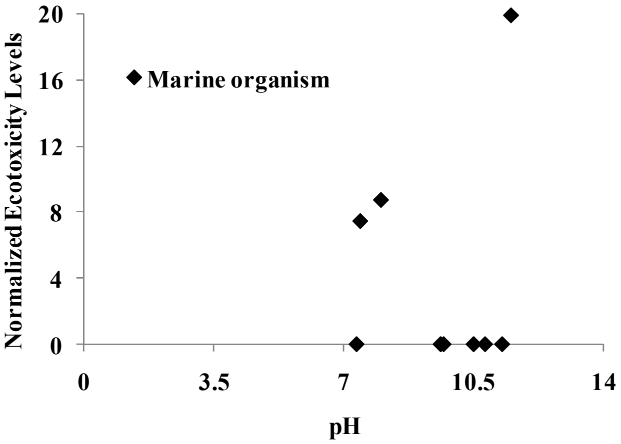


Figure 2.6 - Relationship between pH and NEL based on the Ecotoxicity Levels of the marine bio-indicator (*V. fischeri*)

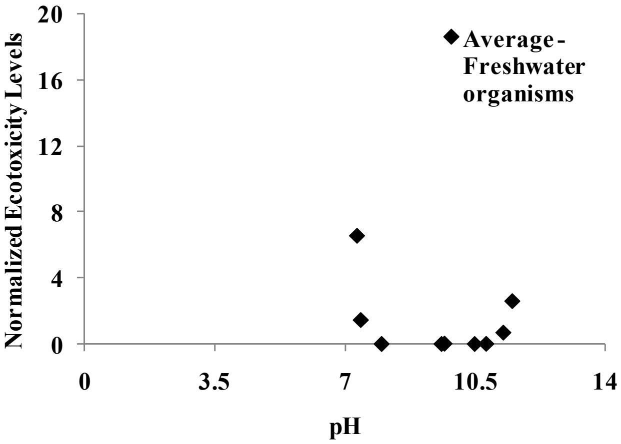


Figure 2.7 - Relationship between pH and NEL based on the average of the Ecotoxicity Levels of the freshwater bio-indicators (*D. magna* and *P. subcapitata*)

Figure 2.8 to Figure 2.10 show the relationship between Mo and the NEL values of the three bio-indicators, the NEL values based on the results of the marine bio-indicator and the NEL values based on the results of the freshwater bio-indicators, respectively. In what concerns the remaining chemical parameters, it was not observed any positive relationship between the NEL values and those parameters. Therefore, they will not be shown in this work. It is only interesting to stress that in what concerns the remaining parameters, the results have demonstrated generally that the relationship between them and the biological response was similar to that observed for Mo.

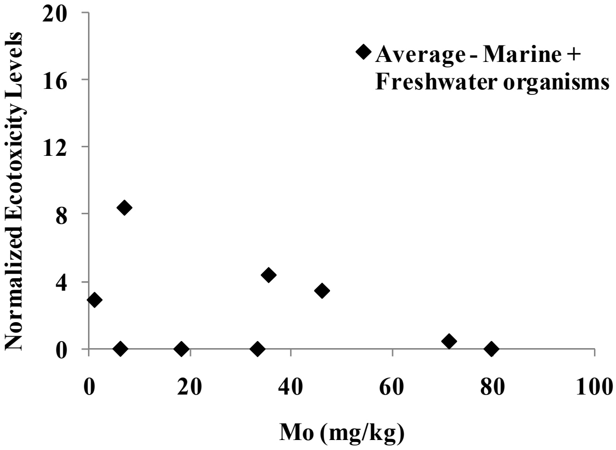


Figure 2.8 - Relationship between the concentration of Mo and NEL based on the average of the Ecotoxicity Levels of the three bio-indicators

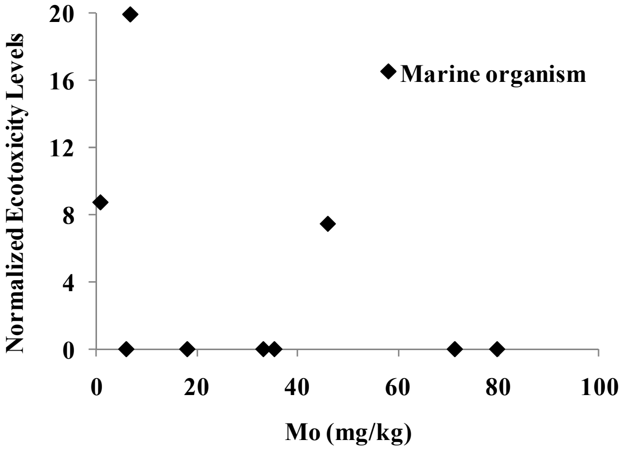


Figure 2.9 - Relationship between the concentration of Mo and NEL based on the Ecotoxicity Levels of the marine bio-indicator (*V. fischeri*)

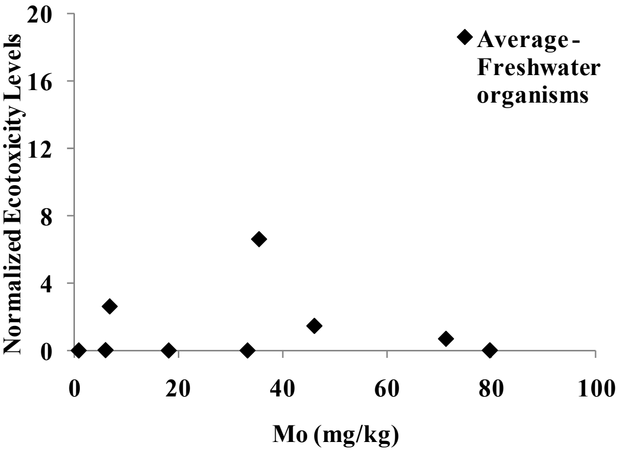


Figure 2.10 - Relationship between the concentration of Mo and NEL based on the average of the Ecotoxicity Levels of the freshwater bio-indicators (*D. magna* and *P. subcapitata*)

According to Komjarova and Blust (2009) and Deleebeeck et al. (2008), the concentrations of Ca, Na, Mg and pH can affect the kinetics of Cd, Cu, Ni, Pb and Zn uptake by *D. magna*. Those authors have concluded that increasing concentrations of Ca, Mg and Na, in an aqueous matrix submitted to ecotoxicological tests have had a protective effect over the organisms. According to the data shown in Table 2.4, the eluate of the fly ashes produced during the combustion of MBM has presented high levels of Ni, which could have promoted high levels of ecotoxicity. Since it was not observed high levels of ecotoxicity, it is possible that the high levels of Na and Ca in this eluate may have reduced the ecotoxic effects of Ni. Park et al. (2009) have indicated that Dissolved Organic Carbon (DOC) and hardness can affect the toxicity to *D. magna* due to, respectively, Cu II and Cr VI. Nevertheless, it is necessary further studies to evaluate the relationship between the chemical parameters and the NEL values, i.e., it is necessary to identify how the chemical parameters affect the biological responses in this type of matrix. This study would be important in order to reduce the ecotoxicity of the eluates produced by ashes.

Figure 2.11 to Figure 2.13 show the relationship between the Lowest Toxicity Levels and the NEL values of the three bio-indicators, the NEL values based on the results of the marine bio-indicator and the NEL values based on the results of the freshwater bio-indicators, respectively.

The results indicate that low values of the Lowest Toxicity Levels have promoted, generally, low NEL values. It was identified some exceptions but it was not identified the reason for this behavior, revealing the necessity of more studies in this area.

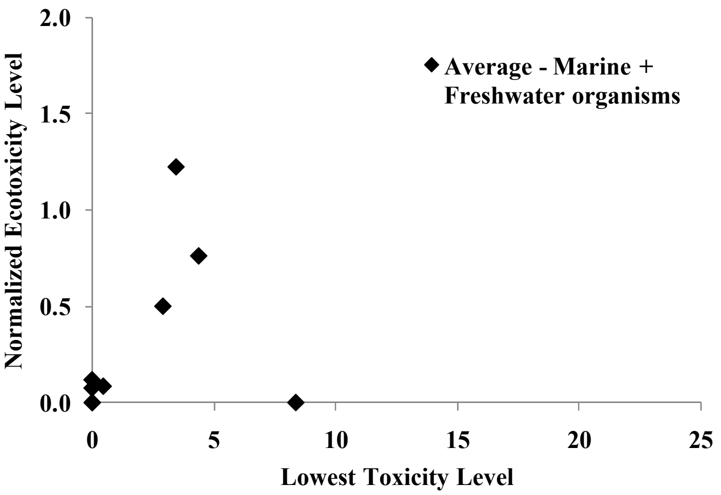


Figure 2.11 - Relationship between the Lowest Toxicity Level and NEL based on the average of the Ecotoxicity Levels of the three bio-indicators

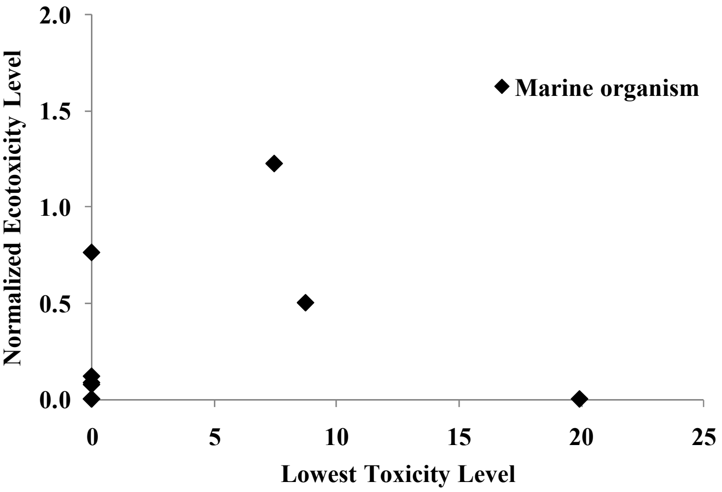


Figure 2.12 - Relationship between the Lowest Toxicity Level and NEL based on the Ecotoxicity Levels of the marine bio-indicator (*V. fischeri*)

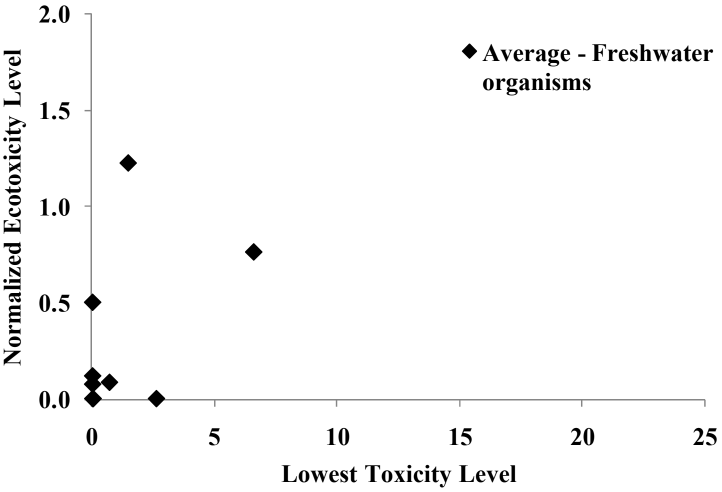


Figure 2.13 - Relationship between the Lowest Toxicity Level and NEL based on the average of the Ecotoxicity Levels of the freshwater bio-indicator

2.1.3.5 Classification of the ashes according to CEMWE and to the Council Decision 2003/33/EC

Based on CEMWE, the ashes produced during the combustion of coal and co-combustion of coal and MBM have not shown evidences of ecotoxicity. All ashes produced during the combustion of MBM were classified as ecotoxic, due to the chemical composition of the eluates.

Table 2.6 shows the classification of ashes according to the Council Decision 2003/33/EC. Fly ashes need to be stabilized prior to landfilling, except the 1st cyclone ashes produced during the co-combustion of coal and MBM. These can be landfilled in a landfill for hazardous waste. The bottom ashes were classified as non-hazardous residues.

Table 2.6 - Classification of the ashes according to the Council Decision 2003/33/EC (N-H: Non Hazardous; H: Hazardous; DnA: Deposition not Allowed)

Classification	Bottom ashes			1st cyclone ashes			2nd cyclone ashes		
	Coal	Coal + MBM	MBM	Coal	Coal + MBM	MBM	Coal	Coal + MBM	MBM
	N-H	N-H	N-H	DnA	H	DnA	DnA	DnA	DnA
Due to…	Mo, Se, F^-, SO_4^{2-}, TDS	Mo, SO_4^{2-}, TDS	Cr, Ni, Cl^-, F^-, SO_4^{2-}, TDS	Mo, Se	Mo, F^-	Mo	Mo	Mo, Se	Mo, Ni, F^-, TDS

2.1.4 Conclusions

Generally, the leaching rates of metals in the ashes were low. The substitution of coal by MBM produced ashes with higher content of heavy metals. It was not observed any pattern in the release of metals in the ashes. The release of chloride and alkali (Na and K) was higher in the eluates of ashes from the co-combustion of coal and MBM and combustion of MBM than in the eluates of ashes resulting from the coal combustion.

The biological responses of the organisms tested are, probably, associated with the pH of the eluates. Nevertheless, it is necessary to develop more studies in order to identify the factors that promote the high levels of ecotoxicity in some eluates.

According to CEMWE, the ashes produced during the combustion of coal and co-combustion test did not show evidences of ecotoxicity. All ashes produced during the combustion of MBM were classified as ecotoxic due to the chemical composition of the eluates.

According to the Council Decision 2003/33/EC, all fly ashes need stabilization prior to their landfilling, except the 1st cyclone ashes produced in the co-combustion test that were classified as a hazardous residue. The bottom ashes were classified as non-hazardous residues.

Despite the differences in the scope of CEMWE and Council Decision 2003/33/EC, it can be stated that its application to ashes has led to different conclusions about the classification of these materials.

2.2 Stabilization/solidification of fly ashes and concrete production from bottom and circulating ashes produced in a power plant working under mono and co-combustion conditions

Based on the following paper and oral communication:

Rui Barbosa, Nuno Lapa, Helena Lopes, Ibrahim Gulyurtlu, Benilde Mendes (2011), Stabilization/solidification of fly ashes and concrete production from bottom and circulating ashes produced in a power plant working under mono and co-combustion conditions. Waste Management 31, 2009–2019
doi:10.1016/j.wasman.2011.04.020
IF (2012): 2.485; 5-year IF: 2.926
Waste Management is indexed on Scopus, SCImago and WoS

R. Barbosa, N. Lapa, H. Lopes, B. Mendes (2010), Study of the valorization of ashes produced in a thermoelectric power plant, working under co-combustion of coal and biomass, and in a pulp and paper industry. Workshop "Energy Optimization in Industry and Reduction of CO2 Emissions”. Organized by the Executive Commitee of the International Agreement IETS (Comité Executivo do Acordo Internacional IETS), in the scope of the International Energy Agency (Agência Internacional de Energia) jointly with the Grupo Nacional para a Integração de Processos (GNIP), Lisboa, 3rd November.

Abstract

Two combustion tests were performed in a fluidized bed combustor of a thermo-electric power plant: 1) Combustion of coal; 2) Co-combustion of coal (68.7% w/w), SS (9.2% w/w) and MBM (22.1% w/w). Three samples of ashes (bottom, circulating and fly ashes) were collected in each combustion test. The ashes were submitted to the following assays: a) Evaluation of the leaching behaviour; b) Stabilization/solidification of fly ashes and evaluation of the leaching behaviour of the stabilized/solidified (s/s) materials; c) Production of concrete from bottom and circulating ashes. The eluates of all materials were submitted to chemical and ecotoxicological characterizations. The crude ashes have shown similar chemical and ecotoxicological properties among them. The s/s materials have presented compressive strengths between 25 and 40 MPa, low emission levels of metals through leaching and were classified as non-hazardous materials. The formulations of concrete have presented compressive strengths between 12 and 24 MPa. According to the Dutch Building Materials Decree (BMD), some concrete formulations can be used in both scenarios of limited moistening and without insulation, and with permanent moistening and with insulation.

Keywords: Ashes; Coal; Concrete; Co-combustion; Meat and bone meal; Sewage sludge

2.2.1 Introduction

The best solution for power production has to be profitable, environmentally sound and sustainable. The use of fossil fuels is profitable, but it is neither sustainable nor environmentally sound. The replacement of fossil fuels by renewable sources of primary energy can contribute to improve the environmental performance of electricity production and to move forward in a sustainable way.

The environmental performance is improved due, for example, to the reduction of the emission of Green House Gases (GHG) from the extraction sites of fossil fuels up to the power production at the thermoelectric power plant (Morais et al., 2008; Prochnow et al., 2009; Rourke et al., 2009). Nevertheless, field experience has shown that the availability of biomass can be a serious obstacle for its extensive use for energy production (Richers et al., 2002).

There is a possibility of rendering the use of biomass more viable by blending it with non-hazardous waste materials which are economically unattractive for recycling or which has a high land-filling cost (Khan et al., 2009). The use of such wastes for energy is promising, provided they do not promote negative effect on the combustion system, on the ashes quality and on the quality of gaseous emissions. It is therefore necessary to achieve a satisfactory synergy between coal, biomass and wastes, because their co-firing is a subject of great interest for the sustainability of energy production and reduction of the emissions of GHG (Lopes et al., 2003; Arias et al., 2008).

Under this framework, the European project named COPOWER was developed to assess the possibility to partially replace the coal used in a power plant of 243 MW_{th} by biomass and non-hazardous wastes for the production of electricity. The main aim was to evaluate in what extent the coal could be replaced by renewable sources (biomass and non-hazardous wastes) without the need for technical modifications of the electricity production process, without loss of profitability in the electricity production and without compromising the environmental performance of the power plant in terms of the quality of exhaustion gases and ashes produced.

In this work, the bottom, circulating and fly ashes produced during the combustion assays with coal and co-combustion assays with coal, sewage sludge and MBM were analyzed. A strategy for the stabilization/solidification of fly ashes and for the valorisation of bottom and circulating ashes as concrete was performed.

2.2.2 Materials and Methods

2.2.2.1 Description of the power plant and combustion and co-combustion assays

The power plant studied in this work is located in Duisburg (Germany) and has installed a fluidized-bed furnace with a thermal power of 243 MW_{th}. Its conversion efficiency of thermal energy into electricity is of 40% and uses bituminous coal as the main fuel. Two other renewable fuels were tested in this work: sewage sludge and MBM. Figure 2.14 shows the Duisburg power plant.

Figure 2.14 – Duisburg power plant

The coal came from a Colombian open-pit mine. The sewage sludge was produced in urban wastewater treatment plants located in the vicinity of the power plant, and was collected in primary and secondary treatment systems. The sewage sludge resulted from dehydration processes with iron salts. MBM came from different companies located all over Germany that converts the residues of slaughter houses into MBM. The following two combustion tests were performed in the Duisburg power plant: 1) Combustion of coal. This trial was defined as “1st"; 2) Co-combustion of coal, sewage sludge and MBM. This trial was defined as “2nd". The feeding rates of fuels are shown in Table 2.7. The coal substitution rate in the co-combustion test was defined in energy basis. During the combustions tests, limestone was added for sulphur capture.

Table 2.7 - Feeding rates of fuels in the combustion and co-combustion tests

Fuel	Feeding rate (t/h)	Variation coefficient (%)
Combustion test		
Bituminous Coal	33.5±3.3	5.9
Co-combustion test		
Bituminous Coal	29.40±1.69	5.7
Sewage sludge	3.93±1.25	31.8
MBM	9.46±2.23	23.6

2.2.2.1.1 Chemical characterization of fuels

The bulk content of different metals in fuels was determined according to the USEPA Method 3051A (2007) and EN 13656 (2002) (for Ca, Mg, Na, Al, K, Fe and P). The quantification was achieved through Atomic Absorption Spectrometry (Thermo AAS, M series) after an acidic digestion with HNO_3 (65% v/v) and HCl (37% v/v) (3:1) (USEPA Method 3051A, 2007), or HF, HNO_3 and HCl (EN 13656, 2002), in a microwave oven (Milestone Ethos 1600) using closed vessels. The digestion temperature was permanently controlled during the digestion process. P was determined through UV/Vis. The elemental composition of fuels was determined according to: a) CEN/TS 15104 (2005) (biofuels) and ASTM D5373 (2008) (coal) for C, H and N content; b) CEN/TS 15289 (2006) (biofuels) and ASTM D3177-02 (coal) for S; c) CEN/TS 15289 (2006) (biofuels) and ASTM D 4208-02 (coal) for Cl.

The proximate analysis of fuels is shown in Table 2.8. The moisture content was determined according to ASTM D3173 (2008), the LHV was determined according to ASTM D5865 (2010), the ashes content was determined according to ASTM D3174 (2004), the volatile matter content was determined according to ASTM D3175 (2007) and the fixed carbon content was determined according to ASTM D 3172 (2007).

Table 2.8 -Proximate analysis of the fuels used in the combustion and co-combustion tests (LHV: Low Heating Value; db: dry basis)

Fuels	Water content (% as received)	LHV (GJ/t as received)	Ashes (% db)	Volatile Matter (% db)	Fixed Carbon (% db)
Bituminous coal	13.0	24.79	12.6	37.0	50.4
Sewage sludge	74.6	14.20 (db)	44.9	49.6	5.3
MBM	2.9	13.10	28.8	63.1	8.1

2.2.2.1.2 Ashes analysed

Bottom ashes (WBK), circulating ashes (FBK) and fly ashes (EGR) produced in the combustion tests were collected and maintained in tight vessels with a small atmosphere (<5% of vessel volume), at a temperature of 4ºC, and in the absence of light. The WBK was collected in the bottom of the fluidised-bed furnace, the FBK was collected in the circulating line of ashes from the cyclones to the furnace, and the EGR was collected in the flue gas treatment system after the electrostatic precipitator.

2.2.2.1.3 Chemical and ecotoxicological characterization of ashes

The ashes were submitted to the assays described in Figure 2.15.

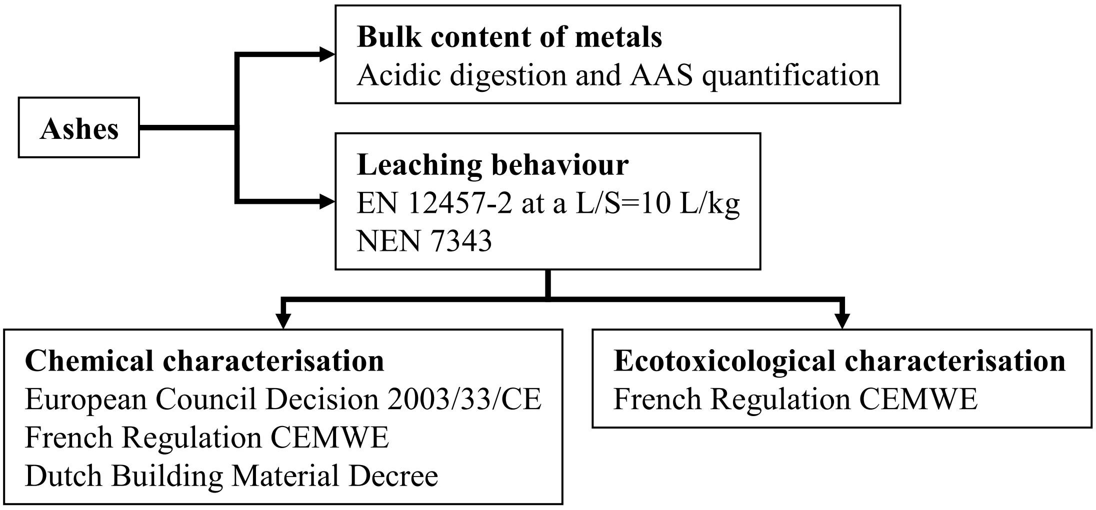


Figure 2.15 - Diagram on the assays to which all ashes were submitted

a) Quantification of the bulk content of metals – The methodology was the same as described before for chemical characterization of fuels in what concerns the USEPA Method 3051A (2007).
b) Leaching behaviour – All ashes were submitted to the leaching tests described in the standards number EN 12457-2 (2002) (completely mixed batch test) and NEN 7343 (1995) (column leaching test – CLT). The extraction cycles were performed under a controlled temperature of 20±2ºC.

The eluates produced in both leaching tests EN 12457-2 (2002) and NEN 7343 (1995) were characterised for chemical and ecotoxicological parameters (Figure 2.15). The chemical parameters analysed were the following: pH (electrometric, method 4500; APHA/AWWA/WEF, 2005), F^- (SPADNS, method 4500 D; APHA/AWWA/WEF, 2005), TDS (gravimetric method; APHA/AWWA/WEF, 2005), DOC (Combustion and detection by Infra-Red; ASTM D7573, 2009), SO_4^{2-} (Turbidimetric, method 4500 E; APHA/AWWA/WEF, 2005), free CN (colorimetric method; APHA/AWWA/WEF, 2005), phenol compounds (colorimetric method; ISO 6439, 1990), Cl^- (Mohr's method; ISO 9297, 1989), As (AAS air-acetylene flame; EN ISO 11969, 1996), Sb (AAS air-acetylene flame; APHA/AWWA/WEF, 2005), Ba, Mo (AAS nitrous-acetylene flame; APHA/AWWA/WEF, 2005), Cd, Cu, Ni, Pb, Zn (AAS air-acetylene flame; ISO 8288, 1986), Se (AAS air-acetylene flame; ISO 9965, 1993), Hg (AAS cold vapour; ISO 5666/1, 1983), Cr (AAS nitrous oxide-acetylene flame; ISO 9174, 2009) and Cr VI (colorimetric method; NF T90-043, 1988).

Figure 2.16 shows the filling procedure of columns with ashes (a) and three columns containing bottom, circulation and fly ashes (b).

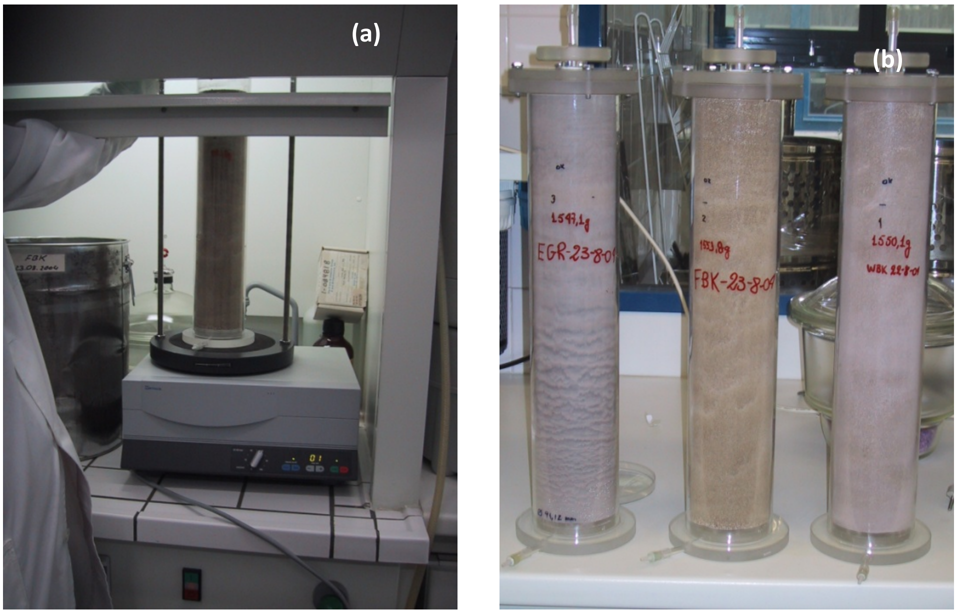


Figure 2.16 - Filling procedure of columns with ashes (a) and detail of three columns containing bottom, circulation and fly ashes (b)

The ecotoxicological characterization of eluates followed the principles defined in the modified version of CEMWE (igure 2.17) (French Ministry of Environment, 1998). This modified version of CEMWE was proposed by Lapa et al. (2002) and was used in different works for the ecotoxicological characterization of ashes. For example, Lapa et al. (2007) and Barbosa et al. (2009) have used it for the characterization of ashes produced in the co-combustion of coal and SS.

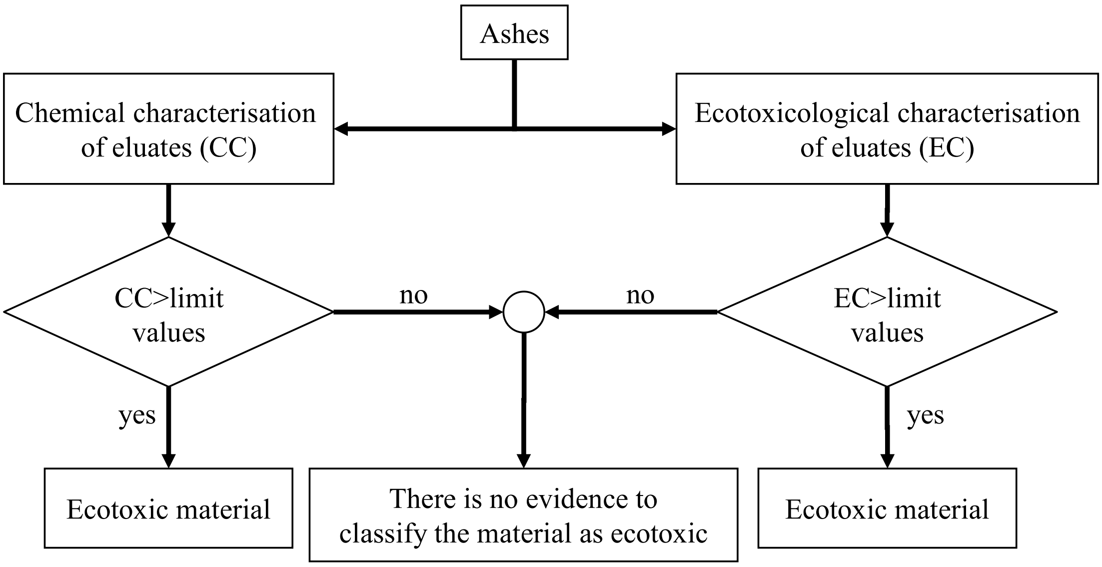


Figure 2.17 - Diagram on the modified methodology of the French regulation CEMWE

The ecotoxicological parameters determined in the eluates are shown in Table 2.9.

Table 2.9 - Ecotoxicological parameters analysed in the eluates

Type of test	Effect analysed, biological indicator and standards used
Short-term test/Acute effect	Luminescence inhibition of *Vibrio fischeri* (bacterium), performed in a miniaturized system of Microtox® according with ISO 11348-3, 2007
	Mobility inhibition of *Daphnia magna* (crustacean), performed in a miniaturized kit of Microbiotests® according with ISO 6341, 1996
Long-term test/Chronic effect	Growth rate inhibition of *Pseudokirchneriella subcapitata* (algae), performed in a miniaturized kit of Microbiotests® according with ISO 8692, 2004

2.2.2.1.4 Stabilization/solidification of fly ashes (EGR) and leaching behaviour evaluation

EGR ashes were submitted to a stabilisation/solidification process with the aim to reduce the emission of chemical species. Cement CEM IV/A(V) 32.5N was used in the stabilisation/solidification of EGR ashes. The formulations were prepared as indicated in Table 2.10 and the mortars were injected in cylindrical moulds of polystyrene.

Table 2.10 - Formulations of the s/s materials prepared with fly ashes obtained in both combustion and co-combustion assays

Ratio ashes:cement:water (wet weight)	Fly Ashes (% w/w)	Cement (% w/w)	Water (% w/w)	Water/Cement ratio (% w/w)
1:0.62:0.70	43.1	26.7	30.2	1.13
1:0.62:0.78	41.7	25.8	32.5	1.26
1:0.62:0.82	41.0	25.4	33.6	1.32
1:0.62:0.86	40.3	25.0	34.7	1.39
1:0.62:0.88	40.0	24.8	35.2	1.42

Before hardening, the moulds were vibrated with a vibratory mill (Retsch AS 200 digit) with amplitude of 0.3 for 2 minutes, in order to release the air bubbles retained inside them. Then, they were sealed and maintained at 20±1ºC, during 28 days, for cure. After the cure cycle, the s/s materials were submitted to a compressive strength test which was performed under their longitudinal axis. The s/s materials were coded as shown in Table 2.11.

Table 2.11 - Codes of the formulations of s/s materials

Ratio ashes:cement:water (wet weight)	Fly ashes (EGR) from the combustion test	Fly ashes (EGR) from the co-combustion test
1:0.62:0.70	A	F
1:0.62:0.78	B	G
1:0.62:0.82	C	H
1:0.62:0.86	D	I
1:0.62:0.88	E	J

Figure 2.18 shows the s/s formulations prepared with fly ashes produced in both combustion and co-combustion tests.

Figure 2.18 - Formulations of the s/s materials prepared with fly ashes

Then, the s/s materials were also submitted to the leaching test defined in the French standard number AFNOR X31-211. This is a batch leaching test performed over monolithic materials, with demineralized water and a liquid to solid (L/S) ratio of 10 L/kg, during 24h. The eluates were submitted to chemical and ecotoxicological characterizations. The chemical characterization followed the same parameters, standards and methods indicated in sub-chapter 2.2.2.1.3. Also the following parameters were determined: Ca (AAS nitrous oxide-acetylene flame; ISO 7980, 2010), Na (AAS air-acetylene flame; ISO 9964-1, 1993), K (AAS air-acetylene flame; ISO 9964-2, 1993), Mg (AAS air-acetylene flame; APHA/AWWA/WEF, 2005). The ecotoxicological characterization comprised the following bio-indicators: *Vibrio fischeri* (performed in a miniaturized system of Microtox® according with ISO 11348-3, 2007); b) Mobility inhibition of the crustacean *Daphnia magna* (performed in a miniaturized kit of Microbiotests® according with ISO 6341, 1996); and c) growing inhibition of the algae *Pseudokirchneriella subcapitata* (performed in a miniaturized kit of Microbiotests® according with ISO 8692, 2004).

2.2.2.1.5 Development of concrete formulations based on bottom and circulating ashes

Several concrete formulations were prepared through the mixture of bottom and circulating ashes produced in the same combustion test (Table 2.12). Portland cement CEM I 42.5R was used to produce these concretes. Coarse aggregates of siliceous gravel (dimension <4mm) and fine aggregates of washed sand (dimension <0.3mm) were used.

Table 2.12 - Formulations of concretes prepared with the mixture of bottom and circulating ashes obtained in the combustion and co-combustion assays (w/w: weight/weight; w/c: water/cement)

Formulation parameters	Formulation Codes					
	BET1	BET4	BET2	BET5	BET3	BET6
Substitution of cement by ashes (% w/w)	10		20		33	
Deionised water (g)	100		100		100	
Mixture of bottom+circulating ashes (1:1 w/w) from the combustion of coal (g)	16.9	0	33.8	0	55.8	0
Mixture of bottom+circulating ashes (1:1 w/w) from the co-combustion of coal+sewage sludge+MBM (g)	0	16.9	0	33.8	0	55.8
Cement CEM I 42.5R (g)	152.1		135.2		113.2	
Fine aggregates (g)	358		358		358	
Coarse aggregates (g)	526		526		526	
w/c ratios	0.66		0.74		0.88	

The formulations of concrete were placed in sealed cylindrical moulds of polystyrene and maintained at 20±1ºC, during 28 days, for cure. Once the cure was completed, concretes were submitted to a compressive strength test which was performed under their longitudinal axis.

Concretes were also submitted to the diffusion leaching test defined in the Dutch standard number NEN 7345 (1995). In this leaching test, monolithic samples are placed in contact with demineralized water, in a closed vessel, with a liquid to volume (L/V) ratio of 5 L/dm^3. This leaching test lasts for 64 days. During this extraction time, the leaching agent is substituted and collected several times at the following days: 0.25, 1.0, 2.25, 4, 9, 16, 32 and 64 d. Based in the diffusion test results, an assessment can be made of the time dependency of the leaching behaviour of the chemical species analysed under real conditions of use of a monolithic material (Marion et al., 2005; Alonso-Santurde et al., 2010).

The eluates were submitted to chemical and ecotoxicological characterizations. The chemical characterization followed the same parameters, standards and methods indicated in sub-chapter 2.2.2.1.4. The ecotoxicological characterization comprised the bio-indicator *Vibrio fischeri* (performed in a miniaturized system of Microtox® according with ISO 11348-3, 2007).

2.2.3 Results and Discussion

2.2.3.1 Bulk content and elemental composition of fuels

Table 2.13 shows the bulk content and elemental composition of fuels.

Table 2.13 - Average bulk content and elemental composition of coal, SS and MBM (n=2; ± SD; n: number of replicates; SD: standard deviation; db: dry basis; n.a.: not applicable)

Parameter	Unit	Coal	SS	MBM
C	% db (m/m)	66.4 (±5.0)	28.8 (±3.0)	39.2 (±4.1)
H	% db (m/m)	4.7 (±0.4)	6.0 (±0.7)	4.8 (±0.4)
N	% db (m/m)	1.4 (±0.1)	3.7 (±0.4)	8.5 (±1.0)
S	% db (m/m)	0.96 (±0.01)	1.40 (±0.1)	0.43 (±0.04)
Cl	% db (m/m)	0.070 (±0.001)	0.070 (±0.001)	0.29 (±0.03)
Ca	% db (m/m)	0.23 (±0.02)	4.0 (±0.5)	13.4 (±1.1)
Fe	% db (m/m)	0.64 (±0.04)	6.7 (±0.7)	0.020 (±0.003)
Al	% db (m/m)	1.29 (±0.10)	2.5 (±0.3)	0.080 (±0.001)
K	% db (m/m)	0.24 (±0.02)	0.43 (±0.05)	0.26 (±0.03)
Na	% db (m/m)	0.08 (±0.01)	0.18 (±0.02)	0.63 (±0.07)
Mg	% db (m/m)	0.19 (±0.02)	0.50 (±0.06)	0.24 (±0.03)
P	% db (m/m)	0.0040 (±0.0003)	2.52 (±0.21)	5.0 (±0.5)
Ba	mg/kg db	<3.65 (n.a.)	1150 (±91)	452 (±36)
Sb	mg/kg db	<0.07 (n.a.)	1.91 (±0.21)	0.13 (±0.01)
Mo	mg/kg db	<22.4 (n.a.)	326 (±41)	117 (±16)
Se	mg/kg db	<0.21 (n.a.)	853 (±106)	0.30 (±0.02)
As	mg/kg db	<0.73 (n.a.)	4.5 (±0.55)	<0.65 (n.a.)
Hg	mg/kg db	<0.27 (n.a.)	0.85 (±0.09)	<0.24 (n.a.)
Cd	mg/kg db	<7.3 (n.a.)	<21.6 (n.a.)	<6.52 (n.a.)
Pb	mg/kg db	<22.8 (n.a.)	281 (±31)	<20.4 (n.a.)
Cu	mg/kg db	<9.4 (n.a.)	654 (±89)	9.9 (±1.2)
Ni	mg/kg db	<14.4 (n.a.)	<43.4 (n.a.)	<14.0 (n.a.)
Zn	mg/kg db	36.8 (±4.9)	3333 (±401)	94.3 (±17.1)
Cr	mg/kg db	33.5 (±4.1)	147 (±19)	<10.2 (n.a.)

In coal, Zn and Cr were detected above the quantification limits and the concentrations were similar to those found by Miller et al. (2004) and Reddy et al. (2005). Other works have found lower levels of Cr than those found in this work (Lopes et al., 2003; Miller et al., 2004; López-Antón et al., 2008, Ward et al., 2011). The concentrations of As, Cu, Pb and Se were lower than those found by Miller et al. (2004) and Reddy et al. (2005) which have reported levels of As of

1.83 mg/kg and 41.9 mg/kg, Cu of 25.0 and 43.0 mg/kg, Pb of 34.0 and 29.4 mg/kg, and Se of 2.4 and 12.1 mg/kg, respectively. Lopes et al. (2003) and Ward et al. (2011) have reported similar levels of As and Cu to those found in this work. The concentrations of Mg, Al, Fe, Ca, K, Na and P found in coal were lower than those found by Shao et al. (2011), but higher than those found by Gulyurtlu et al. (2005). These differences in the bulk content of coal may be attributed to the different geological origins and type of coals analysed. In this work, a bituminous coal coming from an open-pit mine in Colombia was studied, while all the other authors have analysed this and other types of coals from different geographic and geological origins.

Among the renewable fuels tested in this work, sewage sludge has presented the highest concentrations of Hg, Sb, Ba, Mo, Se, Pb, Zn and Cr. Similar results in a different sewage sludge were reported by Miller et al. (2004), Rule et al. (2006) and Üstün (2009). Yuan et al. (2011) have found similar levels of Cu, lower levels of Zn, Pb and Cr and higher levels of Ni than those determined in this work. Elled et al. (2007) and Miller et al. (2004) have determined similar concentrations of Hg to those shown in Table 2.13, but higher levels of Sb.

MBM has presented high levels of Ba and Mo probably because these elements are rapidly transported in blood plasma from food or airborne exposure mainly to bones (World Health Organization, 2003; World Health Organization, 2004). The concentrations of K, Fe, Mg and Na determined in the MBM analysed in this work were similar to those found by Dybowska et al. (2009). Among the fuels analysed, MBM has presented the highest concentrations of Ca and P. This fact may explain the high levels of some metals in the ashes produced during the combustion test as it will be referred in the following section.

2.2.3.2 Bulk content of metals in ashes

Table 2.14 shows the average bulk content of metals in ashes. Globally, the concentrations of Cr, Zn, Ni, Cu, Pb and Cd were similar in bottom and circulating ashes of both combustion and co-combustion tests. In their study related with the characterization of fly ashes from coal, Johnson et al. (2010) have found lower concentrations of Zn, Cu and Mo (37, 37 and 13 mg/kg, respectively) but higher concentrations of Ni, Pb and Ba (28, 39 and 3800 mg/kg) than those shown in Table 2.14.

Table 2.14 - Average bulk content of bottom, circulating and fly ashes obtained in the combustion, “1st", and co-combustion assay, “2nd" (n: number of replicates; SD: standard deviation; db: dry basis; n.a.: not applicable)

Sample	Cr	Zn	As	Ni	Cu	Pb	Cd	Hg	Ba	Mo	Sb	Se
Combustion of coal (n=2; ± SD; mg/kg db)												
WBK-1st	56.2 (±5.5)	268 (±15)	<0.63(n.a.)	33.9 (±2.5)	32.5 (±4.0)	<19.7 (n.a.)	<6.3 (n.a.)	<0.24 (n.a.)	660 (±78)	39.4 (±4.2)	0.14 (±0.01)	<0.18 (n.a.)
FBK-1st	61.0 (±6.0)	551 (±52)	<0.64(n.a.)	23.2 (±3.1)	23.9 (±2.6)	<19.9 (n.a.)	<6.4 (n.a.)	<0.24 (n.a.)	742 (±85)	27.4 (±3.1)	0.21 (±0.01)	<0.18 (n.a.)
EGR-1st	59.1 (±10.5)	93.9 (±2.1)	<0.64(n.a.)	23.3 (±15.1)	59.6 (±0.6)	<19.9 (n.a.)	<6.4 (n.a.)	<0.24 (n.a.)	779 (±90)	27.4 (±3.8)	0.070 (±0.008)	1.7 (±0.2)
Co-combustion of coal+sewage sludge+MBM (n=2 ; ± SD; mg/kg db)												
WBK-2nd	74.2 (±19.4)	255 (±16)	11.8(±0.8)	33.0 (±0.3)	46.2 (±8.5)	<19.9 (n.a.)	<6.4 (n.a.)	0.39 (±0.21)	1259 (±120)	23.3 (±2.1)	0.28 (±0.03)	0.31 (±0.04)
FBK-2nd	60.6 (±4.4)	260 (±9)	12.2(±0.1)	24.6 (±2.8)	41.0 (±3.3)	<20.0 (n.a.)	<6.4 (n.a.)	0.29 (±0.07)	851 (±93)	31.0 (±4.0)	<0.06 (n.a.)	0.29 (±0.03)
EGR-2nd	171 (±18)	331 (±25)	5.8(±0.8)	29.4 (±5.3)	108 (±11)	33.2 (±2.3)	<6.3 (n.a.)	0.48 (±0.06)	2369 (±240)	20.5 (±3.7)	3.35 (±0.41)	0.38 (±0.04)

The concentration of Zn in circulating ashes produced in the co-combustion test was less than a half of the concentration in the same type of ashes produced in the combustion test, but it was about three times higher in the fly ashes collected in the co-combustion test. The co-combustion test may have produced unburned carbon which can cause, according to Nakayama et al. (2008), the reduction of ZnO to Zn contributing for its volatilization. This process associated to the condensation over fine particles in the coldest parts of the furnace might increase the concentration of Zn in fly ashes.

The concentration of Cu in bottom ashes produced during the co-combustion test was about 46.2 mg/kg. This concentration is slightly lower than the concentration found by Cyr and Ludmann (2006) (70.3 mg/kg). The ashes produced during the co-combustion test have presented higher concentration of Cu than the ashes produced during the combustion of coal. The increasing rate was about 1.5, 1.7 and 1.8 in the bottom, circulating and fly ashes, respectively. The higher concentrations of Cu obtained in the ashes produced in the co-combustion test can be attributed to the higher concentration of this metal in the sewage sludge used in this co-combustion test.

The concentrations of As and Hg were, generally, higher in all ashes produced during the co-combustion test than in the ashes produced in the combustion assay. This can be attributed to the higher concentrations of Hg and As in the sewage sludge used in the co-combustion test. The concentration of As in the fly ashes produced during the combustion of coal was low. Narukawa et al. (2005) have found higher levels of this element in fly ashes resulting from the combustion of the same fuel (5.4 to 22.3 mg/kg).

It was also observed a tendency for a higher accumulation of Cr, Zn, Cu, Pb, Hg and As in the fly ashes of the co-combustion test than in the fly ashes of the combustion test. This may be explained, in part, by the sum of the concentrations of these metals in the SS and MBM and also by the influence of Cl present in the MBM that might have promoted the formation of metal chlorides (Folgueras et al., 2003; Polettini et al., 2004; Sun et al., 2004; Mizuno et al., 2006).

Cyr and Ludmann (2006) have found, in a study related with the combustion of MBM, that the concentration of Cr in bottom ashes was about half of the concentration found in this work (32.42 mg/kg). The reason for this difference may be related with the highest concentration of Cr obtained in MBM that was used in this work.

Zn, Cu and Pb have presented high concentrations in fly ashes produced during the co-combustion test which may be explained by the high concentrations of Ca and P in MBM. High concentrations of Ca and P may lead to the production of higher levels of apatite, which can contribute for the retention of Zn, Cu and Pb in the ashes as Ca substitutes (Coutand et al., 2008; Dybowska et al., 2009).

The high concentrations of Mo and Sb in sewage sludge and MBM and Se in sewage sludge have conducted to the production of ashes with high concentrations of these metals. Narukawa et al. (2005) have found levels of Se slightly higher in this type of ashes (2.3 to 5.2 mg/kg) than those observed in this work. In what concerns Mo, these authors have found lower levels of this element (1.0 to 3.9 mg/kg) than those determined in this work.

2.2.3.3 Leaching behaviour of ashes based on EN 12457-2

In Table 2.15 it is shown the characterization of eluates produced according to EN 12457-2. pH values were extremely alkaline. In what concerns the parameter cyanides, it was expected its presence in the ashes, especially in those produced during the combustion of biomass (Barber et al., 2003). The analytical results show that the concentration of cyanides was lower in the eluates produced by the ashes resulting from the co-combustion test than in the eluates produced by the ashes of the combustion assay. This may be explained by the presence of higher levels of limestone in the ashes of the co-combustion assay, which promoted a faster hydrolysis of cyanides (Schäfer and Bonn, 2002).

Cr and Cr VI were not detected in the eluates produced by the bottom and circulating ashes from both combustion tests. In what concerns the fly ashes, the concentration of Cr was very similar in these ashes produced in both combustion tests. In the fly ashes obtained from the combustion of coal, Cr was present almost in the oxidation state VI, which is in agreement with the results obtained by Chai et al. (2009).

In the fly ashes produced during the combustion of coal, the concentration of Cr was two times higher than the concentration found by Koukozas et al. (2011) in the same type of material. Nevertheless, the concentration of Zn in the coal fly ashes obtained in this work was five times lower than the concentration found by those authors. In the eluates produced by the fly ashes from the co-combustion test, the concentration of Cr VI was less than one third of the concentration of Cr. The differences in the speciation of Cr may be explained by the reduction of the redox potential in ashes eventually caused by the oxidation conditions during the combustion and formation of ashes in the treatment system of exhaustion gases (Chai et al., 2009).

Table 2.15 - Chemical characterization of the eluates of bottom, circulating and fly ashes, produced according to the European leaching standard number EN 12457-2 (“1st”: ashes produced in the combustion trial; “2nd": ashes produced in co-combustion trial; n: number of replicates; SD: standard deviation; n.a.: not applicable)

Sample	Phenol Compounds	Sulphates	Fluorides	Chlorides	CN^-	pH	TDS	DOC	Cr	Cr VI
Combustion of coal (n=2; ± SD; mg/kg db, except for pH – Sorensen scale)										
WBK-1st	1.15 (±0.14)	11500 (±284)	73.2 (±6.0)	7445 (±459)	0.24 (±0.01)	13.7 (±0.2)	40659 (±623)	50.5 (±2.1)	<0.50 (n.a.)	<0.50 (n.a.)
FBK-1st	0.80 (±0.07)	11400 (±706)	68.2 (±7.4)	1395 (±35)	0.23 (±0.01)	13.2 (±0.9)	41897 (±1017)	10.0 (±1.4)	<0.50 (n.a.)	<0.50 (n.a.)
EGR-1st	0.70 (±0.07)	12000 (±1,415)	68.2 (±6.7)	1645 (±35)	0.18 (±0.01)	13.6 (±0.3)	47778 (±738)	62.5 (±6.4)	1.29 (±0.02)	1.28 (±0.04)
Co-combustion of coal+sewage sludge+MBM (n=2; mg/kg db, except for pH – Sorensen scale)										
WBK-2nd	0.70 (±0.22)	10509 (±708)	20.5 (±2.7)	1220 (±142)	<0.13 (n.a.)	13.0 (±0.1)	39536 (±882)	25.9 (±1.2)	<0.50 (n.a.)	<0.50 (n.a.)
FBK-2nd	<0.50 (n.a.)	11308 (±704)	53.0 (±7.2)	1270 (±71)	<0.13 (n.a.)	13.2 (±0.1)	41182 (±1956)	37.6 (±4.3)	<0.50 (n.a.)	<0.50 (n.a.)
EGR-2nd	<0.50 (n.a.)	14308 (±1702)	53.0 (±4.3)	1280 (±142)	<0.13 (n.a.)	13.4 (±0.1)	45740 (±1702)	39.7 (±5.1)	1.27 (±0.03)	<0.50 (n.a.)

Sample	Zn	As	Ni	Cu	Pb	Cd	Hg	Ba	Mo	Sb	Se
Combustion of coal (n=2; ± SD; mg/kg db)											
WBK-1st	0.15 (0.02)	<0.03 (n.a.)	<0.63 (n.a.)	<0.41 (n.a.)	<1.00 (n.a)	<0.32(n.a.)	<0.01 (n.a.)	<0.16 (n.a.)	5.0 (±2.6)	0.010 (±0.002)	0.01 (<0.001)
FBK-1st	<0.13 (n.a.)	<0.03 (n.a.)	<0.63 (n.a.)	<0.41 (n.a.)	1.56 (±0.78)	<0.32(n.a.)	<0.01 (n.a.)	<0.16 (n.a.)	3.5 (±0.72)	0.010 (±0.002)	0.01 (<0.001)
EGR-1st	0.17 (0.07)	<0.03 (n.a.)	<0.63 (n.a.)	<0.41 (n.a.)	<1.00 (n.a.)	<0.32(n.a.)	<0.01 (n.a.)	<0.16 (n.a.)	5.7 (±0.91)	0.0050 <0.0005	0.06 (±0.04)
Co-combustion of coal+sewage sludge+MBM (n=2; ± SD; mg/kg db)											
WBK-2nd	<0.13 (n.a.)	<0.03 (n.a.)	<0.63 (n.a.)	<0.41 (n.a.)	<1.00 (n.a.)	<0.32 (n.a.)	<0.01 (n.a.)	<0.16 (n.a.)	1.4 (±0.1)	<0.003. (n.a.)	<0.01 (n.a.)
FBK-2nd	<0.13 (n.a.)	<0.03 (n.a.)	0.95 (±0.14)	<0.41 (n.a.)	<1.00 (n.a.)	<0.32 (n.a.)	<0.01 (n.a.)	<0.16 (n.a.)	2.3 (±0.1)	<0.003. (n.a.)	<0.01 (n.a.)
EGR-2nd	<0.13 (n.a.)	<0.03 (n.a.)	0.68 (±0.07)	<0.41 (n.a.)	<1.03 (n.a.)	<0.32 (n.a.)	<0.01 (n.a.)	<0.16 (n.a.)	4.2 (±0.3)	<0.003. (n.a.)	0.030 (±0.003)

The concentration of Mo in the eluates of all ashes was between the limit values for inert and for non-hazardous residues (0.5 to 10 mg/kg). The leaching rate of Sb was very low. According to Cornelis et al. (2006), at pH>12, calcium antimonite comes into solution due to portlandite formation, but the subsequent increase in Sb leaching is reduced due to the interaction of Sb with portlandite and ettringite. In a study performed by Miravet et al. (2006) it is concluded that Sb is strongly bound to fly ashes.

Based on the limits defined in the European Council Decision 2003/33/EC, the bottom ashes produced in the combustion test were classified as non-hazardous materials, due to the concentrations of sulphates, fluorides, chlorides, TDS, and Mo that were above the limits for inert materials and below the limits for non-hazardous materials.

Circulating ashes were also classified as non-hazardous. Those produced by the combustion of coal have obtained this classification due to the concentration of sulphates, fluorides, chlorides, TDS, Mo, and Pb, while those produced during the co-combustion test were classified as non-hazardous due to the concentration of sulphates, fluorides, chlorides, TDS, Mo, and Ni.

Fly ashes were classified as non-hazardous residues due to the concentrations of sulphates, fluorides, chlorides, TDS, Mo, and Cr. The fly ashes produced during the combustion test were classified as non-hazardous due also to the concentration of Ni.

Fly ashes produced in the co-combustion test have shown concentrations of Cr VI higher than the limit defined in CEMWE. The concentration of phenolic compounds in the bottom ashes produced in the combustion of coal was higher than the limit defined in CEMWE, therefore, they were also classified as ecotoxic materials.

2.2.3.4 Ecotoxicological characterization of eluates obtained by EN 12457-2 leaching test

In Table 2.16 it is shown the ecotoxicological levels of the eluates of ashes produced with the European leaching standard number EN 12457-2 (2002), and the ecotoxicological limit values defined in the CEMWE. High ecotoxicity levels of the eluates were observed for all bio-indicators.

Similarly to the observations of Lapa et al. (2002 and 2007), the biological indicator with the highest sensitivity was *V. fischeri*. The effect on the bio-indicators may be attributed to the pH of the eluate and/or to the bioavailability of heavy metals (Lapa et al., 2002, Tsiridis et al., 2006; Lapa et al., 2007; Barbosa et al., 2009). Comparing the ecotoxicological levels obtained in the eluates of ashes to CEMWE limit values, it is possible to conclude that all ashes have shown ecotoxic characteristics for the bio-indicators tested.

Table 2.16 - Ecotoxicological levels of the eluates of bottom, circulating and fly ashes, produced according to the European leaching standard number EN 12457-2 and limit values defined in the CEMWE

Eluate of the ashes	*V. fischeri* (EC_{50} – 30 min, %)	*P. subcapitata* (EC_{20} – 72 h, %)	*D. magna* (EC_{50} – 48 h, %)
WBK–1st (Combustion test)	<1	5	2
WBK–2nd (Co-combustion test)	<1	<1	3
FBK–1st (Combustion test)	<1	3	3
FBK–2nd (Co-combustion test)	<1	<1	3
EGR–1st (Combustion test)	<1	4	3
EGR–2nd (Co-combustion test)	<1	<1	3
CEMWE limit values	10	0.1	10

2.2.3.5 Leaching behaviour of ashes based on the leaching test NEN 7343

Several authors argue that CLT, such as the leaching test NEN 7343 (1995), are better simulations of the real conditions of leaching than the batch leaching tests such as EN 12457-2 (2002). According to Jones (1995), the composition of eluates produced as a function of time by the percolation of water through ashes can be better predicted by a long term CLT than by a batch leaching test performed in a unique cycle. Reemtsma and Mehrtens (1997) have argued that dynamic CLT appears to better simulate natural conditions. CLT removes, initially, the most mobiles elements from ashes, hence they will not be in solution for continued interaction with other elements as it is observed in batch leaching tests (Wang et al., 2008b).

Figure 2.19 shows the variation of DOC, chlorides and Cr VI in the eluates produced by CLT NEN 7343 (1995) when applied to the three types of ashes produced in the combustion and co-combustion assays. Generally, fly ashes showed a tendency to release higher concentrations of chlorides and Cr VI than bottom and circulating ashes. High leaching rates of chlorides are common in fly ashes produced during the combustion of coal and biomass as observed by

Aguiar del Toro et al. (2009) and Ahmaruzzaman (2010). López-Antón et al. (2008) have verified high dissolution rates of Cr VI from fly ashes in a similar column leaching test.

The concentrations of Pb, Cd, As, Cu, Ni, Hg, Zn and Sb were below the limit values for inert materials, but the concentrations of Mo and Ba were between the limit values for inert and non-hazardous materials.

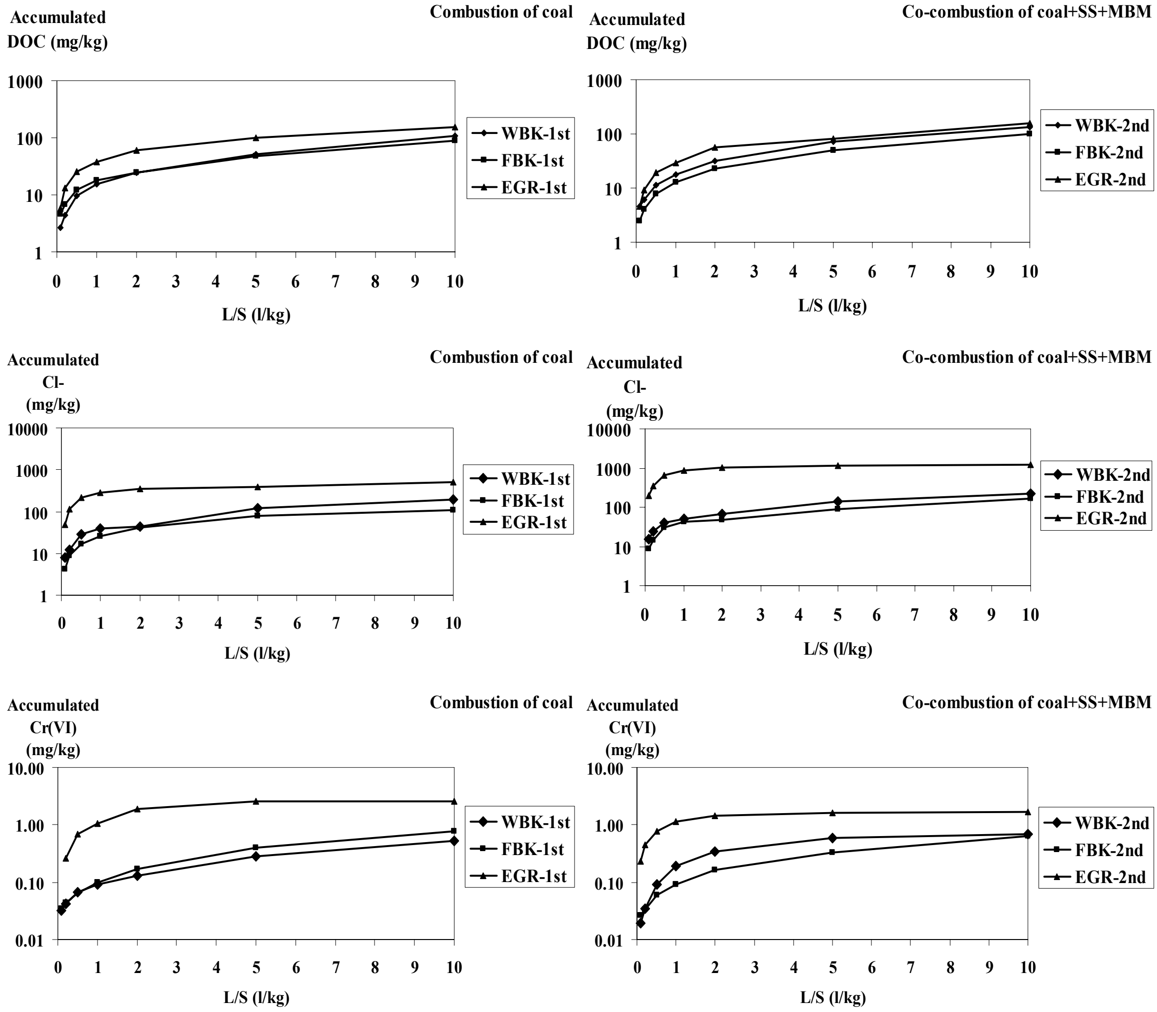


Figure 2.19 - Accumulated concentration of DOC, Cl, and Cr (VI) in the eluates of NEN 7343 column leaching test to which the ashes were submitted (1st: combustion test; 2nd: co-combustion test)

Table 2.17 shows the classification of ashes based on the analytical results obtained in the eluates, after a L/S ratio of 0.1 L/kg has been achieved in NEN 7343 (1995) leaching test, and considering the limit values defined in the Council Decision 2003/33/EC.

The bottom and circulating ashes from both combustion tests were classified as non-hazardous, while fly ashes were classified as hazardous materials.

Table 2.17 - Classification of the ashes produced in the combustion and co-combustion tests, based on the results obtained in the leaching test NEN 7343 for C_0 of L/S=0.1 L/kg and according to the limits defined in the Council Decision 2003/33/EC

Ashes	Classification according Council Decision 2003/33/EC
WBK – Combustion test	Non-hazardous material
WBK – Co-combustion test	Non-hazardous material
FBK – Combustion test	Non-hazardous material
FBK – Co-combustion test	Non-hazardous material
EGR – Combustion test	Hazardous material
EGR – Co-combustion test	Hazardous material

2.2.3.6 Ecotoxicological characterization of eluates obtained by NEN 7343 leaching test

The ecotoxicity levels of eluates produced by NEN 7343 (1995) leaching test (Figure 2.20) were high for both biological indicators used, particularly for *V. fischeri*. The eluates produced in the first L/S ratio of NEN 7343 (1995) (0.1 L/kg) leaching test seemed to have, generally, higher ecotoxicity levels than the eluates produced with L/S ratios >2 L/kg. This fact may be related with the higher releasing rates of different chemical species in the beginning of the CLT. No significant differences were observed between the ecotoxicity levels of the eluates of ashes produced in both combustion and co-combustion tests.

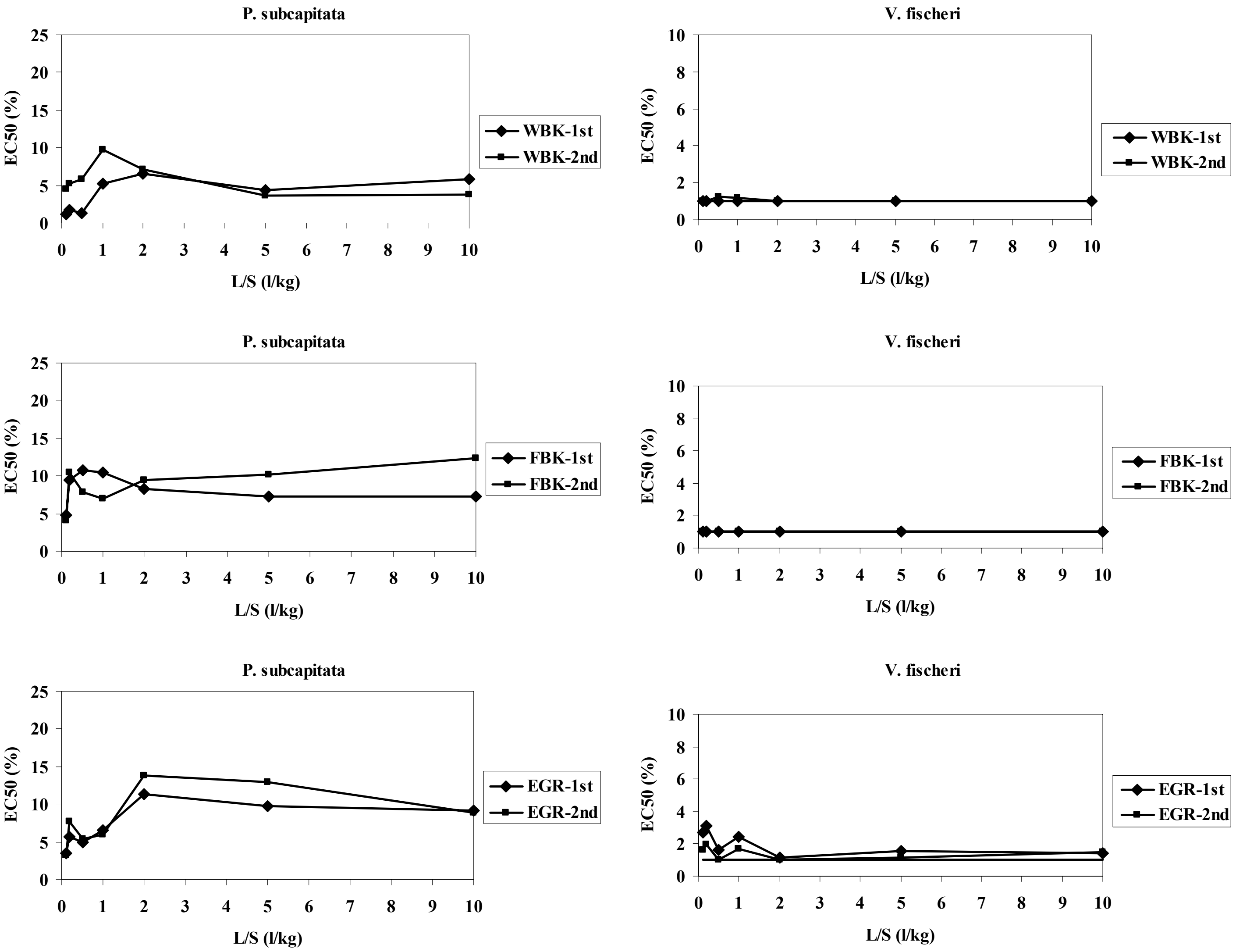


Figure 2.20 - Ecotoxicity levels for *P. subcapitata* and *V. fischeri* of the eluates produced through NEN 7343 column leaching test to which the ashes were submitted (1^{st}: combustion test; 2^{nd}: co-combustion test)

2.2.3.7 Mechanical characterization and leaching behaviour of s/s materials produced with fly ashes (EGR)

The addition of coal fly ashes to Portland cement concrete improves its workability (United States Department of Transportation – Federal Highway Transportation, 2012). If other combustion residues are added to Portland cement concrete, a reduction in workability can generally be observed. However, alternative combustion residues may have different pozzolanic activities, which may influence some properties of the concrete, namely its strength (Payá et al., 2002; Donattelo et al., 2010; Johnson et al., 2010).

In Figure 2.21 it is shown the compressive strength of s/s mortars produced with the mixture of fly ashes, Cement CEM IV/A(V) 32.5N and water, as presented in Table 2.10. The compressive strengths obtained were between 25 and 40 MPa which can be considered to be a range of normal to high compressive strength values. These results clearly show the good properties of the fly ashes produced in both combustion and co-combustion assays. The compressive strength variation within each group of s/s materials was mainly due to the variation of the water/cement ratio. High water/cement ratios have promoted the reduction of the compressive strength. According to Felekoglu (2007), this is due to the increase of the micro-pores in mortar structure after the solidification period.

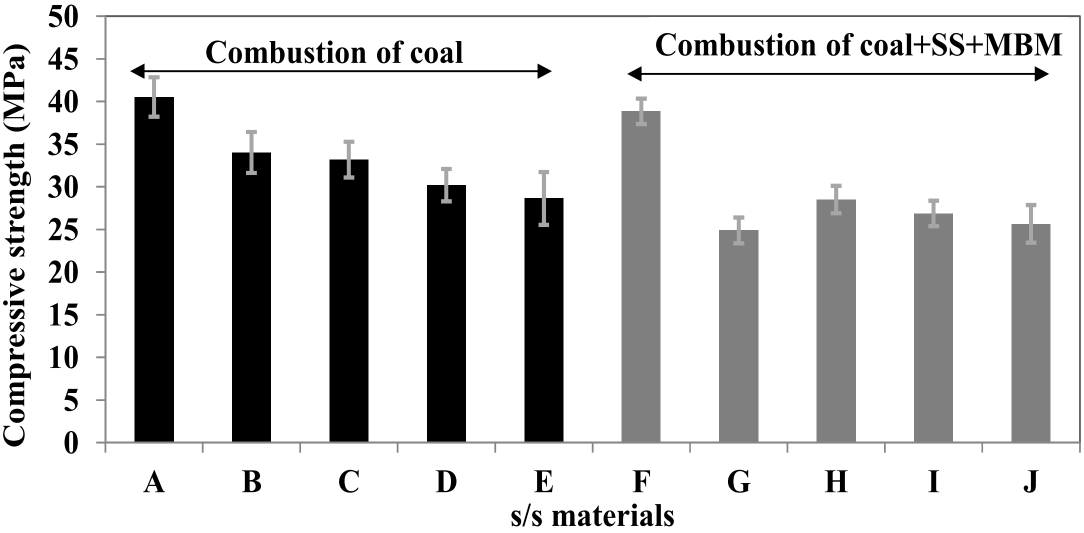
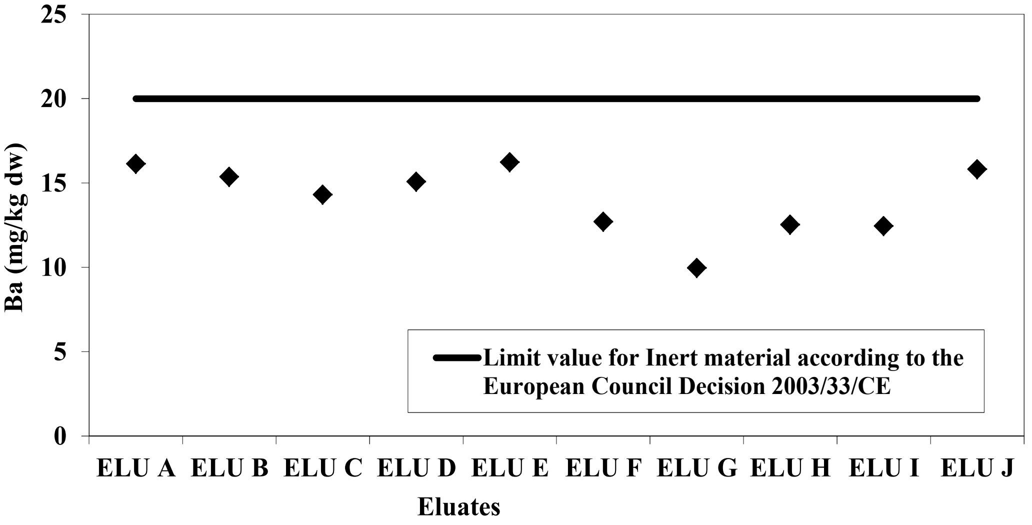


Figure 2.21 - Compressive strength, after 28 days of cure, of s/s materials produced with the fly ashes of the combustion assay with coal and co-combustion assay with coal+SS+MBM (SD are presented in error bars)

Concentrations of Ba and Mo in the eluates of the s/s materials, obtained through the AFNOR X31-211 leaching test, are shown in Figure 2.22. The majority of the chemical species quantified in the eluates, namely phenol compounds, sulphates, fluorides, chlorides, DOC, TDS, Sb, Se and Ba, have presented concentrations below the limit values defined for inert materials in the European Council Decision 2003/33/EC. Only Mo was detected in concentrations slightly above the limit value for inert materials.

It was observed a significant reduction on the emission of all chemical species from the s/s materials when compared with the same levels emitted by crude fly ashes. The matrix was effective on retaining the chemical species that easily released from the crude fly ashes.



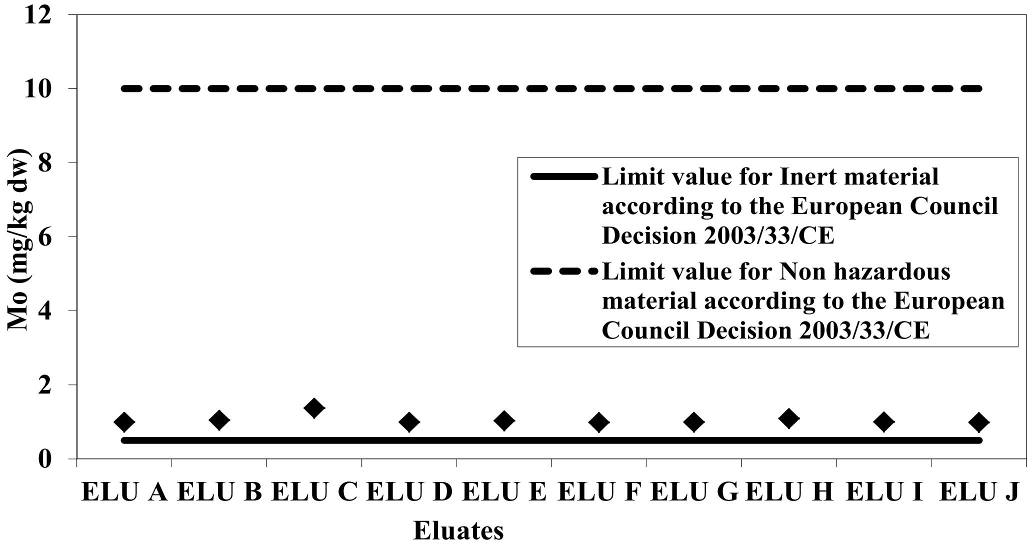


Figure 2.22 - Concentrations of Ba and Mo in the eluates of s/s materials, produced through the standard leaching test AFNOR X31-211

2.2.3.8 Ecotoxicological characterization of s/s materials produced with fly ashes (EGR)

The ecotoxicity levels of the eluates of the s/s materials (Table 2.18) were lower than the levels determined for crude fly ashes and were also lower than CEMWE limit values, except for *V. fischeri*. The ecotoxicity levels obtained for *V. fischeri* can be attributed to the extreme alkaline pH values of the eluates to which the bacterium is highly sensitive, or to other chemical species that were not quantified (Lapa et al., 2007; Barbosa et al., 2009; Ghirardinia et al., 2009).

Table 2.18 - Ecotoxicity levels of the eluates of s/s materials and CEMWE limit values

s/s formulation eluate	*V. fischeri* (EC_{50} – 30 min, %)	*P. subcapitata* (EC_{20} – 72 h, %)	*D. magna* (EC_{50} – 48 h, %)
ELU A	5	24	25
ELU B	7	29	22
ELU C	6	39	24
ELU D	6	22	21
ELU E	5	36	22
ELU F	6	35	24
ELU G	6	22	24
ELU H	6	27	24
ELU I	6	41	24
ELU J	5	20	24
CEMWE limit values	*10*	*0.1*	*10*

2.2.3.9 Mechanical characterization and leaching behaviour of concretes

Figure 2.23 shows the compressive strength of the concretes produced after 28 days of cure. The compressive strength is directly related to the microstructure of the hardened concrete and to the w/c ratio. As w/c ratio decreases, the compressive strength increases. Furthermore, the strength of the coarse aggregate, mineralogical origin and quality can become controlling factors at high compressive strengths (United States Department of Transportation - Federal Highway, and Technology, 2001). In the concretes produced in this work, the compressive strength varied between 12 and 24 MPa. Generally, these results were lower than would be expected based on the high quality of the cement used. This can be attributed to the following factors: a) High percentages of ashes used; b) Bad chemical properties of ashes; c) Substitution of cement by the mixtures of bottom and circulating ashes instead of using these mixtures to substitute the aggregates.

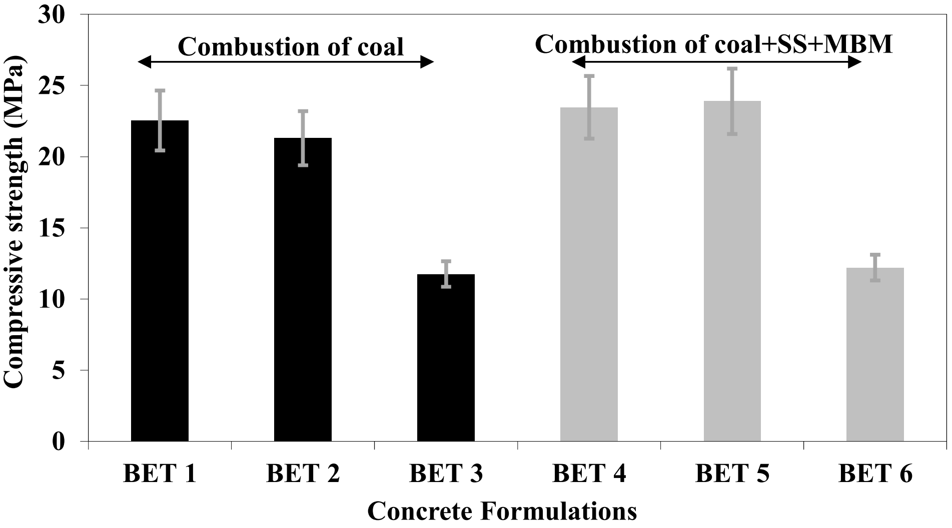


Figure 2.23 - Compressive strength, after 28 days of cure, of concretes produced with the mixtures of bottom and circulating ashes

The cumulative releases of chlorides and sulphates from concretes are shown in Figure 2.24. Chlorides and sulphates were selected because their release patterns are representatives of the two basic release patterns that were observed for all the leachable chemical species. Chlorides represent the chemical species that present a biphasic release with an initial release rate higher than the release rate observed for the second phase. This leaching behaviour is of type I according to Chandler et al. (1997). Sulphates represent the chemical species with a monophasic release in which the release rate are constant all over the leaching process (type II leaching behaviour).

In Table 2.19 it is shown the calculated emission factors (I_c) of each chemical species released from the concretes according to the BMD. The I_c values were calculated according with Eq. 2.2:

$$I_c = \mathrm{E}_{64\mathrm{d}} * \mathrm{f}_{\mathrm{temp}} * \mathrm{f}_{\mathrm{ext}} * \sqrt{\mathrm{f}_{\mathrm{bev}} * \mathrm{f}_{\mathrm{iso}}} \qquad \text{Eq. 2.2}$$

E_{64d} means the emission after 64 days of leaching, in the diffusion leaching test (NEN 7345, 1995) (mg/m^2);

f_{temp} means the correction factor of the temperature, from the laboratory to environment (=0.7);

f_{ext} means the extrapolation factor from 64 days to 1 or 100 years. This factor is 2.4 for sulfates and chlorides and 15 for the remaining parameters;

f_{bev} means the correction for the moistening conditions of exposure. This factor is 1 and 0.1 for conditions of permanent and limited moistening conditions, respectively;

F_{iso} means the correction factor for the isolation conditions. This factor is 1 without insulation conditions and is 0.1 with insulation conditions.

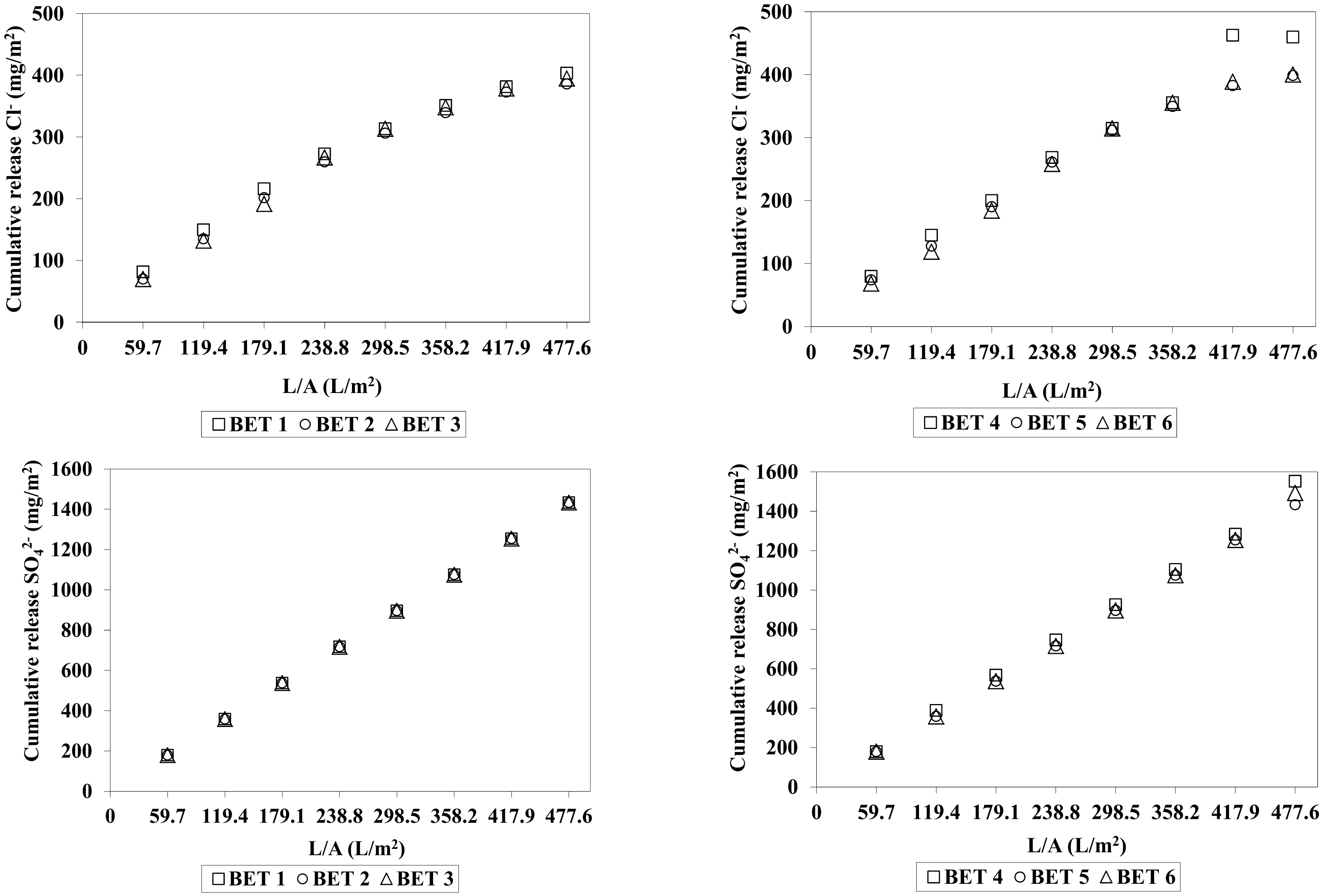


Figure 2.24 - Cumulative releases of chlorides and sulphates from the concretes, obtained through the NEN 7345 column leaching test

Depending on the moisture and isolation conditions there are, in BMD, three categories, which are:

- Category 1A: permanent moistening and without insulation conditions. In this category, the expression $\sqrt{f_{bev} * f_{iso}}$ will assume the value of $\sqrt{1*1}$.

- Category 1B: limited moistening and without insulation conditions. In this category, the expression $\sqrt{f_{bev} * f_{iso}}$ will assume the value of $\sqrt{0.1*1}$.

- Category 2: permanent moistening and with insulation conditions. In this category, the expression $\sqrt{f_{bev} * f_{iso}}$ will assume the value of $\sqrt{1*0.1}$.

Based on the values of I*max* of BMD and indicated in last column of Table 2.19, it is possible to conclude that all concretes with a substitution level of cement by ashes of 10% and 20% (w/w) ashes, except BET 5, can be used with limited moistening and without insulation, or with permanent moistening and with insulation, respectively. These concretes (BET1, BET 2 and BET 4) cannot be used in permanent moistening and without insulation conditions due to the emission factors of cyanide, mercury, and cadmium (underlined values).

The emission factor of cyanide was above the I_{max}, for all categories, in concretes BET3 and BET6, while the emission factor of mercury was above the I_{max} in concrete BET5. Therefore, concretes that were prepared with 33% (w/w) ashes (BET3 and BET6) and BET 5 formulation cannot be used as civil engineering materials.

Table 2.19 - Calculated emission factors (I_c) of concretes BET1 to BET 6, maximum emission factors (I_{max}) and assessment on the possibility of using concretes as civil engineering materials (emission factors expressed as mg/m^2; Underlined numbers means that the I_c level of that category is above the I_{max}; NU: Not usable in the category; U: Usable in the category)

Chemical species	BET 1		BET 2		BET 3		BET 4		BET 5		BET 6		I_{max}
	I_c (Catg. 1A)	I_c (Catg. 1B and 2)	I_c (Catg. 1A)	I_c (Catg. 1B and 2)	I_c (Catg. 1A)	I_c (Catg. 1B and 2)	I_c (Catg. 1A)	I_c (Catg. 1B and 2)	I_c (Catg. 1A)	I_c (Catg. 1B and 2)	I_c (Catg. 1A)	I_c (Catg. 1B and 2)	
Chloride	677	214	648	205	663	210	772	244	670	212	672	213	30000
Fluoride	138	43.6	62.7	19.8	62.7	19.8	179	56.5	50.2	15.9	50.2	15.9	14000
Sulphate	2407	761	2407	761	2407	761	2608	825	2407	761	2507	793	45000
Cyanide	34.1	10.8	34.1	10.8	56.3	17.8	26.3	8.33	31.5	9.96	50.0	15.8	15
Antimony	1.81	0.57	1.59	0.50	1.84	0.58	2.01	0.63	2.30	0.73	1.67	0.53	39
Barium	305	96.3	498	157	449	142	304	96.0	218	69.1	525	166	6300
Cadmium	17.9	5.65	14.7	4.66	12.9	4.06	16.6	5.25	24.5	7.73	14.4	4.56	12
Lead	441	139	420	133	404	128	404	128	251	79.3	284	89.8	1275
Copper	50.2	15.9	50.2	15.9	50.2	15.9	50.2	15.9	50.2	15.9	59.9	18.9	540
Mercury	6.02	1.90	6.02	1.90	6.02	1.90	6.79	2.15	21.2	6.69	12.5	3.94	4.5
Zinc	213	67.3	211	66.6	93.4	29.5	45.1	14.3	26.3	8.33	25.1	7.93	2100
Classification	*NU*	*U*	*NU*	*U*	*NU*	*NU*	*NU*	*U*	*NU*	*NU*	*NU*	*NU*	--

2.2.3.10 Ecotoxicological characterization of concretes

Figure 2.25 to Figure 2.30 show the evolution of the ecotoxicity levels of the eluates, expressed as Toxicity Units (TU=100%/EC_{50}), as a function of the accumulated L/A.

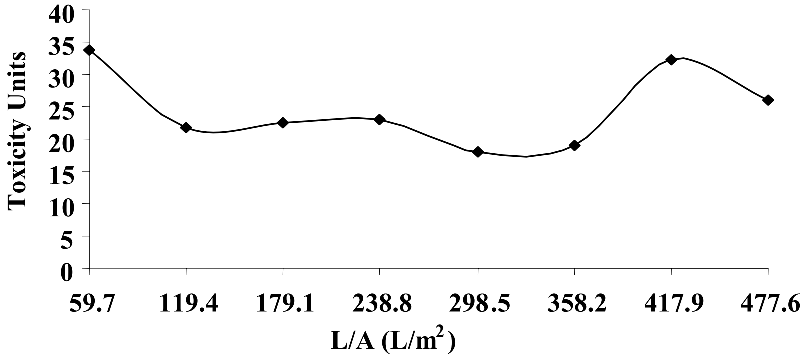


Figure 2.25 - Evolution of the TU as function of the accumulated L/A (L/m^2) of the eluates of BET 1

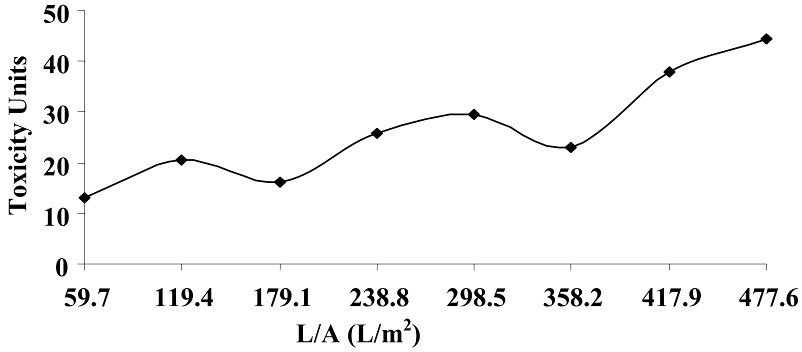


Figure 2.26 - Evolution of the TU as function of the accumulated L/A (L/m^2) of the eluates of BET 2

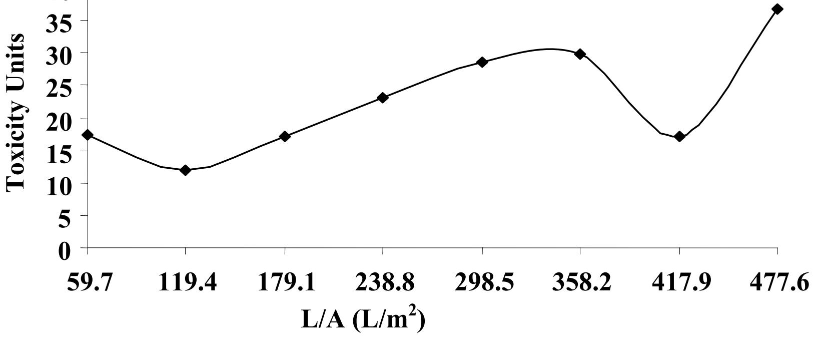


Figure 2.27 - Evolution of the TU as function of the accumulated L/A (L/m^2) of the eluates of BET 3

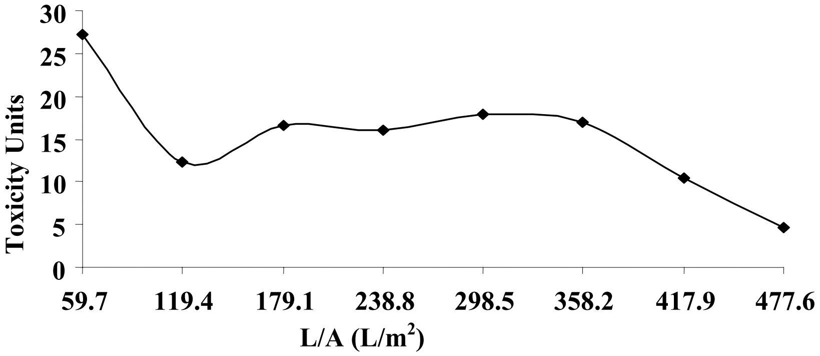


Figure 2.28 - Evolution of the TU as function of the accumulated L/A (L/m^2) of the eluates of BET 4

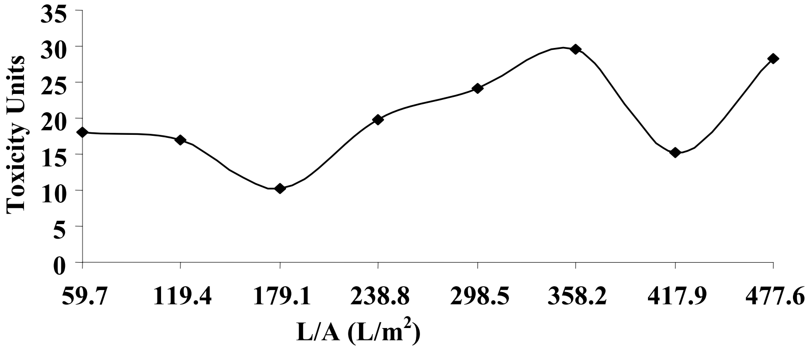


Figure 2.29 - Evolution of the TU as function of the accumulated L/A (L/m^2) of the eluates of BET 5

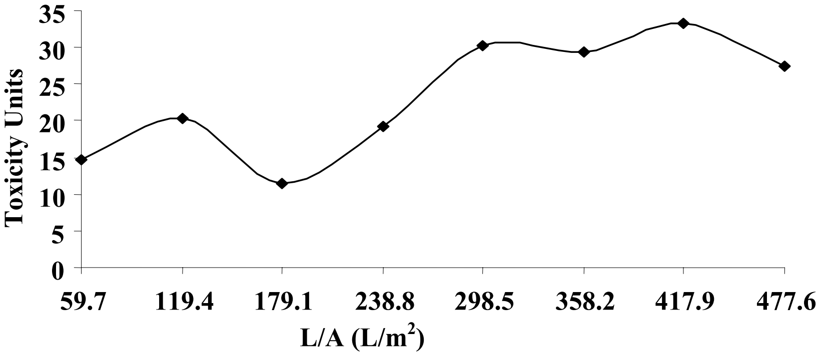


Figure 2.30 - Evolution of the TU as function of the accumulated L/A (L/m^2) of the eluates of BET 6

There is no specific pattern in the evolution of the TU of the elautes. Nevertheless, it was observed a reduction in the TU in concrete formulations in which were used co-combustion ashes instead of coal ashes. The reduction in the TU was evident in BET 1 (10% coal ashes) *vs.* BET 4 (10% co-combustion ashes) and BET 2 (20% coal ashes) *vs.* BET 5 (20% co-combustion ashes). This means that the incorporation of co-combustion ashes in concrete has promoted lower ecotoxicological levels than those observed in the concretes in which it was incorporated coal ashes.

2.2.4 Conclusions

Generally, the use of co-fuels has no promoted significant changes in the leaching behaviour of the ashes. It was observed similar chemical and ecotoxicological properties of the eluates of the same type of ashes.

It was possible to stabilise adequately the fly ashes produced in both combustion and co-combustion tests. All s/s mortars achieved a good degree of stabilisation, being characterized by medium to high compressive strengths and being classified as non-hazardous materials.

The compressive strengths of concretes produced with the mixture of bottom and circulating ashes were in the range of low to medium values. Based on the BMD, the concretes prepared with 10% and 20% (w/w) ashes, except the formulation BET 5, could be used in real conditions with limited moistening and without insulation, and with permanent moistening and with insulation, respectively.

It was observed a reduction in the TU in concrete formulations in which were used co-combustion ashes instead of coal ashes. The reduction in the TU was evident in BET 1 (10% coal ashes) vs. BET 4 (10% co-combustion ashes) and BET 2 (20% coal ashes) vs. BET 5 (20% co-combustion ashes). This means that the incorporation of co-combustion ashes in concrete has promoted lower ecotoxicological levels than those observed in the concretes in which it was incorporated coal ashes.

3 Study on the valorization of ashes produced in the combustion of forestry residues in a pulp and paper industry

3.1 Chemical and ecotoxicological properties of size fractionated biomass ashes

Based on the following paper and oral communication:
Rui Barbosa, Diogo Dias, Nuno Lapa, Helena Lopes, Benilde Mendes (2013), Chemical and ecotoxicological properties of size fractionated biomass ashes. Fuel Processing Technology 109, 124-132
dx.doi.org/10.1016/j.fuproc.2012.09.048
IF (2012): 2.819; 5-year IF: 3.493
Fuel Processing Technology is indexed on Scopus, SCImago and WoS

R. Barbosa, N. Lapa, H. Lopes, B. Mendes (2010), Study of the valorization of ashes produced in a thermoelectric power plant, working under co-combustion of coal and biomass, and in a pulp and paper industry. Workshop "Energy Optimization in Industry and Reduction of CO2 Emissions”. Organized by the Executive Commitee of the International Agreement IETS (Comité Executivo do Acordo Internacional IETS), in the scope of the International Energy Agency (Agência Internacional de Energia) jointly with the Grupo Nacional para a Integração de Processos (GNIP), Lisboa, 3rd November.

ABSTRACT

The main aim of this work was to study the chemical and ecotoxicological properties of ashes produced in a biomass boiler of a pulp and paper industry and evaluate possible differences depending on the particle size of bottom and fly ashes. The pulp and paper industry in which the ashes were collected produces electricity by burning eucalyptus bark and pine bark in a Bubbling Fluidized Bed Combustor. Crude bottom and fly ashes and their size fractions, obtained through sieving, were analysed for a set of metals and for leaching behaviour. The eluates were also submitted to ecotoxicological characterization, using five bio-indicators. The highest concentrations of metals and metalloids were found in the lower particle size fractions of bottom and fly ashes. However, generally, it could not be observed any specific releasing pattern of metals depending on the particle size, except for fly ashes in which the releasing rate of some earth and alkali-earth metals seemed to increase for lower particle size fractions. No specific pattern of the ecotoxicity levels could be associated to the different particle size fractions of ashes. However, the fractions of bottom ashes with 4000-10000 µm and >10000 µm have presented the lowest ecotoxicity levels. All the samples were classified as ecotoxic, except the fraction of bottom ashes >10000 µm.

Keywords: biomass ashes; bulk content; chemical properties; ecotoxicological properties; leachability; particle size fractionation.

3.1.1 Introduction

Coal combustion and co-firing of low cost alternative fuels, such as tires, fuel oil and sewage sludge, have been tested for many years (Callén et al., 1998; Alvarez et al., 2004a; Alvarez et al., 2004b; Reddy et al., 2005; Izquierdo et al., 2008). These studies have demonstrated that when some wastes are used as alternative fuels in high blending percentages with coal (for example when using tyre rubber at a substitution level of 30%) can contribute to higher emissions levels of pollutants on flue gases and on the ashes produced during the thermal valorisation. More recently, the scientific community and the energy industry sector has started to study other types of wastes, such as the biomass residues, in order to find fuels with lower content of pollutants that can be blended with fossil fuels (Vamvuka et al., 2009; Singh et al., 2011).

In the case of the pulp and paper industry, a huge fraction of the biomass received is not appropriate for pulp and paper production. This residual fraction of biomass is considered to be a bio-waste that can be valorised. The most common valorisation route of these forest residues is the thermal valorisation through combustion, since the energy content is high enough for energy recovery (Sami et al., 2001; Acma et al., 2003; Al-Kassir et al., 2010; González et al., 2011b). In the Portuguese pulp and paper industry, one of the largest worldwide, the thermal valorisation of forest residues is widely used, contributing to reduce the forest fires, to improve the environmental performance of the energy production sector and, particularly, to reduce the emissions of GHG (Fruergaard et al., 2009; Morais et al., 2011).

Nevertheless, the combustion of forest residues gives rise to important quantities of ashes which requires sustainable management strategies. The type of ashes produced depends on the type of boiler and the treatment system of the exhaustion gases. Currently, two types of ashes are produced: bottom and fly ashes. In the systems with a circulating ashes line implemented, also there are circulating ashes, but normally they are mixed with bottom ashes due to similar properties and composition (please, see sub-chapter 2.2). The bottom ashes are collected at the bottom of the boilers, while the fly ashes are collected in the cooler zones of the boilers and/or retained in the treatment systems of the exhaustion gases.

These two types of ashes usually present different physical and chemical properties, depending on the type of biomass used and on the combustion conditions (furnace temperature profile, residence time of fuels and gases, biomass mixtures, fuel feeding systems and gas treatment systems, among other factors). The average size and particle size distribution of ashes are also different as it was observed by different authors (Rajamma et al., 2009; Singh et al., 2011; Esteves et al., 2012; Sata et al., 2012).

The hazardous nature of ashes is normally associated to the presence of contaminants, such as heavy metals, halogens and sulphates, among others. However, ashes are mainly composed by silica and salts of alkali and alkali-earth metals, which may influence the release of contaminants and their global toxicity. Stiernström et al. (2011) revealed that the presence of non-hazardous metals in the eluates, such as Ca and K, plays an important role on the overall toxicity of complex ashes eluates. In addition to Ca compounds, also the presence of Fe and Al hydrates interfere with the release of heavy metals due to sorption processes (Saffarzadeh et al., 2011).

Fly ashes present lower particle sizes than bottom ashes, while the concentrations of heavy metals and other contaminants, such as Cl, are generally higher than that of bottom ashes (Obernberger et al., 1997; Camerani et al., 2002; Sarkar and Rano, 2007). Several bibliographic references reveals that fly ashes present usually higher toxicity levels than bottom ashes (Aguiar del Toro et al., 2009; Dahl et al., 2009; Dahl et al., 2010).

There also are several studies dedicated to the leaching behaviour of ashes. For example, Lindberg et al. (2013) have studied the leaching rate of Sb, Mo, Ba and Cr VI in this type of matrix. Sloot et al. (2001) and Klemm (1998) have performed a deep study of the leaching behaviour of Mo and have concluded that this element leaches as molybdate and the leaching rate is pH-dependent. They have also observed an association of Mo to ettringite which, under high pH levels, produce water-soluble oxyanions species. Goumans et al. (1994) and Kent et al. (2007) have studied the mechanisms that influence the solubility of Ba. Goumans et al. (1994) have observed a high influence of sulphate in the leaching behaviour of Ba while Kent et al. (2007) have demonstrated the important role of chromate in the leaching behaviour of Ba. These two studies have concluded that the solubility of Ba is influenced either by sulphate and chromate.

The study of the leaching behaviour of Cr VI was studied by several authors (Allison et al., 1991; Perkins, 2000; Chirenje et al., 2002; Jing et al., 2006). These authors have observed that Cr VI may leachate in the presence of dissolved organic carbon (Chirenje et al., 2002), associated with ettringite (Perkins, 2000) or as calcium metalates (Allison et al., 1991; Jing et al., 2006).

However studies focusing on both chemical and ecotoxicological properties of size fractionated biomass ashes are scarce (Poykio et al., 2009; Dahl et al., 2010; Singh et al., 2011), being not possible to know if any patterns on the distribution of chemical species can be defined among the different size fractions of biomass ashes and even any kind of ecotoxicological pattern is associated to them.

The main aim of this study was to assess the chemical and ecotoxicological properties of size fractionated biomass ashes, which were produced during the combustion of forest residues in a boiler of a pulp and paper industry. Several ecotoxicological indicators were tested in order to evaluate the different toxicity responses and possible correlations with the chemical parameters. As there is a growing interest in the reutilization of these ashes, e.g. in civil engineering materials, this work intended to find out if any specific particle size fractions might be less interesting for this type of valorisation due to eventual high metal content and high ecotoxicity levels. This study will allow the development of new works, which will consist in the preparation of new formulations of concrete constituted, partially, by biomass ashes. These new formulations of concrete will be used for coastal zone protection. This study will also allow identifying if there are fractions less interesting, from the chemical and ecotoxicological point of view, for the removal of pollutants from industrial wastewater samples.

3.1.2 Materials and Methods

3.1.2.1 Origin of biomass ashes

The biomass ashes – fly and bottom ashes – were produced in a Portuguese biomass boiler of a pulp and paper industry that produces electricity by burning eucalyptus bark and pine bark in a Bubbling Fluidized Bed Combustor (BFBC). Bottom ashes were collected at the bottom of the BFBC and the fly ashes were collected in the hopper of the electrostatic precipitator used for flue gas treatment. The BFBC uses sand as fluidizing agent. The ashes were stored in air-tight polypropylene containers and maintained at a temperature of 4±1ºC, in the absence of light, to reduce ageing and to prevent weathering by uptake of moisture and carbonation.

3.1.2.2 Size fractionation of biomass ashes

Bottom and fly ashes were sieved using the following meshes (Retsch): 20, 50, 200, 500, 850, 2000, 4000 and 10000 μm (ISO 3310-2, 1999), depending on the type of ashes. The sieving process was performed in a vibratory sieve shaker AS 200 Digit (Retsch), during 90 min and with amplitude of 1.5 mm. The significant size fractions (mass higher than 5% w/w) were selected for detailed characterization.

3.1.2.3 Ashes inorganic composition

The ashes were submitted to acidic and alkaline digestions to determine the metal bulk contents. The quantification of Cr, Zn, Ni, Cu, Pb, Cd, Ba, Mo, Sb, Se, As, Hg, Mg, Al, Fe, Ca, Na and K was performed over samples submitted to an acidic digestion according to the USEPA Method 3051A (2007) (9 ml of concentrated nitric acid, 65% v/v, + 3 ml of concentrated hydrochloric acid, 37% v/v). The digestion was developed in microwave oven (Milestone Ethos 1600) using closed vessels and with controlled temperature (175 ± 5 °C, 10 min). The digested samples were filtered through glass fiber filters (Schleicher & Schuell) and the quantification of metals was achieved through AAS (Thermo AAS, M series): As (AAS air-acetylene flame; EN ISO 11969, 1996), Hg (AAS cold vapour; ISO 5666/1, 1983), Cd, Cu, Ni, Pb, Zn (AAS air acetylene flame; ISO 8288, 1986), Cr (AAS nitrous oxide-acetylene flame; ISO 9174, 2009), Se (AAS air-acetylene flame; ISO 9965, 1993), Mg, Sb, Fe (AAS air-acetylene flame, method 3111; APHA/AWWA/WEF, 2005), Ca (AAS nitrous oxide flame; ISO 7980, 2010), Na (AAS air-acetylene flame; ISO 9964-1, 1993), K (AAS air acetylene flame; ISO 9964-2, 1993), Mo, Ba, Al (AAS nitrous oxide-acetylene flame, method 3111; APHA/AWWA/WEF, 2005).

The alkaline digestion was performed following USEPA Method 3060A using a mixture of 20 g NaOH + 30 g Na_2CO_3 in 1 L of deionized water. The digested samples were filtered through 0.45 µm membrane filters (Schleicher & Schuell) and the final pH values were adjusted to 7.5±0.3 for quantification of Cr VI (USEPA Method 7196A, 1992).

The sulphur content was measured in the as-received ashes and in their particle sizes using an automatic analyser Leco SC-144DR (ASTM Method D 5016, 2008).

3.1.2.4 Impure silica content

The glass fibre filters with the filtration residues resulting from the acidic digestion was heated up to 1200°C, during 10 min, in a microwave oven (CEM, model MAS 7000). The remaining residue was weighted with an analytical balance (Metler Toledo; precision ±0.0001 g) and assumed to be the impure silica.

3.1.2.5 Leaching test and chemical and ecotoxicological characterizations of aqueous eluates

The as-received ashes and the particle size fractions selected were submitted to leaching according to the European standard EN 12457-2 (2002). The leaching test was performed with deionized water, using a L/S ratio of 10 L/kg, during 24 hours, at a temperature of 20±2ºC. The suspensions were then filtered through 0.45 µm porosity nitrate cellulose membranes (Schleicher & Schuell).

The chemical characterization of the filtered eluates comprised the following parameters: pH (electrometric, method 4500; APHA/AWWA/WEF, 2005), DOC (Dissolved Organic Carbon) (Combustion and detection by Infra-Red; ASTM D7573, 2009), SO_4^{2-} (Turbidimetric, method 4500 E; APHA/AWWA/WEF, 2005), F^- (SPADNS, method 4500 D; APHA/AWWA/WEF, 2005), TDS (gravimetric method; APHA/AWWA/WEF, 2005), Cl^- (Mohr's method; ISO 9297, 1989), As (air-acetylene flame; EN ISO 11969, 1996), Hg (AAS cold vapour; ISO 5666/1, 1983), Cd, Cu, Ni, Pb, Zn (AAS air acetylene flame; ISO 8288, 1986), Cr (AAS nitrous oxide-acetylene flame; ISO 9174, 2009), Cr VI (NF T90-043, 1988), Se (AAS air acetylene flame; ISO 9965, 1993), Sb, Mg, Fe (AAS, air-acetylene flame; APHA/AWWA/WEF, 2005), Na (AAS air acetylene flame - ISO 9964-1, 1993), K (AAS air acetylene - ISO 9964-2, 1993), Ca (AAS nitrous oxide flame - ISO 7980, 2010), Al, Ba, Mo, (AAS, nitrous oxide-acetylene flame; APHA/AWWA/WEF, 2005).

The ecotoxicological characterization of the eluates comprised the following assays: a) Luminescence inhibition of the bacterium *Vibrio fischeri* (performed in a miniaturized system of Microtox® according with ISO 11348-3, 2007); b) Mobility inhibition of the freshwater micro-crustacean *Daphnia magna* (performed in a miniaturized kit of Microbiotests® according with ISO 6341, 1996); c) Mobility inhibition of the marine micro-crustacean *Artemia franciscana* (miniaturized test kit from MicroBioTests Inc. according with ASTM E1440–91, 2004); d) Growth inhibition of the freshwater microalgae *Pseudokirchneriella subcapitata* (performed in a miniaturized kit of Microbiotests® according with ISO 8692, 2004); e) Growth inhibition of the marine microalgae *Phaeodactylum tricornutum* (performed in a miniaturized kit of Microbiotests® according with ISO 10253, 2006).

The Effective Concentration (EC_{xx}) of each eluate was determined for each biological indicator. EC_{xx} means the eluate concentration, expressed in percentage, which caused a specific reference effect of *xx*% for each biological population tested.

Each EC_{xx} has been transformed in Toxicity Units (*TU*) (dimensionless) according to Eq. 3.1:

$$TU = 100\%/EC_{xx} \qquad \text{Eq. 3.1}$$

Three types of *TU* were calculated for each sample: a) a global *TU*, which was based on the average of the *TU* of all biological indicators; b) a TU based on the average values of *TU* of the marine biological indicators (*V. fischeri*, *P. tricornutum* and *A. franciscana*); and c) a *TU* based on the average values of *TU* of the freshwater biological indicators (*D. magna* and *P. subcapitata*). If EC_{xx} values were below or above the extreme concentrations tested, the calculation of *TU* was based on the extreme concentrations (ex. when $EC_{xx} < 1\%$ it was considered $EC_{xx} = 1\%$; when $EC_{xx} > 90\%$ it was considered $EC_{xx} = 90\%$). The eluates were not submitted to the correction of the pH levels prior the ecotoxicological tests, since the correction of the pH may promote changes in the solubilisation or speciation of metals and it was also an aim of this work to include the pH effect on the global ecotoxicity of ashes and their size fractions.

3.1.2.6 Ecotoxicological classification of the ashes

The evaluation of the ecotoxic properties (Hazardous property H14, according to the Council Directive 91/689/EEC, of the Council of the European Communities) of the ashes were based on the CEMWE (Lapa et al., 2002; Barbosa, 2005). The original CEMWE methodology was adapted as it was discussed in a previous work (Lapa et al., 2002). The ecotoxicological classification of the ashes was based on chemical and ecotoxicological characterization of the eluates of the ashes. The chemical parameters comprised in the ecotoxicological classification, through CEMWE, were As, Cd, Cr, CrVI, Cu, Hg, Ni, Pb, Zn and phenolic compounds. The ecotoxicological parameters comprised in the ecotoxicological classification, through CEMWE, were *D. magna* and *V. fischeri*.

3.1.3 Results and Discussion

3.1.3.1 Size fractionation

Figure 3.1 shows the particle size distribution of bottom and fly ashes as the cumulative undersize distributions. The horizontal lines crossing *yy*=10%, *yy*=50% and *yy*=90% define the parameters D_{10}, (cumulative undersize distribution of 10%), D_{50} (cumulative undersize distribution of 50%), and D_{90}).

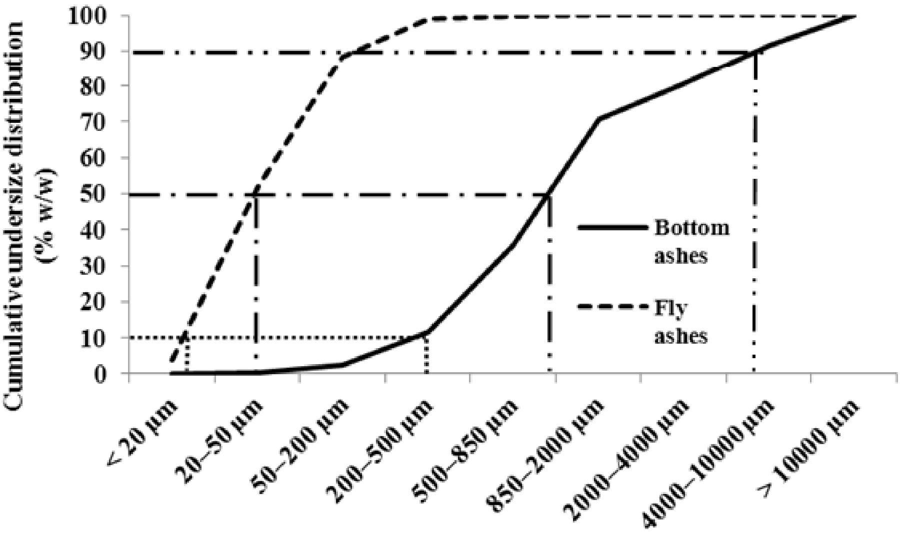


Figure 3.1- Particle size distribution of biomass ashes (cumulative undersize distribution of 90%), respectively.

The bottom ashes were mainly constituted by particles with dimensions falling in the size ranges of: 200-500 µm (9.2% w/w), 500–850 µm (24.1% w/w), 850–2000 µm (34.9% w/w), 2000–4000 µm (10.0% w/w), 4000–10000 µm (10.8% w/w) and > 10000 µm (8.5% w/w). These six particle size fractions comprised 97.5% of the total mass of bottom ashes. The bottom ashes presented D_{10}= 307 µm, D_{50}= 980 µm and D_{90} = 6444 µm.

The fly ashes were composed by finer particles. The majority of their mass (94.8% w/w) was obtained in three size ranges: 20–50 µm (48.0% w/w), 50–200 µm (36.3% w/w) and 200–500 µm (10.5% w/w). The fly ashes presented D_{10}= 13 µm, D_{50}=34 µm and D_{90}= 161 µm.

This size distribution of fly ashes is similar to that found by Singh et al. (2011) (D_{90} = 135 µm). The studies performed by Rajamma et al. (2009) have shown that the particle sizes of fly ashes were typically below 50 µm. These authors have cut the ashes at 500 µm in order to remove the elongated particles, which can explain the lower dimension of the particles. Esteves et al. (2012) have found a slightly lower particle dimension (D_{50}=21 µm) in a study related with fly ashes produced in a co-generation process of a pulp and paper industry. The works developed by Sata et al. (2012) have also shown a lower particle dimension of the fly ashes, since their D_{50} were between 10 and 13 µm. The differences in the particle size can be related with several aspects, namely the combustion system, the characteristics of the fluidizing agent, the system treatment of the gaseous effluents and the fuels used.

3.1.3.2 Bulk content in metals

Figure 3.2 and Figure 3.3 show the bulk inorganic composition of bottom ashes and their particle size fractions for a set of elements. The concentration of Hg, Cd, Ni, Mo, Pb, Cu, Ba, and Cr (not shown in these Figures) were below the quantification level.

Bottom ashes were mainly composed by alkali and alkali-earth metals and trace concentrations of heavy metals and metalloids. Alkali (Na, K) and alkali-earth elements (Ca, Mg) were the major components of biomass ashes, due to high concentrations of these elements in forest biomass. Some of the metals and metalloids determined are also present in forest biomass due to their role as minor nutrients (Steenari et al., 1999a; Dahl et al., 2009; Singh et al., 2011).

Generally, the highest concentrations of alkali and alkali-earth metals, heavy metals and metalloids were found in the lowest particle size fractions of 200-500 and 500-800 µm. Dahl et al. (2009) have found in their work related with ashes produced by the co-combustion of biomass-derived fuels (wood chips, sawdust, bark, and peat) similar concentrations of Cu and Zn (3.7 mg Cu/kg and 41 mg Zn/kg), but lower concentrations of K (90 mg K/kg), Mg (2100 mg Mg/kg) and Na (100 mg Na/kg) and a higher concentration of Ca (19200 mg Ca/kg). In a work dedicated to chemical extraction of heavy metals from bottom and fly ashes produced in a biomass combustion system of a pulp and paper mill plant, Nurmesniemi et al. (2008) have found higher values of Ca (29300 mg /kg) than those found in the present work. These differences may be related with the composition of the fuels or with the combustion conditions, namely, with the temperature in the combustion chambers.

It was not possible to measure S content in the higher size fractions, due to the heterogeneity and dimension of the particles. Nevertheless, in the other particle size fractions it was observed a tendency for the increase of S content with the increase of the particle size, namely in the fractions higher than 500-850 µm. In a review paper of Khan et al. (2009), the composition of several biomass types, sewage sludge and bituminous coal and the composition of the ashes produced by these fuels were presented. In what concerns the S content, its concentration has ranged between the detection limit and 2000 mg/kg in the biomass fuels and between the detection limit and 56000 mg S/kg in the bottom ashes produced by this fuel.

The work developed by Vamvuka et al. (2009) related with the combustion of lignite, olive kernel and olive tree wood has indicated that the biomass fuel presented an S content much more reduced than that indicated by Khan et al. (2009), namely 800 mg S/kg, for olive kernel and 300 mg S/kg for olive tree wood, which has produced bottom ashes with lower S content

(14000 mg S/kg and 8400 mg S/kg in the bottom ashes obtained in the combustion of olive kernel and olive tree wood, respectively). Ingerslev et al. (2011) have studied some properties of wood chips (*Pinus sylvestris L.*) and the ashes produced by the combustion of this material. These authors have found an S content of 5260 mg/kg in the ashes they have characterized.

The wide range of the S content, in the bottom ashes, found by Khan et al. (2009), Vamvuka et al. (2009) and Ingerslev et al. (2011) may be related with the composition of the biomass used in the combustions assays. The concentration of S in the as-received bottom ashes characterized in the present work falls (376 mg/kg db) is below the concentrations found by those authors.

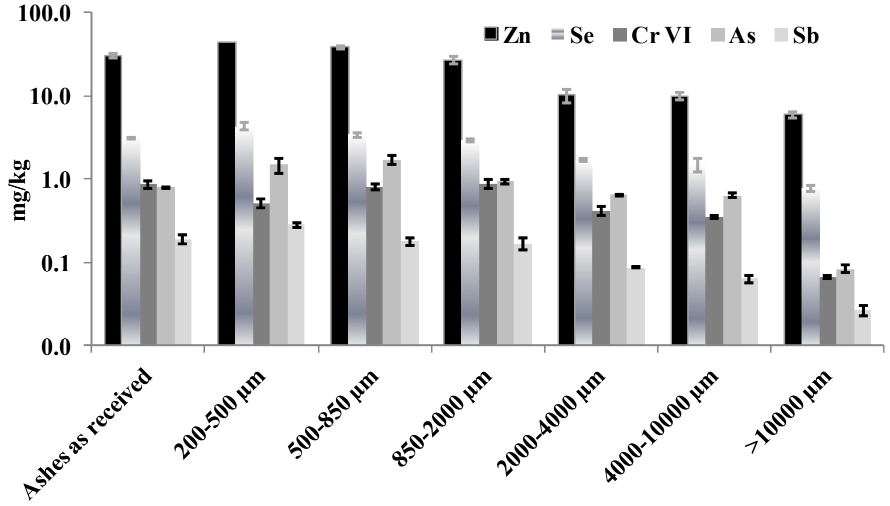


Figure 3.2 - Inorganic bulk content of bottom ashes and their particle size fractions for Zn, Se, CrVI, As, and Sb (n=2)

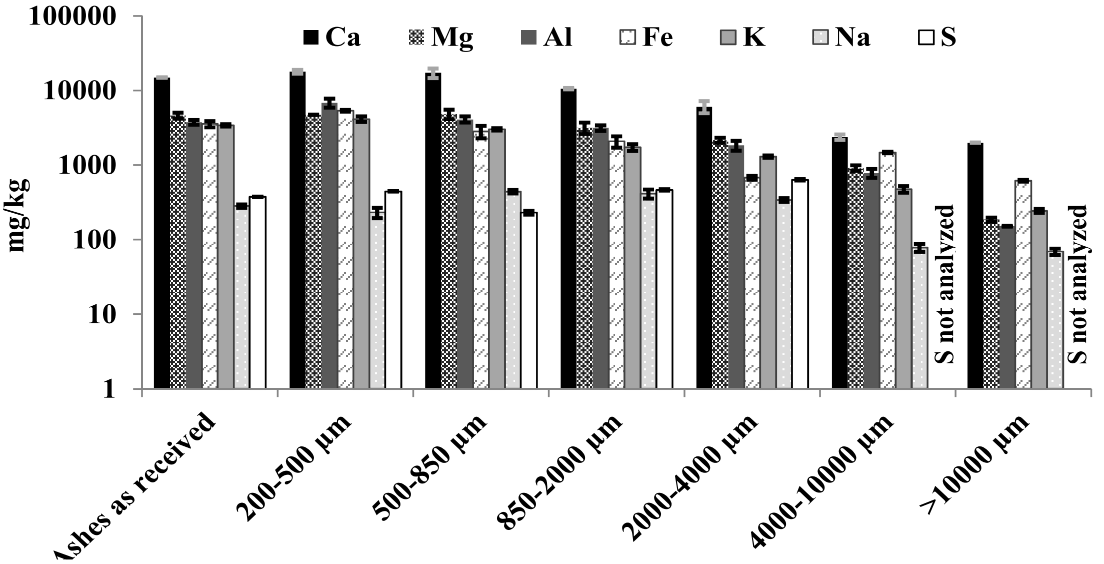


Figure 3.3 - Inorganic bulk content of bottom ashes and their particle size fractions for Ca, Mg, Fe, K, Na, and S (n=2)

Figure 3.4 to Figure 3.7 show the results of bulk content of metals present in fly ashes. The concentrations of Hg, Cd, Ni, and Mo were below the quantification limit.

These ashes were mainly composed by alkali and alkali-earth metals, and vestigial concentrations of heavy metals and metalloids. Globally, the highest concentrations of metals were also determined in the lowest particle size fraction (20-50 μm) and the lowest concentrations were detected in the highest particle size fraction (200-500 μm).

The concentrations of heavy metals were globally higher in fly ashes than those determined for bottom ashes. For instance, Pb and Ba contents were higher in the size fractions of 20-50 μm and 50-200 μm, ranging from 27.9 mg Pb/kg to 306 mg Ba/kg. The Hg content was <0.503 mg/kg in the as-received ashes and ranged between 0.408 and 0.598 mg/kg in the size fractionated samples. Cu and Cr were above the quantification limits in all size fractions in concentrations ranging from 8.96 mg Cu/kg (200-500 μm) up to 59 mg Cr/kg (20-50 μm). The presence of these elements in the fly ashes can be explained by the fact that some trace metals are often volatilized during combustion and condense in the cooler parts of the exhaustion system. Condensation over the surface of particles that constitute fly ashes leads to higher concentrations of heavy metals in fly ashes rather than in bottom ashes (Steenari et al., 1999b).

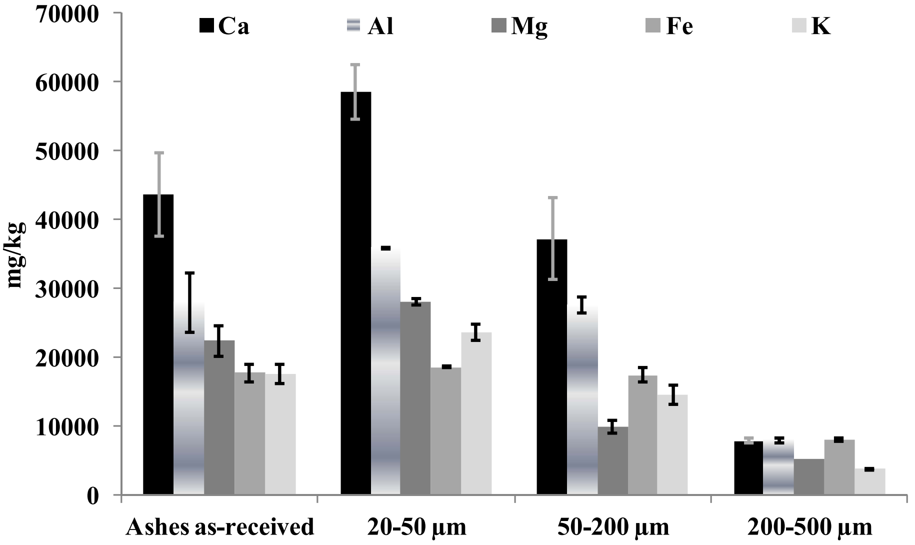


Figure 3.4 - Inorganic bulk content of fly ashes and their particle size fractions for Ca, Al, Mg, Fe and K (n=2)

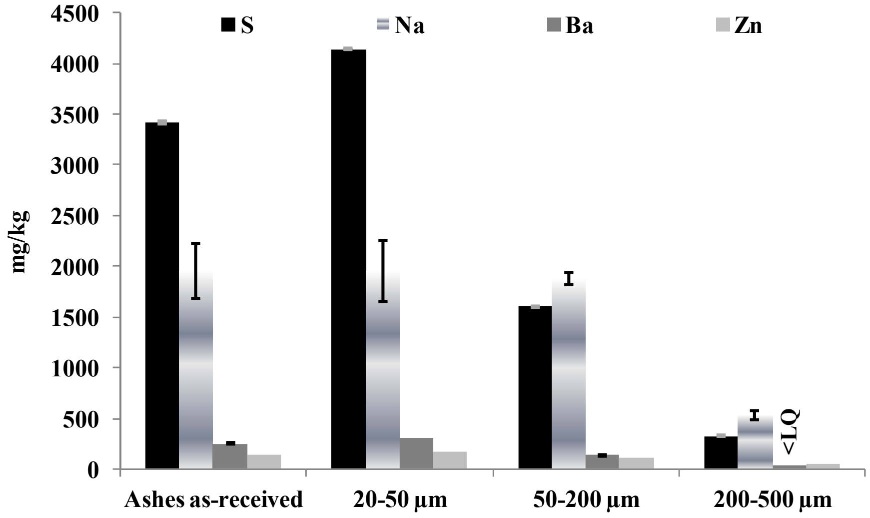


Figure 3.5 - Inorganic bulk content of fly ashes and their particle size fractions for S, Na, Ba, and Zn (n=2)

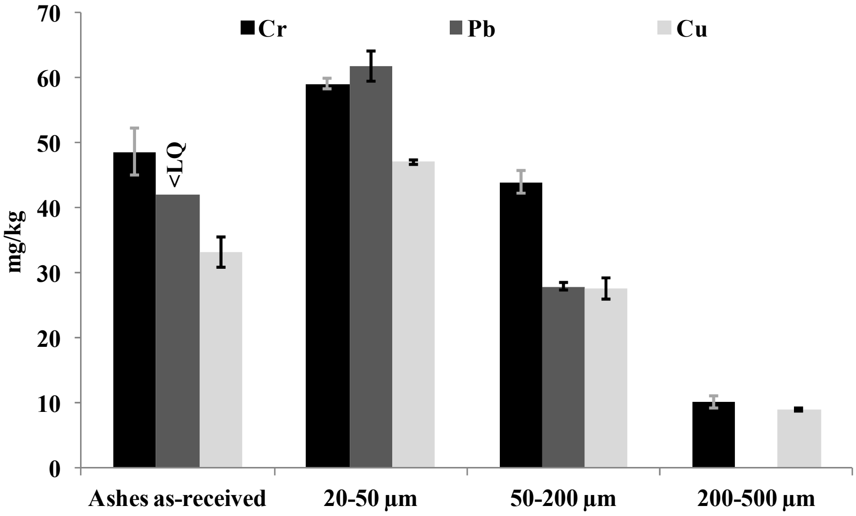


Figure 3.6 - Inorganic bulk content of fly ashes and their particle size fractions for Cr, Pb, and Cu (n=2)

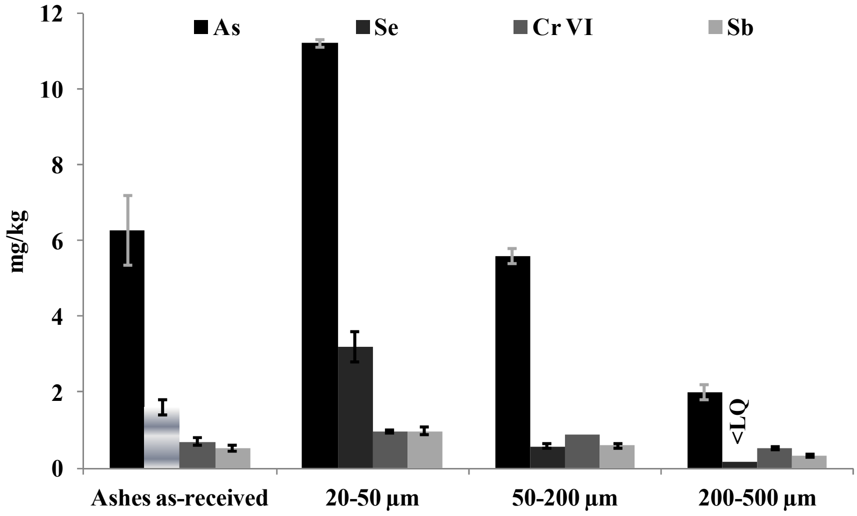


Figure 3.7 - Inorganic bulk content of fly ashes and their particle size fractions for As, Se, CrVI, and Sb (n=2)

Rajamma et al. (2009) have characterized two types of fly ashes. One of them was produced in a biomass thermal power plant dedicated to electricity production from forest residues, while the other one was produced in a biomass co-generation plant located in a pulp and paper industry. These authors have found similar concentrations of, for example, Hg (<1.0 mg/kg), Cd (1 and 1.3 mg/kg) and Ni (27 to 35 mg/kg) to those determined in the present work. The concentrations of Pb and Cu were also similar to those found by Rajamma et al. (2009) in the fly ashes from the biomass co-generation plant (12 mg Pb/kg and 27 mg Cu/kg). Nevertheless, these authors have found higher concentrations of these two metals in fly ashes collected at the biomass thermal power plant dedicated to electricity production (191 mg Pb/kg and 99 mg Cu/kg).

Ingerslev et al. (2011) have found slightly higher levels of Cd (14.6 mg/kg), Ni (18.8 mg/kg) and lower Pb (19.3 mg/kg) than those determined in the present study, but higher concentrations of Cu (110 mg/kg) and Cr (159 mg/kg). Dahl et al. (2009) have found lower concentrations of Cu (22 mg/kg), but higher concentrations of Zn (370 mg/kg).

Singh et al. (2011) have performed an extensive characterization of fly ashes produced from different fuels. Concerning the biomass fly ashes, these authors have found similar concentrations of Hg (<0.1 mg/kg), Mo (10 mg/kg), Zn (161 mg/kg), Pb (26 mg/kg), Ba (376 mg/kg) and Cr (61 mg/kg) to those determined in the present work. The concentration of Cu was higher (113 mg/kg) and As and Se concentrations reported were 60-fold and about 15-fold lower, respectively, than those found in the present work.

According to IAWG (1997), the metals that may form oxyanions, As, Se and Sb, tend to form volatile compounds at relatively low temperatures and are easily partitioned into the fly ashes and other air pollution control residues. Nearly all As and Sb volatilize at temperatures above 500 °C. If these elements condense in fly ashes surface, they tend to be oxidized by the metal oxides and form the corresponding non-volatile metal arsenates or antimonates (Mahuli et al., 1997; Paoletti, 2002; Sterling and Helble, 2003; Paoletti et al., 2001). This fact may explain the higher concentrations of As, Se and Sb in fly ashes than in bottom ashes.

Dahl et al. (2009), Ingerslev et al. (2011) and Esteves et al. (2012) have found similar concentrations of Mg to those presented in Figure 3.4: 25000 mg/kg, 19860 mg/kg and 17000 mg/kg, respectively. In what concerns K, Esteves et al. (2012) have found a similar concentration (17177 mg/kg), but the concentrations found by Ingerslev et al. (2011) (43500 mg/kg) and Dahl et al. (2009) (9700 mg/kg) were slightly different. Esteves et al. (2012) have determined a similar concentration of Ca (37000 mg/kg), while Ingerslev et al. (2011) and Dahl et al. (2009) have found higher concentrations (129000 mg/kg and 140000 mg/kg, respectively). The concentrations of Na determined in the present study were similar to those found by Ingerslev et al. (2011) (5970 mg/kg) and Dahl et al. (2009) (1400 mg/kg).

The S content in the as-received fly ashes was higher than in the as-received bottom ashes and has shown a tendency to decrease with the increasing of the particle size of fly ashes, which was very marked. Nevertheless, the S content seems low when compared with the results of other works. For instance, the work developed by Ingerslev et al. (2011), related with the properties of fly ashes from forest biomass, has shown an S content about four times higher than that observed in the present work.

3.1.3.3 Impure silica content

Figure 3.8 shows the content on impure silica for both as-received bottom and fly ashes and for their particle size fractions.

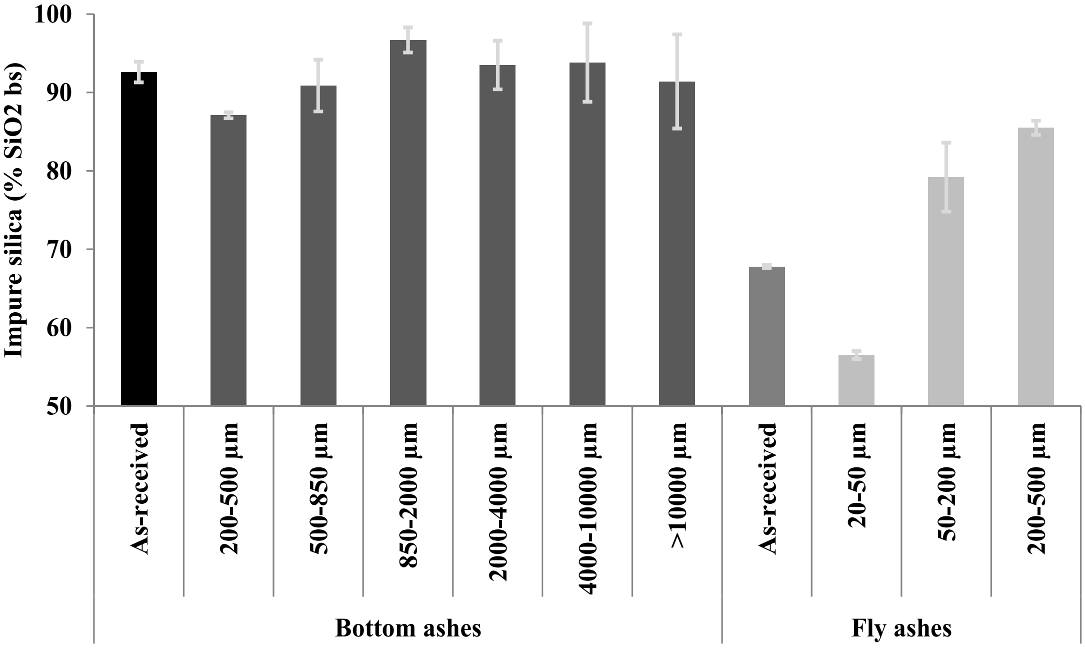


Figure 3.8 - Impure silica content of bottom and fly ashes and their particle size fractions (n=2)

The content on impure silica was found to be higher in bottom ashes than in fly ashes. It was not observed any pattern in the distribution of this parameter with the particle size increasing of bottom ashes, except that the lower size fraction presented the lower contents.

On the contrary, the concentration of impure silica in fly ashes has risen with the particle size increase, which may be related with the elutriation effect of sand that was used as fluidizing agent.

3.1.3.4 Chemical characterization of aqueous eluates

Figure 3.9 to Figure 3.12 show the chemical characterization of eluates of bottom ashes and their particle size fractions. The concentrations of As, Se, Hg, Cd, Ni, Zn, Pb, Cu, Cr, and Fe were below the limit of quantification. Figure 3.13 to Figure 3.16 show the chemical characterization of eluates of fly ashes and their particle size fractions. The concentrations of Se, Hg, Cd, Ni, Zn, Pb, Cr, and Fe were below the limit of quantification.

The eluates of both biomass ashes were highly alkaline, due to the presence of oxides that are formed during the combustion process in excess air. All eluates have demonstrated the high mobility of chlorides and sulphates from the bottom and fly ashes, although they present a different mobility pattern, depending on the particle size increase. For both ashes, the concentration of chlorides have decreased with the particle size increase from 200-500 μm up to >10000 μm, while sulphates have shown an increasing mobility with the increase of particle size distribution. The increase was more evident in the higher size fractions. Nevertheless, due to the higher concentrations of chlorides than sulphates in the eluates of both ashes, TDS have shown a variation similar to chlorides, i.e., a decrease of their concentration with the increase of the particle dimensions, although this variation has been more pronounced in fly ashes.

The different mobility of alkali and alkali-earth metals, namely Ca, Na and K, from both bottom and fly ashes, was the most evident characteristic of these biomass ashes. No mobility pattern of these metals from bottom ashes was evident, as their release may be highly controlled by the presence of other chemical species, such as sulphates. In a different way, the release patterns of Ca, K, and in a lower extent of Na, seemed to follow a decreasing leaching rate with the particle size increase of fly ashes. This is probably due to the lower concentration of controlling chemical releasing species in fly ashes, such as sulphates, than in bottom ashes.

The eluates of both biomass ashes were characterized, as stated previously, by low or undetectable concentrations of heavy metals and metalloids showing the low content and low mobility of these metals in fly and bottom ashes. No special mobility pattern from both biomass ashes was possible to define for these groups of metals, due to their low concentrations. It was observed some exceptions in what concerns the solubilisation rate of Sb, Mo, Ba and Cr VI in bottom ashes. According to Lindberg et al. (2013), these elements can form compounds such as oxides, sulphides and sulphates, which are easily soluble.

According to a study performed by van der Sloot et al. (2001) related with the water leachable metal forms in bottom ashes from MSW incineration plants, at a L/S ratio of 2 L/kg, almost all the water-soluble Mo was released, in the form of molybdate (oxyanion). These authors have concluded that the leaching of Mo from that type of ashes was pH-dependent, with the highest leaching rates being observed for pH levels above 8. According to Klemm (1998), it is possible to find ettringite in ashes. This mineral may contain oxyanions of amphoteric heavy metals, which under high pH levels usually form water-soluble oxyanions species. The combination of pH level and oxyanion-substituted ettringite may explain the high leaching levels observed for Mo.

According to Goumans et al. (1994), the solubility of Ba is sulphate-dependent. The ratio between the concentrations of sulphate and Ba, in the eluates of as-received bottom ashes, was 31 mmol SO_4^{2}/mmol Ba. This means that the concentration of sulphate was clearly higher than the concentration of Ba, which may indicate that Ba might be solubilized as barium sulphate. In the eluates from the size fractionated bottom ashes, the ratio between the concentrations of sulphate and Ba were 23 mmol SO_4^{2-}/mmol Ba (200-500 µm), 48 mmol SO_4^{2-}/mmol Ba (500-850 µm) and 58 mmol SO_4^{2-}/mmol Ba (850-2000 µm). Once again, this may indicate that Ba has probably solubilized as barium sulphate. According to Kent et al. (2007), Ba can also be mobilized as barium chromate ($BaCrO_4$) at high pH levels. In the eluates of the higher particle size fractions, the concentrations of Ba were below the quantification limit despite the high concentration of sulphates.

Although the sensibility of the quantification methods of Cr and Cr VI are different, one can deduce that at least 50% of Cr may exist in the hexavalent oxidation state. Cr VI is more mobile than Cr III under alkaline conditions and it does not exist as free ion, but as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), or chromium trioxide (CrO_3). Therefore, Cr VI behaves as divalent anions rather than hexavalent cations (Chirenje et al., 2002).

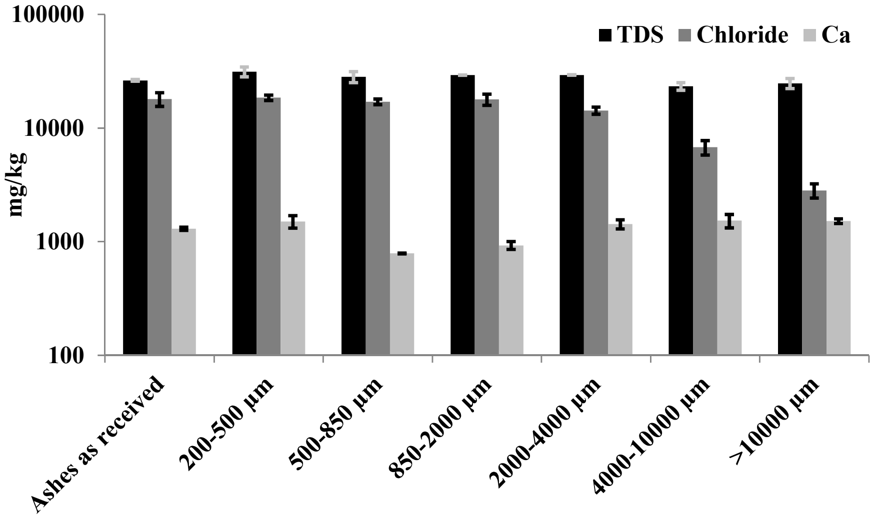


Figure 3.9 - Content on TDS, chloride and Ca of the eluates of bottom ashes and their particle size fractions (n=2)

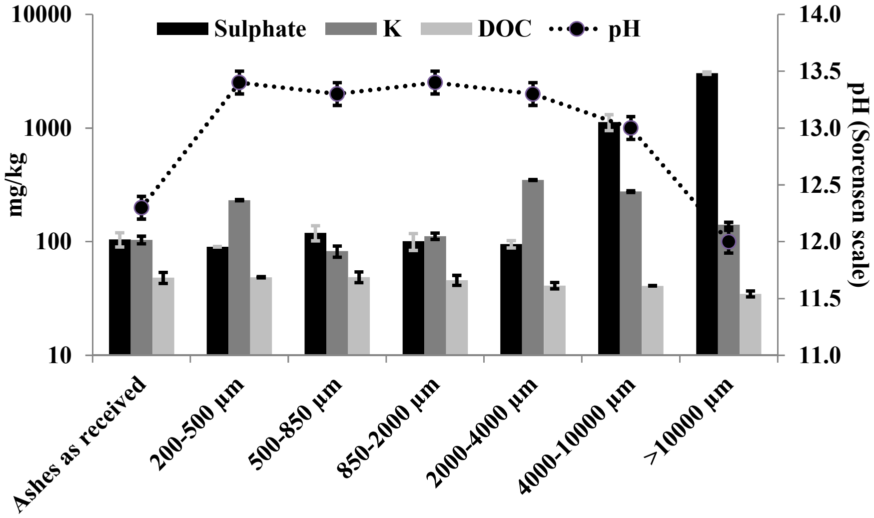


Figure 3.10 - Content on sulphate, potassium, DOC and pH level of the eluates of bottom ashes and their particle size fractions (n=2)

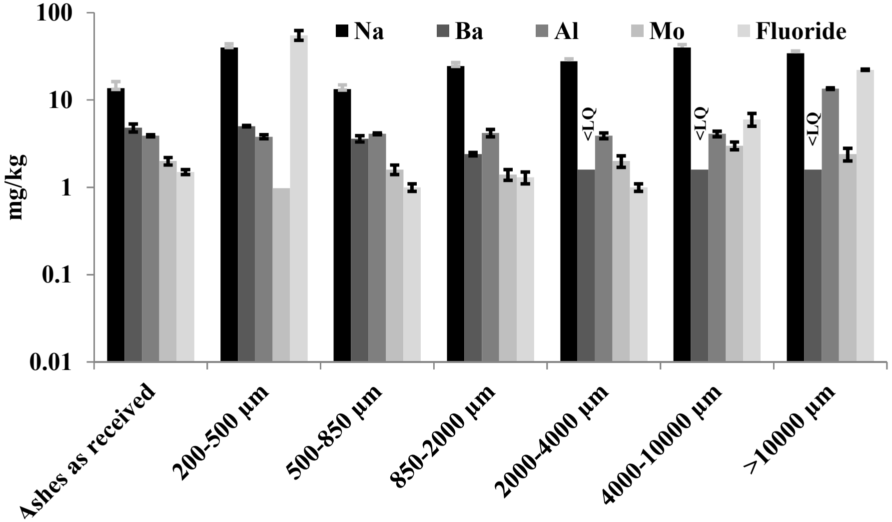


Figure 3.11 - Content on Na, Ba, Al, Mo, and fluoride of the eluates of bottom ashes and their particle size fractions (n=2)

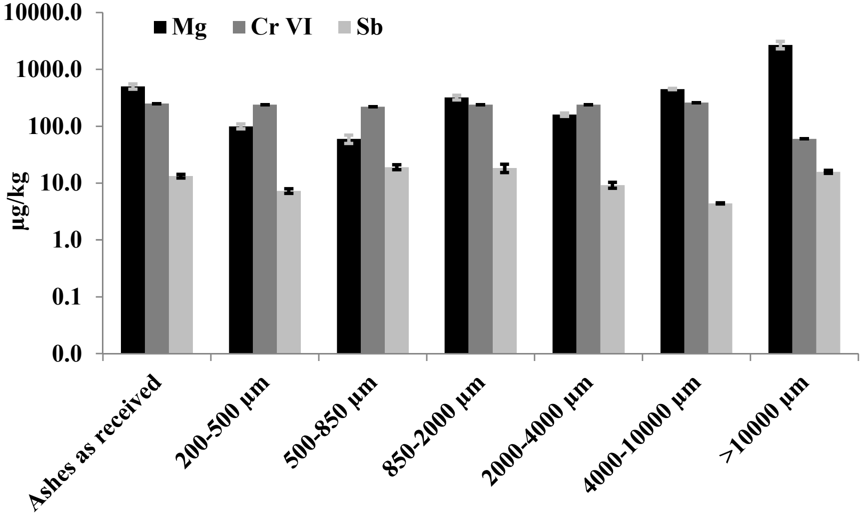


Figure 3.12 - Content on Mg, CrVI, and Sb of the eluates of bottom ashes and their particle size fractions (n=2)

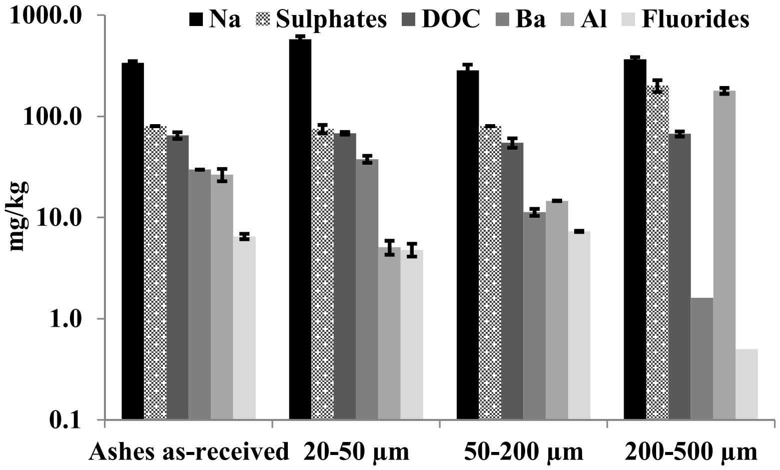


Figure 3.13 - Content on Na, sulphates, DOC, Ba, Al, and Fluorides of the eluates of fly ashes and their particle size fractions (n=2)

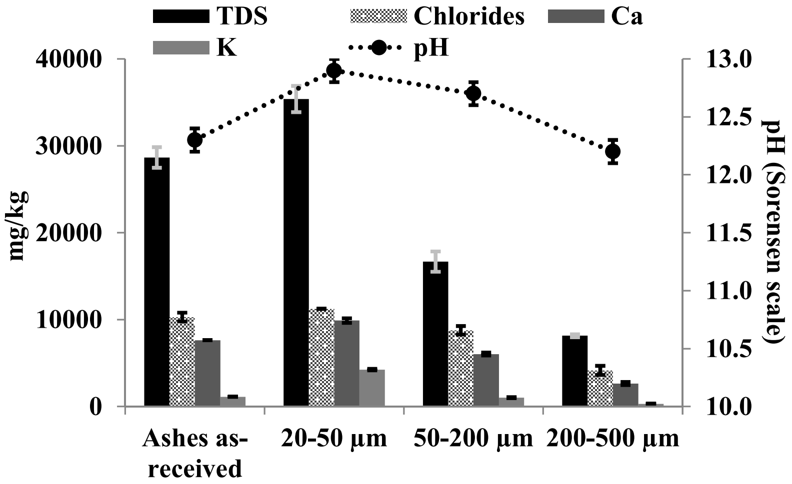


Figure 3.14 - Content on TDS, chlorides, K, and pH levels of the eluates of fly ashes and their particle size fractions (n=2)

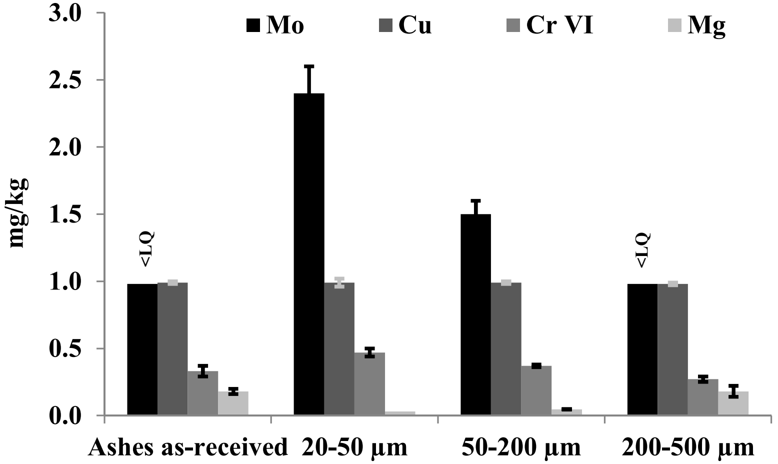


Figure 3.15 - Content on Mo, Cu, CrVI, and Mg of the eluates of fly ashes and their particle size fractions (n=2)

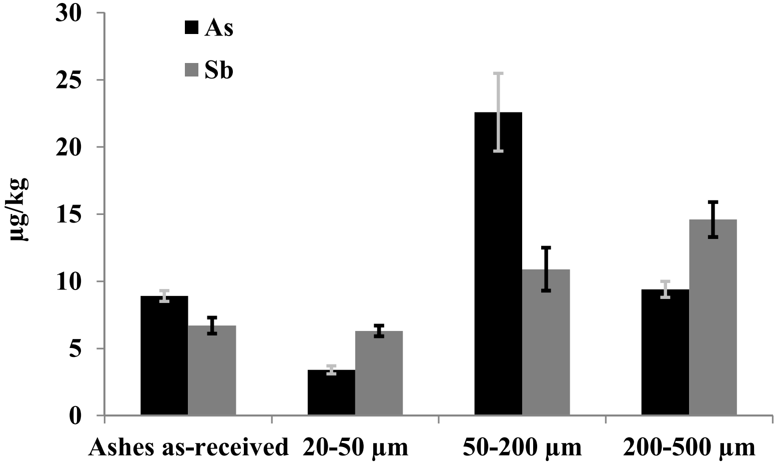


Figure 3.16 - Content on As, and Sb of the eluates of fly ashes and their particle size fractions (n=2)

According to Chirenje et al. (2002), the solubilisation of Cr VI may be associated with the presence of DOC, if the organic carbon compounds form complexes of cations, like Fe or Al. Since the concentrations of Fe in the eluates of the ashes are below the quantification limit, the mobilization of Cr VI from the ashes may be associated to the complex DOC-Al-Cr VI. As it was indicated previously, Cr VI might have also leached as barium chromate (Kent et al., 2007). Perkins (2000) has shown that Cr VI-ettringite precipitated from Ca- and Al-containing solutions at pH values greater than 10. At high pH levels, when there is an excess of carbonate over the available Ca, Cr VI-ettringite is unstable due to the formation of calcite and gibbsite. Therefore, Cr VI-ettringite and related minerals are most likely to be important in systems at high pH values when there is a large excess of Ca over carbonate or when precipitation of calcium carbonate is inhibited. Allison et al. (1991) and Jing et al. (2006) have also observed that the release of CrVI and CrIII is essentially associated to calcium metalates ($CaCrO_4.xH_2O$, $Ca_2Cr_2O_5.yH_2O$) and the solubility of CrVI as calcium metalate is higher than the solubility of CrIII as calcium metalate. Besides this, Cornellis et al. (2008) have indicated that the most common oxidation state of Cr in the ashes is the hexavalent state. These facts may explain the presence of CrVI in the eluates.

The concentrations of As, Sb and Ba in fly ashes were all above the quantification limits. Nevertheless, the leaching rates were very low, especially for As and Sb. According to Cornelis et al. (2008), the release of As and Sb is associated to Ca and Ba metalates. Nevertheless, the solubilities of Ca and Ba metalates are relatively low, especially for pH around 12, which may explain the low leaching rates of As and Sb.

The release of sulphates was similar to what happened for the bottom ashes, presenting an increase in the higher size fractions of ashes. In the bottom ashes, the release of S, as sulphate, has not followed any pattern and has ranged between 5% and about 17%. In what concern the fly ashes, the release of S, as sulphate, has ranged between 0.6% and about 20%. In the fly ashes it was observed a very marked tendency, since the release of S as sulphates has increased with the increasing of the particle size of fly ashes.

The concentrations of Cu in the eluates of fly ashes and in the eluates of the particle size fractions were similar. Cappai et al. (2012) have studied the mobility of a set of metals from fresh fly ashes of MSW combustion plants and from fly ashes submitted to accelerated carbonation. In what concerns the leaching behaviour of Cu, Cappai et al. (2012) have concluded, for pH levels similar to those observed in the present work (around 12-13), that the solubilisation of Cu was slightly higher in the treated fly ashes than in the fresh ashes. In this study, despite the ashes have not been submitted to accelerated carbonation, the leaching behaviour of Cu was similar to that observed by Cappai et al. (2012) for treated fly ashes.

Quina et al. (2009) have studied the influence of pH on the leaching behaviour of a set of metals from municipal solid waste air pollution control residues. They have concluded that the leaching level of Cu was similar to those observed in the present work (about 1 mg Cu/kg for pH levels of 12-13). Those authors have observed, for pH levels of about 12-13, concentrations levels of Pb (300-800 mg/kg), Zn (30-60 mg/kg), Cr (5-20 mg/kg) and Ni (1-4 mg/kg) higher than those found in the present study. These relative high differences in eluates, especially in what concerns Pb, may be related with the different composition of fuels used.

3.1.3.5 Ecotoxicological characterization and classification of eluates

Figure 3.17 and Figure 3.18 show the ecotoxicological characterization of eluates.

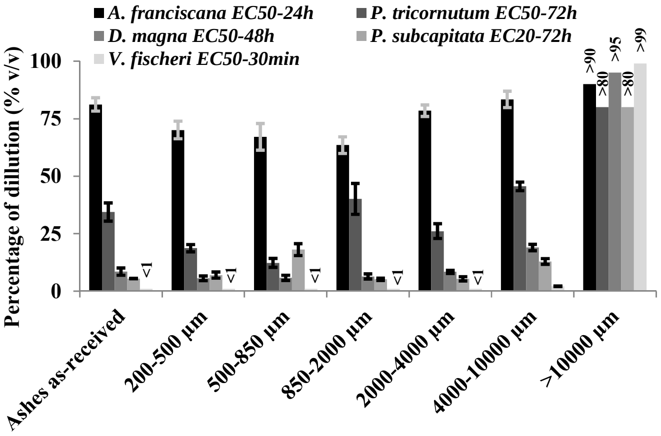


Figure 3.17 - Ecotoxicological characterization of eluates from bottom ashes and their particle size fractions (n=2)

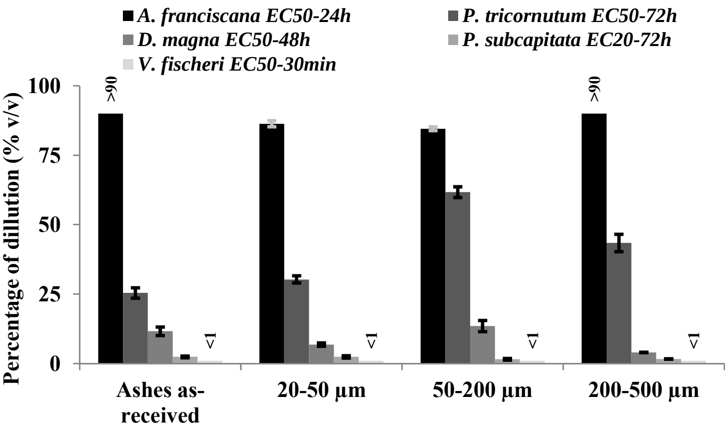


Figure 3.18 - Ecotoxicological characterization of eluates from fly ashes and their particle size fractions (n=2)

Figure 3.19 to Figure 3.21 show the TU values for all biological indicators tested, for marine biological indicators, and for the freshwater biological indicators, respectively.

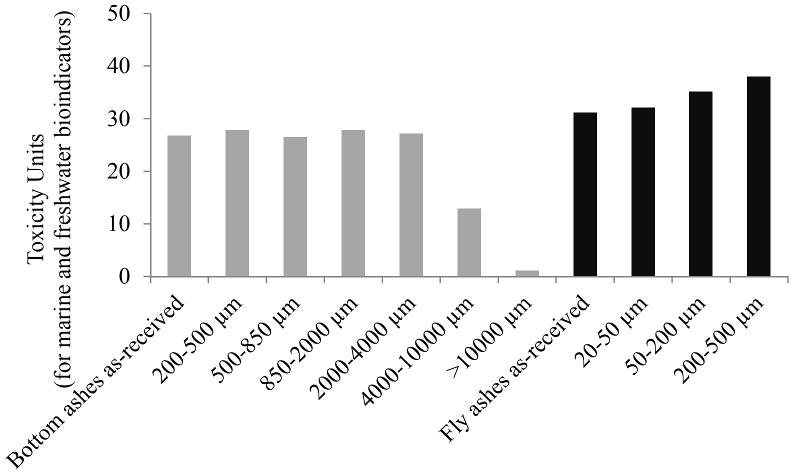


Figure 3.19 - Toxicity Units of bottom and fly ashes and their particle size fractions for both marine and freshwater biological indicators

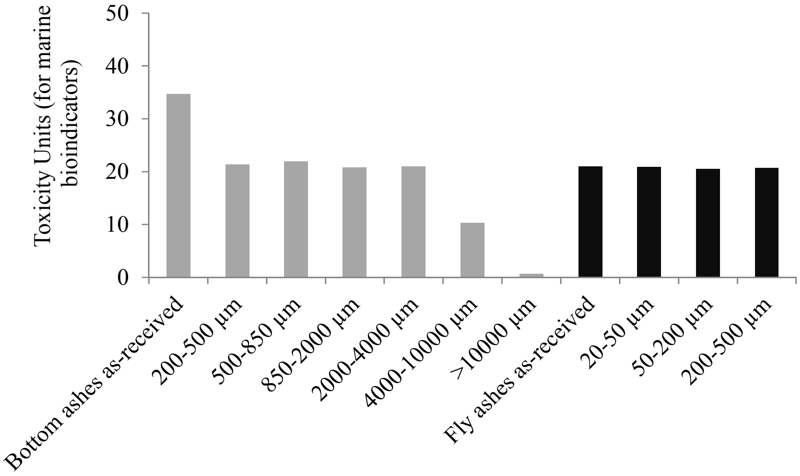


Figure 3.20 - Toxicity Units of bottom and fly ashes and their particle size fractions for marine biological indicators

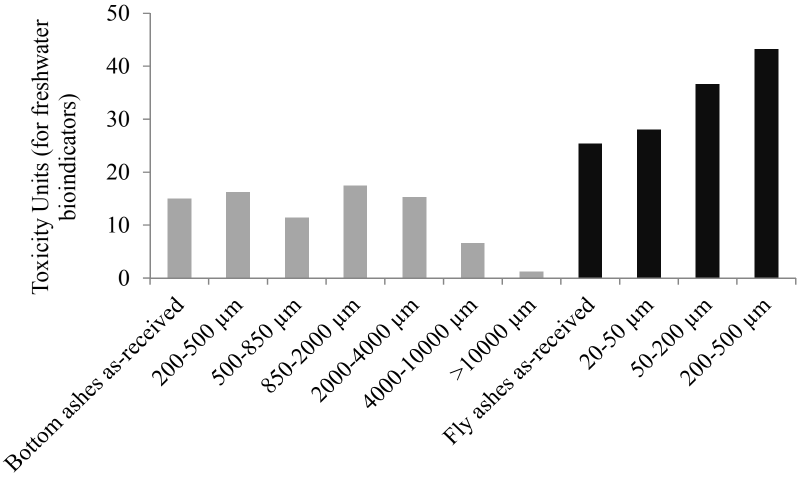


Figure 3.21 - Toxicity Units of bottom and fly ashes and their particle size fractions for freshwater biological indicators

Generally, *V. fischeri* was found to be the most sensitive biological indicator and *A. franciscana* the least sensitive for all eluates. Excluding the bacterium *V. fischeri*, the biological indicators from marine environment (*P. tricornutum* and *A. franciscana*) have shown lower sensitivity to the toxicity levels of all eluates than the organisms from fresh water environments (*P. subcapitata* and *D. magna*). This behaviour may be related with the fact that the marine environment may have promoted a reduction of the toxicity of the compounds, due to salt concentration. The higher degree of the toxicity level determined for fresh water organisms may be also due to osmotic effects on these organisms caused by high salt concentration in eluates.

The eluate of the particle size fraction >10000 µm of bottom ashes has presented the lowest ecotoxicological levels. Marine organisms were more sensitive to the eluate produced by the bottom ashes as-received than to the eluates produced by the different particle size fractions of these ashes. In what concerns the ecotoxicological levels of fly ashes for marine organisms, it was not observed any significant difference between the as-received samples and the size fractionated samples.

Once again, the eluate of the particle size fraction >10000 µm of bottom ashes has presented the lowest ecotoxicological levels. In what concerns the fly ashes it was observed that the as-received ashes have present lower ecotoxicological levels than the size fractions. It was observed an increase in the *TU* with the particle size increasing.

All the samples were classified as ecotoxic based on CEMWE, except the fraction of bottom ashes > 10000 µm. The ecotoxic classification was mainly due to the effects on *V. fischeri* and *D. magna* (bottom ashes as-received and their particle size 200-500 µm, 500-850 µm, 850-2000 µm and 2000-4000 µm and the fractions 20-50 µm and 200-500 µm of fly ashes), and *V. fischeri* (bottom ashes fraction of 4000-10000 µm, fly ashes as-received and its fraction of 50-200 µm).

3.1.4 Conclusions

The bulk characterization has shown that bottom and fly ashes were mainly composed by earth metals, alkali-earth metals and silica compounds. The concentrations of heavy metals and metalloids were found to be vestigial or undetectable. The highest concentrations of metals and metalloids were found in the lower particle size fractions of both bottom and fly ashes.

Chlorides, sulphates, Ca, K, and in a lower extent Na were the main elements leached from all fractions of bottom and fly ashes. It was not observed any releasing pattern from the particle size fractions, except in the fly ashes for which the releasing rate of some earth and alkali-earth metals seemed to increase with the decrease of particle size fractions.

The freshwater organisms revealed to be more sensitivity to the eluates of bottom and fly ashes and of their particle size fractions than marine organisms. The larger particle size fractions of bottom ashes of 4000-10000 µm and >10000 µm have presented lower ecotoxicity levels than the other particle size fractions. All the samples were classified as ecotoxic, except the fraction of bottom ashes > 10000 µm.

It was not found any relationship between the chemical and the ecotoxicological behaviour of the eluate of the ashes, which demonstrates that both chemical and ecotoxicological characterisations are complementary and not exclusive.

3.2 Concretes containing biomass ashes: Mechanical, chemical and ecotoxic performances

Based on the following paper and oral communication:

Rui Barbosa, Nuno Lapa, Diogo Dias, Benilde Mendes (2013), Concretes containing biomass ashes: Mechanical, chemical and ecotoxic performances. Construction and Building Materials 48, 457-463
dx.doi.org/10.1016/j.conbuildmat.2013.07.031
IF (2012): 2.293; 5-year IF: 2.818
Construction and Building Materials is indexed on Scopus, SCImago and WoS

Rui Barbosa, Diogo Dias, Nuno Lapa, Benilde Mendes (2012), Using biomass ashes in concretes exposed to salted water and freshwater: mechanical and chemical properties. International Conference on Civil Engineering Materials 2012 (ICCEM'12). 7th-8th July, Paris, France

ABSTRACT

The objective of this work was to assess the possibility of using biomass ashes as substitutes for cement and natural aggregates in concretes, without compromising their mechanical, chemical, and ecotoxic properties. Thirteen concrete formulations were prepared with different percentages of bottom and fly ashes produced in the power plant of a pulp and paper industry. These formulations were submitted to mechanical compressive strength assays, after 28, 60, and 90 days of cure. The reference formulation (without biomass ashes) and two formulations with biomass ashes were selected for further characterization. After 90 days of cure, the selected formulations were submitted to the leaching test described in the EN12457-2 (2002) (L/S=10 L/kg, 24h batch cycle) by using two leaching agents: a synthetic marine water (ASPM medium based on ISO 10253, 2006) and a synthetic freshwater (medium ISO 6341, 1996). The eluates produced were submitted to chemical characterization (a set of 19 metals, pH, SO_4^{2-}, F^-, dissolved organic carbon, chlorides, phenolic compounds, and total dissolved solids) and to an ecotoxicological characterization (marine eluates: bioluminescence inhibition of the bacterium *Vibrio fischeri*; growth inhibition of the microalgae *Phaedactilum tricornutum*; mobility inhibition of the microcrustacean *Artemia franciscana*; freshwater eluates: mobility inhibition of the microcrustacean *Daphnia magna*; growth inhibition of the microalgae *Pseudokirchneriella subcapitata*). The substitution of 10% cement by fly ashes has promoted similar to higher levels of the compressive strength than those registered for the reference formulation. The new formulations presented emission levels of chemical species similar to, or even lower than, those observed for the reference formulation. The ecotoxicological levels were reduced for all of the formulations.

Keywords: Biomass ashes; chemical behavior; concrete; ecotoxicological levels; leachability; mechanical properties; salted and freshwater environments

3.2.1 Introduction

The production of electric energy through the use of forest residues is one of the possible ways to increase the production of renewable energy and to promote sustainable development through the reduction of the direct emission of greenhouse gases associated with the energy sector (Morais et al., 2011).

A considerable amount of the forest biomass received by pulp and paper industries is not appropriate for pulp and paper production. This biomass is considered a residue that can be valorized. As it was referred in a previous work, the most common valorization route of these forest residues is their thermal valorization through combustion, since the energy content is high enough for energy recovery (Acma, 2003; Al-Kassir et al., 2010; González et al., 2011b; Sami et al., 2001).

In the Portuguese pulp and paper sector, the thermal valorization of forest residues through combustion is widely used. Nevertheless, the combustion of biomass produces ashes that need an adequate management strategy.

The types of ashes produced depend on the characteristics of the boiler and the treatment system of the exhaustion gases. Usually, two types of ashes are produced: bottom and fly ashes. The former type is collected at the bottom of the boilers, while the latter is collected in the treatment system of the exhaustion gases. Two main strategies have been adopted in the last years for the management of these ashes: the addition of the ashes to the forest soils (as soil conditioner) and their incorporation in cement production. The first solution has some limitations imposed by the European legislation, due to the high content of biomass ashes in alkali and alkali-earth metals. The second option is also limited since the cement industries are not able to receive all fly ashes produced by the pulp and paper industry, due to a low incorporation rate in the cement production process. Therefore, it is necessary to find new applications for biomass ashes.

Several studies have shown that the production of construction materials, mainly cement-based mortars and concretes, is actually part of the solution for the management of biomass ashes, with a higher level of utilization, despite some technical and commercial barriers (Baxter, 2005; Pels et al., 2005; van Loo and Koppejan, 2008). In fact, there are concerns about the availability and quality of biomass ashes and blends of coal and biomass ashes, when used in cement and concrete industries (Baxter, 2005; Pels et al., 2005; Wang and Baxter, 2007; van Loo and Koppejan, 2008; Zheng et al., 2007; Umamaheswaran and Batra, 2008; Rajamma et al., 2009; Wang et al., 2012). Some standards, such as EN 197-1 (2011) and EN 450-1 (2012) which are related with the use of ashes for cement preparation, or as concrete additives do not allow or at least establish limitations for the use of ashes other than coal ashes. For example, the standard EN 450-1 (2012) allows the use of fly ashes from the co-combustion of coal and biomass in concrete manufacturing, but it introduces the requirement for a minimum content of coal in fuel mixture of 60% by mass (or 50% if wood residues recently produced are used as co-fuel) and a maximum content of ashes of 30%.

Several tests have been performed regarding the use of coal ashes (Aydın et al., 2007; Ha et al., 2007; Singhal et al., 2008) and ashes blends (coal and biomass) in concrete production and cement-based mortars (with up to 10-25% of cement replaced by ashes) (Wieck-Hansen et al., 2000; Baxter, 2005; Miller and Miller, 2007; Zheng et al., 2007; van Loo and Koppejan, 2008; Rajamma et al., 2009; Wang et al., 2008a; Wang et al., 2008c; Ban and Ramlim, 2011). The main conclusions were that the ashes blends do not promote significant changes in the bulk cement chemistry. The materials produced in such conditions have equal or even better performances than those produced by coal ashes.

Concrete incorporating biomass ashes for coastal protection and embankment reinforcement of inland water flow systems is a potential solution for using these ashes (Melchers and Li, 2009; Pack, 2010). Moreover, the use of concrete in the shore can reduce the eroding action of waves and promote the development of high quality waves for water sports as for example surf practice.

To the authors’ knowledge, it is the first time that concretes incorporating biomass ashes from a pulp and paper industry are simultaneously submitted to mechanical characterization and leaching under marine and freshwater conditions. The use of both chemical and ecotoxicological parameters is a follow-up of the previous works in which the authors have stressed the need for gathering these two types of characterizations to support the eco-compatibility assessment of new materials for civil engineering works (Barbosa et al., 2011; Lapa et al., 2012).

The main objective of this work was to produce concrete formulations by using biomass ashes as substitutes of cement and natural aggregates, without compromising their mechanical performance, the emission of chemical species and the ecotoxicological properties. Therefore, the compressive strength resistance of concretes produced with bottom and fly ashes from the combustion of forest residues was studied, and the chemical and ecotoxicological properties of some selected concrete formulations was assessed. These chemical and ecotoxicological properties were assessed under marine and freshwater leaching conditions.

3.2.2 Materials and Methods

3.2.2.1 Origin of biomass ashes

The fly and bottom ashes used in this work were produced in a Portuguese biomass boiler from a pulp and paper Company. This Company produces electricity through the combustion of bark from eucalyptus and pine, and other forest residues, in a BFBC. The bottom ashes were collected at the bottom of the combustion chamber and the fly ashes were collected in the electrostatic precipitator of the air pollution control system. The BFBC uses sand as a fluidizing agent. During the transport and conservation in the laboratory, the ashes were stored in dark airtight polypropylene containers and maintained at a temperature of 4±1°C, in the absence of light, to prevent their weathering and carbonation.

3.2.2.2 Concrete formulations

Thirteen formulations of concrete were prepared (Figure 3.22) with the codes F10B0, F10B9, F10B18, F10B36, F20B0, F20B9, F20B18, F20B36, F30B0, F30B9, F30B18, and F30B36. "F" means fly ashes, "B" means bottom ashes and the numbers represent the mass substitution percentage in wet basis.

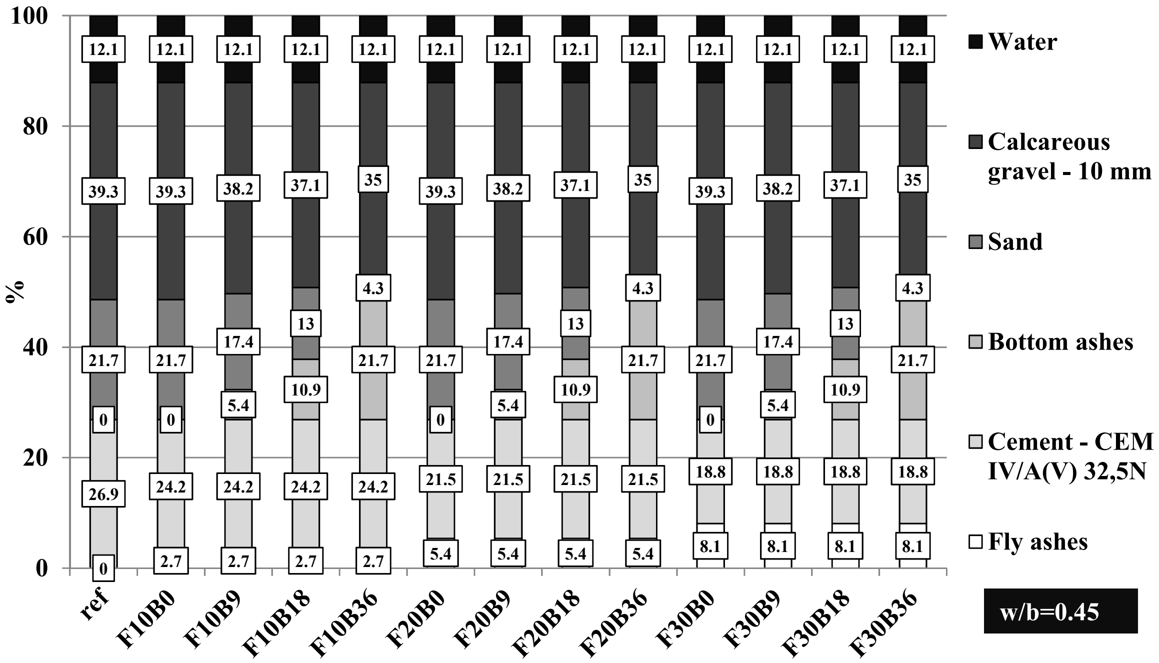


Figure 3.22 - Composition of the thirteen formulations of concrete (w/b: water/binder ratio; % wet basis)

The reference formulation (ref) was composed by the usual materials used in concretes: cement, sand, 10 mm calcareous gravel, and water. The composition of the reference formulation was adapted from Nawy (2008). The water/cement (w/c) ratio was slightly higher than that defined by Nawy (2008) due to the high water absorbance by pozzolanic materials, namely the biomass fly ashes. This behavior was to be expected as it was observed by other authors (Elinwa and Mahmood, 2002; Abdullahi, 2006).

The remaining formulations were prepared with bottom and fly ashes. Three levels of cement substitution by fly ashes were used: 10% (formulations **F10**B0, **F10**B9, **F10**B18, **F10**B36), 20% (formulations **F20**B0, **F20**B9, **F20**B18, **F20**B36) and 30% (formulations **F30**B0, **F30**B9, **F30**B18, **F30**B36). In each of these formulations, four substitution percentages of aggregates (sand and calcareous gravel) by bottom ashes were tested: 0% (F10**B0**, F20**B0**, F30**B0**), 9% (F10**B9**, F20**B9**, F30**B9**), 18% (F10**B18**, F20**B18**, F30**B18**), 36% (F10**B36**, F20**B36**, F30**B36**).

The fresh concrete was prepared in a concrete mixer (Matest B025-SP), and then was placed in cylindrical plastic molds with 80 mm height and 70 mm diameter. Each mold containing the fresh concrete was submitted to a vibration process, with an amplitude of 0.3 mm, in a mechanical vibrator (Retsch AS 200 digit), in order to remove air bubbles. The molds were then capped in order to avoid air contact, and stored at 20±1°C, in a climate chamber, on the absence of light, all over the cure periods.

3.2.2.3 Compressive strength test

The concrete formulations were submitted to cure periods of 28, 60, and 90 days, in the absence of light, at 20±1°C, and in airtight plastic molds to avoid their carbonation. In each of these cure periods, duplicate samples of each formulation were submitted to a compressive strength test in a Form+Test Digimess-M10 press, according to the standard NP EN 12390-3 (2011). After 90 days of cure, three formulations were selected for further characterization: the reference formulation (ref) and formulations F10B18, and F30B18. The criteria for the selection of the two new formulations were the following: formulation with the highest compressive strength result from all of the formulations; and formulation with the highest compressive strength result among the set of formulations with the highest substitution level of cement by fly ashes (formulations F30B0, F30B9, F30B18, and F30B36).

Figure 3.23 shows the compressive strength tests over the concrete formulations.

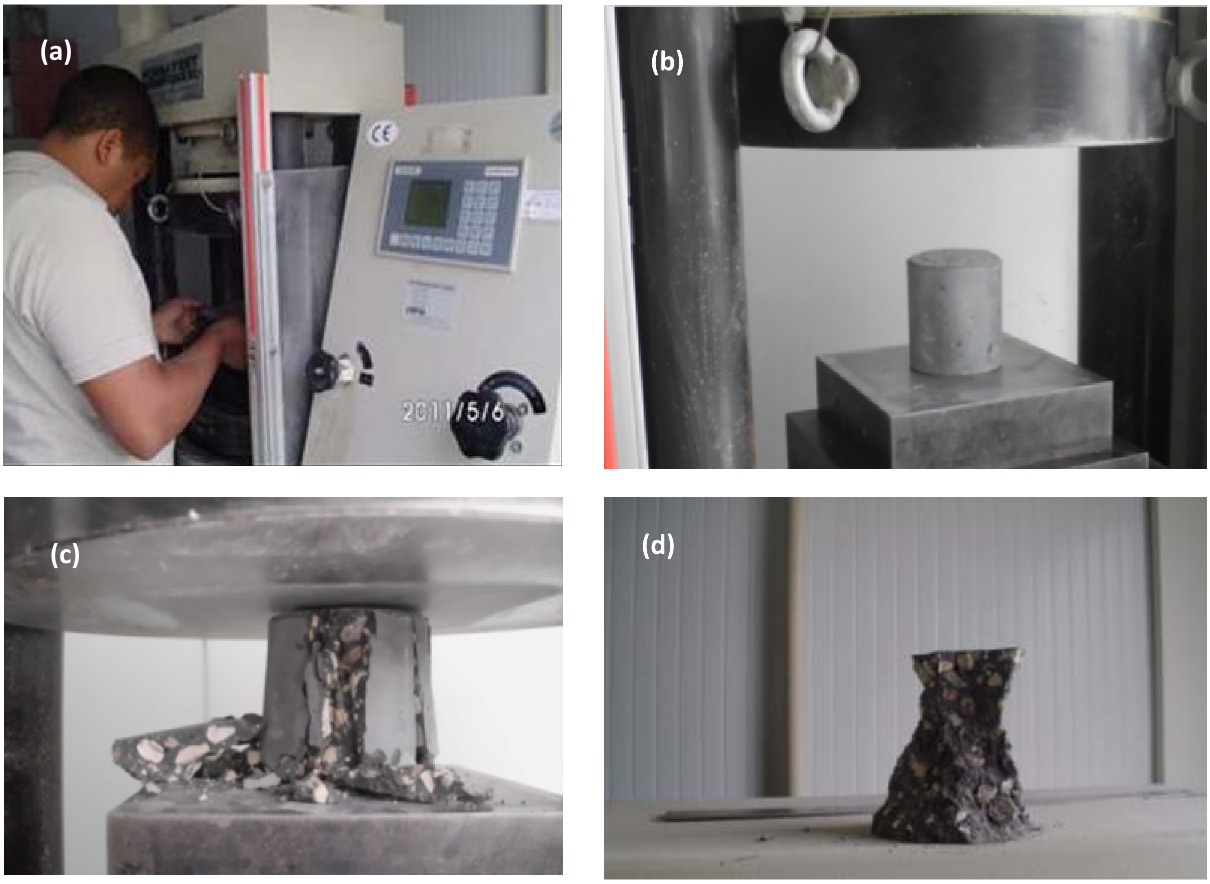


Figure 3.23 - Compressive strength tests over the concrete formulations; (a) preparation of the Form+Test Digimess-M10 press; (b) placing the concrete in Form+Test Digimess-M10 press; (c) first phase of roture; (d) concrete formulation after compressive strength test

3.2.2.4 Leaching tests and chemical and ecotoxicological characterization of the eluates

The selected formulations (formulation ref and two other formulations) were submitted to two different leaching tests after 90 days of cure:

a) Leaching test with a liquid to L/S ratio of 10 L/kg (according to the European Standard EN 12457-2, 2002), using a synthetic freshwater medium as a leaching agent (ISO 6341, 1996);

b) Leaching test with a L/S ratio of 10 L/kg, using a synthetic marine water as a leaching agent (ASPM medium, based on ISO 10253, 2006).

The chemical composition of the freshwater medium was: 64.75 mg/L $NaHCO_3$, 294 mg/L $CaCl_2.2H_2O$, 5.75 mg/L KCl and 123.25 mg/L $MgSO_4.7H_2O$. The chemical composition of the marine water media was 26400 mg/L NaCl, 840 mg/L KCl, 1670 mg/L $CaCl_2$, 4600 mg/L $MgCl_2$, 5580 mg/L $MgSO_4$, 170 mg/L $NaHCO_3$ and 30 mg/L H_3BO_3. Despite these chemical compositions, the leaching tests always included blank tests. The chemical compositions of the eluates of the blank tests were deducted from the chemical compositions of the eluates obtained with the concretes. Therefore, the concentrations of the eluates presented in this paper are exclusively due to the emission from the concretes and not to the composition of the leaching media.

The eluates produced in both leaching tests were submitted to a chemical characterization that comprised the following parameters and methodologies: Hg (AAS cold vapor; ISO 5666/1, 19683), As (AAS air-acetylene flame; EN ISO 11969, 1996), Cd, Cu, Ni, Pb, Zn (AAS air-acetylene flame; ISO 8288, 1986), Cr (AAS nitroux oxide-acetylene flame; ISO 9174, 2009), Cr VI (colorimetric method; NF T90-043, 1988), Fe, Mg, Sb (AAS air-acetylene flame; APHA/AWWA/WEF, 2005), Al, Ba, Mo (AAS nitrous oxide-acetylene flame; APHA/AWWA/WEF, 2005), Na (AAS air-acetylene flame; ISO 9964-1, 1993), K (AAS air-acetylene flame; ISO 9964-2, 1993), Ca (AAS nitrous oxide-acetylene flame; ISO 7980, 2010) Se (AAS air-acetylene flame; ISO 9965, 1993), Cl^- (Mohr's method; ISO 9297, 1989), pH (electrometric - method 4500; APHA/AWWA/WEF, 2005), DOC (Dissolved Organic Carbon) (Combustion and detection by Infra-Red; ASTM D7573, 2009), SO_4^{2-} (Turbidimetric - method 4500 E; APHA/AWWA/WEF, 2005), F^- (SPADNS - method 4500 D, APHA/AWWA/WEF, 2005), total dissolved solids (TDS) (gravimetric method; APHA/AWWA/WEF, 2005), and phenolic compounds (colorimetric method; ISO 6439, 1990).

The eluates were also characterized to a set of ecotoxicological parameters. The marine eluates were submitted to the following ecotoxicological characterization: bioluminescence inhibition of the bacterium *Vibrio fischeri* (miniaturized system of Microtox®; ISO 11348-3, 2007), growth inhibition of the microalgae *Phaedactilum tricornutum* (miniaturized kit of Microbiotests®; ISO 10253, 2006), and mobility inhibition of the microcrustacean *Artemia franciscana* (miniaturized kit of Microbiotests®; ASTM E1440-91, 2004). The freshwater eluates were submitted to the following ecotoxicological characterization: mobility inhibition of the microcrustacean *Daphnia magna* (miniaturized kit of Microbiotests®; ISO 6341, 1996), and growth inhibition of the microalgae *Pseudokirchneriella subcapitata* (miniaturized kit of Microbiotests®; ISO 8692, 2004).

3.2.2.5 Ecotoxicological classification of the concretes

The evaluation of the ecotoxic properties of the concretes, based on code H14 of the Council Directive 91/689/EEC (Council of the European Communities), was based on the CEMWE. The original CEMWE methodology was adapted according to Lapa et al. (2007). The ecotoxicological classification was based on the chemical and ecotoxicological parameters common to both the characterization performed in the present work and the CEMWE.

3.2.3 Results and Discussion

3.2.3.1 Compressive strength results

Figure 3.24 to Figure 3.26 show the results of the compressive strength test after 28, 60, and 90 days of cure of the reference formulation (ref) and of all the new formulations.

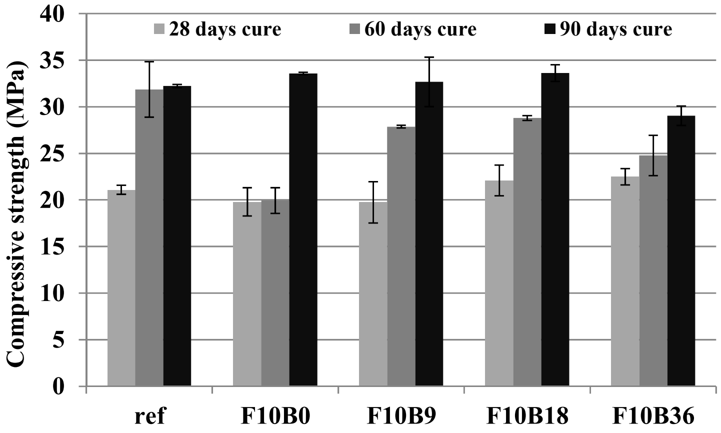


Figure 3.24 - Compressive strength values of the reference formulation (ref) and the formulations F10B0, F10B9, F10B18, and F10B36, after 28, 60 and 90 days of cure (±SD, 2 repl.)

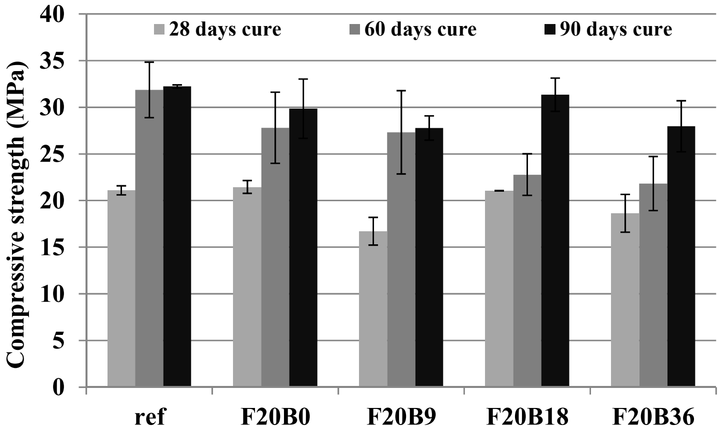


Figure 3.25 - Compressive strength values of the reference formulation (ref) and the formulations F20B0, F20B9, F20B18, F20B36, after 28, 60 and 90 days of cure (±SD, 2 repl.)

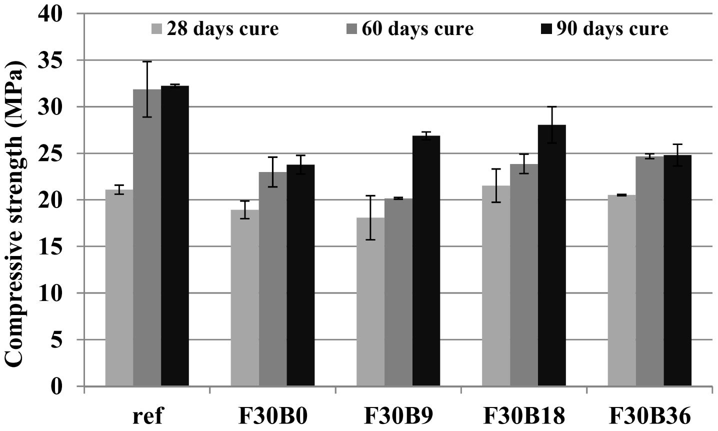


Figure 3.26 - Compressive strength values of the reference formulation (ref) and the formulations F30B0, F30B9, F30B18, and F30B36, after 28, 60 and 90 days of cure (±SD, 2 repl.)

The compressive strengths of the reference formulation were very similar for a cure period of 60 and 90 days (~32 MPa), while the compressive strength values of the new formulations have generally increased with the increase of the cure period.

It also was observed that the compressive strength results of all the new formulations revealed a tendency of reduction with the increasing percentage of fly ashes in the concrete formulations. Only the lowest substitution level of cement by fly ashes (10%) has produced concretes with compressive strength values similar to, or slightly higher than that obtained for the reference material. In the new formulations with substitution levels of 20% and 30% of cement by fly ashes, the highest compressive strength results were obtained in the formulations containing a percentage of substitution of natural aggregates by bottom ashes of 18% (F20B18 and F30B18).

Further studies are needed to identify this mechanical behavior. Nevertheless, some possibilities can be pointed out. In a review paper of Stark (2011), this author summarized some recent advances in the field of cement hydration. It is indicated in this review that the hydration of C_3S proceeds in different stages. In the first period of 1 to 6 hours, there is a very low level of chemical activity (dormant or induction period). After this period, it will occur in an intense hydration, which is associated with the formation of C-S-H and calcium carbonate and release of thermal energy. The extension of these reactions may affect the strength of concrete. According to Nawy (2008), the presence of C_3S promotes a moderate reaction rate of the hydration of Portland cement and contributes to high strength values of concrete.

It seems, as will be discussed further on, that the hydration process has been delayed with the addition of ashes. This may indicate that ashes do not present or present low levels of C_3S.

Therefore, their use in the new formulations of concretes has yielded lower values of compressive strength.

Wang et al. (2008a) have developed a work dedicated to the study of a set of mechanical properties of concrete containing fly ashes from the combustion of biomass. Wang and colleagues have studied eight types of concrete formulations, which included the reference formulation (cement Type I and II) and concrete prepared with wood fly ashes. These authors have substituted 25% of cement by fly ashes. This substitution level is comparable to the formulations F20B0, F20B9, F20B18, and F20B36 (20% substitution of cement by fly ashes) and F30B0, F30B9, F30B18, and F30B36 (30% substitution of cement by fly ashes) tested in the present work. Wang et al. (2008a) have observed that the reference formulation presented compressive strength results of approximately 30, 37, and 37 MPa, for the cure periods of 28, 56, and 91 days, respectively. These compressive strength results are a little higher than the values registered in the present work, namely for 28 days of cure. In what concerns the concrete produced with wood fly ashes, Wang et al. (2008a) have observed compressive strength results of approximately 24, 28, and 27 MPa, for the cure periods of 28, 56, and 91 days, respectively. These compressive strength results are similar to those of the formulations containing 20% and 30% (F20B0, F20B9, F20B18, F20B36, F30B0, F30B9, F30B18, and F30B36) that have been tested in the present work.

Rajamma et al. (2009) have studied the properties of concretes produced with two types of biomass ashes. One of those biomass ashes was produced in a dedicated biomass power plant, while the second one was produced in a boiler of a pulp and paper industry. These authors have tested the compressive strength of three substitution levels of cement by ashes (10%, 20%, and 30%), after 28 days of cure. These conditions are comparable with those associated with formulations F10B0, F20B0, and F30B0 for the same cure period used in the present work.

The reference formulation has presented a compressive strength value of approximately 41.5 MPa. The formulations of concretes produced by the ashes from a dedicated biomass power plant have presented compressive strength values of 43.3, 32.5, and 22.6 MPa, for 10%, 20%, and 30% substitution levels of cement by fly ashes, respectively. The concretes containing fly ashes produced in a pulp and paper industry have presented compressive strength values of 35.8, 30.1, and 26.7 MPa for 10%, 20%, and 30% substitution levels of cement by fly ashes, respectively. The compressive strength values found by Rajamma et al. (2009) are higher than those found in the present work, which were approximately 20, 21, and 19 MPa for F10B0, F20B0, and F30B0, respectively. The differences found on the compressive strength values may be related with the types of cement used. Rajamma et al. (2009) have used cement type 42.5R, which allows high compressive strength values and faster mechanical stabilization than that used in the present work (32.5N).

Wang and Baxter (2007) have studied several properties of concretes produced with fly ashes obtained from the co-combustion of coal and switch grass. One of those properties was the compressive strength. These authors have used Portland cement of types I and II, a water/binder ratio of 0.5 and a substitution level of cement by fly ashes of 25%. Aside from the reference concrete, the authors have studied the properties of concretes with “20% fly ashes + 80% cement” and “10% fly ashes + 90% cement.” The reference concrete has achieved compressive strength values of approximately 29 and 38 MPa, after 28 and 91 days of cure, respectively. The concrete prepared with “20% fly ashes + 80% cement” has attained compressive values of approximately 32 and 37 MPa, after 28 and 91 days of cure respectively. The concrete prepared with “10% fly ashes + 90% cement” has attained compressive values of approximately 25 and 40 MPa, after 28 and 91 days of cure, respectively. These values are higher than those observed in the present work, even for the formulations containing 20% fly ashes. One possible reason for this behavior can be related to the fact that Wang and Baxter (2007) have used fly ashes produced by the combustion of biomass ashes and coal, which may present higher pozzolanic properties than those used in the present work.

Relationship between the cure period and the compressive strength results

Figure 3.27 shows the relationship between the cure period and the compressive strength results for the three substitution levels of cement by fly ashes (0%, 10%, 20%, and 30%). In this Figure, each data point was defined as the average value of the compressive strength results of the four formulations with the same level of substitution of cement by fly ashes, for each cure period.

As it was observed on Figure 3.26, the compressive strength of the reference formulation, after 60 days of cure, was similar to that observed after 90 days of cure. This behavior was not observed for the formulations containing biomass ashes. This may suggest that the use of alternative materials have delayed the hydration process for the cure times considered in the present work. It was also observed that the compressive strength values of the formulations were similar after 28 days of cure, but a higher increase rate of the compressive strength was observed in the formulations in which lower substitution levels of cement by fly ashes were used (Figure 3.27). The increase ratio of the compressive strength results were 0.1801, 0.1577, and 0.0985 MPa/d for 10%, 20%, and 30% of substitution of cement by fly ashes, respectively, which indicates that the higher the substitution level of cement by fly ashes is, the lower the increase of the compressive strength along the cure period is.

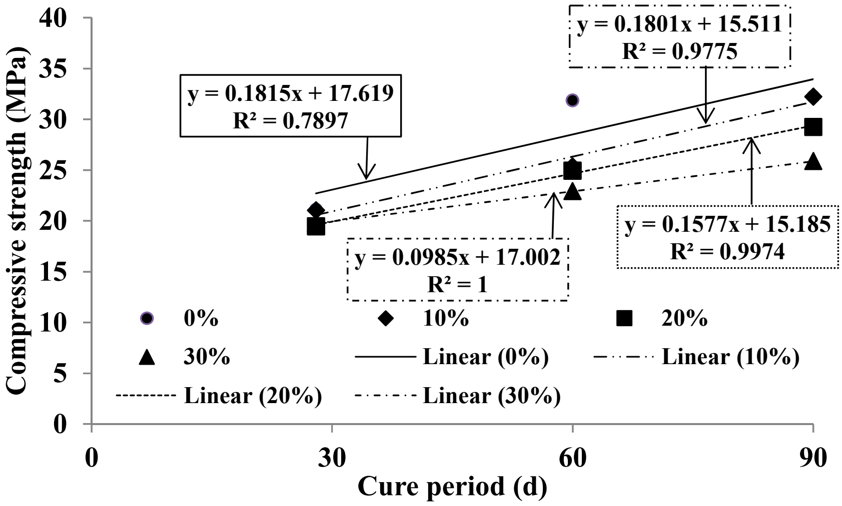


Figure 3.27 - Evolution of the compressive strength values as a function of the cure period for reference concrete and concrete formulations prepared with the three substitution levels of cement by fly ashes (0, 10, 20 and 30%).

3.2.3.2 Chemical characterization of eluates

3.2.3.2.1 Freshwater eluates

Table 3.1 and Figure 3.28 show the chemical characterization of the eluates of concretes with the codes ref, F10B18, and F30B18, submitted to a cure period of 90 days, produced under freshwater leaching conditions.

The pH values produced by the freshwater eluates were approximately 10. These pH levels in the freshwater eluates indicate the release of oxides from the formulations and a low buffer capacity of the leaching agent. Nevertheless, no significant difference was observed between the reference material and the new formulations F10B18 and F30B18.

The other set of parameters presented in Table 3.1 indicate very low emission levels of chemical species, since all of the concentrations were below the respective quantification limits, except for CrVI. Nevertheless, the concentrations of CrVI in the eluates were very low (less than 2 µg/kg db). It is important to stress that the concentrations of this element in the formulation containing biomass ashes (F10B18 and F30B18) were lower than that observed for the reference formulation (ref).

In a previous work (Barbosa et al., 2013) performed by the same authors of these manuscript with the same biomass ashes, the concentrations of CrVI in the bottom and fly ashes were higher than those determined in the freshwater eluates of concretes. The concentrations of CrVI in bottom and fly ashes were, respectively, of 860 and 690 µg/kg (db) and the leachable fractions were, respectively, of 250 and 330 µg/kg (db). The incorporation of biomass ashes in a concrete matrix has led to a high reduction level of the emission of this parameter to a range of 1.66 to 1.69 µg/kg, which corresponds to a reduction ratio of approximately 400-fold (bulk composition) and 100-fold (leachable faction), probably due to the dilution factor of ashes in the cement matrix, but also to the encapsulation of CrVI in the matrix.

Table 3.1 - Chemical characterization of the freshwater eluates of the concrete formulations with the codes ref, F10B18 and F30B18 (n=2, mg/kg db (±SD), except Sb, Hg, As, Se and Cr VI in µg/kg db and pH in Sorensen scale; n.a.: not applicable)

Parameter	ref Freshwater	F10B18 Freshwater	F30B18 Freshwater
pH	10.3 (±0.1)	10.4 (±0.2)	10.1 (±0.1)
Phenolic compounds	< 0.54 (n.a.)	< 0.55 (n.a.)	< 0.55 (n.a.)
F^-	< 0.54 (n.a.)	< 0.55 (n.a.)	< 0.55 (n.a.)
DOC	< 10.9 (n.a.)	< 11.1 (n.a.)	< 11.1 (n.a.)
As	< 3.48 (n.a.)	< 3.54 (n.a.)	< 3.54 (n.a.)
Sb	< 3.26 (n.a.)	< 3.32 (n.a.)	< 3.32 (n.a.)
Se	< 9.90 (n.a.)	< 10.1 (n.a.)	< 10.1 (n.a.)
Cu	< 0.45 (n.a.)	< 0.45 (n.a.)	< 0.45 (n.a.)
Zn	< 0.14 (n.a.)	< 0.14 (n.a.)	< 0.14 (n.a.)
Ba	< 1.74 (n.a.)	< 1.77 (n.a.)	< 1.77 (n.a.)
Hg	< 13.1 (n.a.)	< 13.3 (n.a.)	< 13.3 (n.a.)
Cd	< 0.35 (n.a.)	< 0.35 (n.a.)	< 0.35 (n.a.)
Mo	< 1.07 (n.a.)	< 1.08 (n.a.)	< 1.08 (n.a.)
Pb	< 1.09 (n.a.)	< 1.11 (n.a.)	< 1.11 (n.a.)
Ni	< 0.69 (n.a.)	< 0.70 (n.a.)	< 0.70 (n.a.)
Cr	< 0.54 (n.a.)	< 0.55 (n.a.)	< 0.55 (n.a.)
Cr VI	1.98 (±0.11)	1.66 (±0.20)	1.69 (±0.13)
Al	< 3.70 (n.a.)	< 3.76 (n.a.)	< 3.76 (n.a.)
Fe	< 0.65 (n.a.)	< 0.66 (n.a.)	< 0.66 (n.a.)
Mg	< 0.033 (n.a.)	< 0.033 (n.a.)	< 0.033 (n.a.)

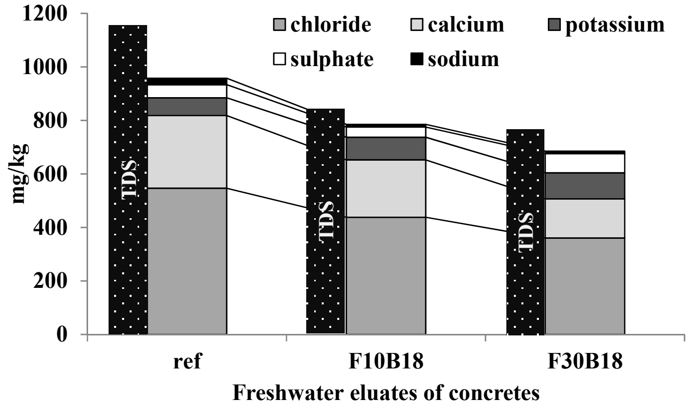


Figure 3.28 - Concentrations of TDS, sodium, sulfate, potassium, calcium and chlorides on the freshwater eluates of the formulations with the codes ref, F10B18 and F30B18

As discussed in a previous work (Barbosa et al., 2013), the bulk content showed that the biomass fly ashes were mainly composed by alkali and earth-alkali elements (K = 17529 mg/kg db, Na = 1953 mg/kg db, Ca = 258639 mg/kg db, Mg = 22317 mg/kg db, and Ba = 336 mg/kg db). Also Fe and Al were present in high concentrations (Fe = 13531 mg/kg db, and Al = 24278 mg/kg db). Nevertheless, the leaching rates of these elements were quite distinct among them. The leaching rates of Ca and Na were approximately 17% of the bulk content, whereas the leaching rate of K was only approximately 6%. Mg has presented a very low leaching rate (<0.001% of the bulk content).

The data shown in Figure 3.28 indicate a clear tendency for the reduction of the concentrations of TDS, Cl^-, Ca^{2+} and Na^+ from the reference formulation (ref) to the formulation with the code F30B18. Nevertheless, an increase in the concentrations of SO_4^{2-} and K^+ was observed in the new concrete formulations (F10B18 and F30B18). This aspect may be related to the high content of S and K, especially in the fly ashes, as was observed by Barbosa et al. (2013) in a previous work.

3.2.3.2.2 Marine eluates

Table 3.2 and Figure 3.29 show the chemical characterization of the eluates of concretes with the codes ref, F10B18 and F30B18, submitted to a cure period of 90 days, obtained in the leaching test with the synthetic marine water.

The pH values of the eluates were approximately 8, which correspond to the typical pH level of the seawater. This demonstrates the high pH buffering capacity of the synthetic marine water, because no significant change in the pH was registered due to the contact with the concrete formulations as it was observed in the synthetic freshwater. The other chemical parameters have presented a very low mobility from all of the formulations of concretes as their concentrations were below the quantification limits, except for CrVI. The emission of CrVI was very low and was below that determined in the freshwater eluates. The lower concentrations of CrVI in the marine eluates can be explained by the differences in the pH values of marine water and freshwater. Since CrVI has an amphoteric behavior, a reduction of its concentration in the pH levels near the neutrality, as registered for the marine water, may be expected.

The results shown in Figure 3.29 indicate a clear tendency for the reduction of the concentrations of TDS, K^+, Ca^{2+} and Na^+ from the ref material to the concrete with the formulation F30B18. Nevertheless, an increase in the concentrations of Cl^- in the formulations containing biomass ashes was observed. The concentrations of SO_4^{2-} have not changed in the new concrete formulations (F10B18 and F30B18).

Table 3.2 - Chemical characterization of the marine eluates of the concrete formulations with the codes ref, F10B18 and F30B18 (n=2, mg/kg db (±SD), except Sb, Hg, As, Se and Cr VI in µg/kg db and pH in Sorensen scale; n.a.: not applicable)

Parameter	ref Marine water	F10B18 Marine water	F30B18 Marine water
pH	8.04 (±0.20)	8.14 (±0.08)	8.02 (±0.04)
Phenolic compounds	< 0.54 (n.a.)	< 0.55 (n.a.)	< 0.55 (n.a.)
F^-	< 0.54 (n.a.)	< 0.55 (n.a.)	< 0.55 (n.a.)
DOC	< 10.9 (n.a.)	< 11.1 (n.a.)	< 11.1 (n.a.)
As	< 3.48 (n.a.)	< 3.55 (n.a.)	< 3.54 (n.a.)
Sb	< 3.26 (n.a.)	< 3.33 (n.a.)	< 3.32 (n.a.)
Se	< 9.90 (n.a.)	< 10.1 (n.a.)	< 10.1 (n.a.)
Cu	< 0.446 (n.a.)	< 0.455 (n.a.)	< 0.453 (n.a.)
Zn	< 0.141 (n.a.)	< 0.144 (n.a.)	< 0.144 (n.a.)
Ba	< 1.74 (n.a.)	< 1.77 (n.a.)	< 1.77 (n.a.)
Hg	< 13.1 (n.a.)	< 13.3 (n.a.)	< 13.3 (n.a.)
Cd	< 0.348 (n.a.)	< 0.355 (n.a.)	< 0.354 (n.a.)
Mo	< 1.07 (n.a.)	< 1.09 (n.a.)	< 1.08 (n.a.)
Pb	< 1.09 (n.a.)	< 1.11 (n.a.)	< 1.11 (n.a.)
Ni	< 0.686 (n.a.)	< 0.698 (n.a.)	< 0.696 (n.a.)
Cr	< 0.544 (n.a.)	< 0.554 (n.a.)	< 0.553 (n.a.)
Cr VI	0.26 (±0.01)	0.35 (±0.01)	0.077 (±0.001)
Al	< 3.70 (n.a.)	< 3.77 (n.a.)	< 3.76 (n.a.)
Fe	< 0.653 (n.a.)	< 0.665 (n.a.)	< 0.663 (n.a.)
Mg	< 0.033 (n.a.)	< 0.033 (n.a.)	< 0.033 (n.a.)

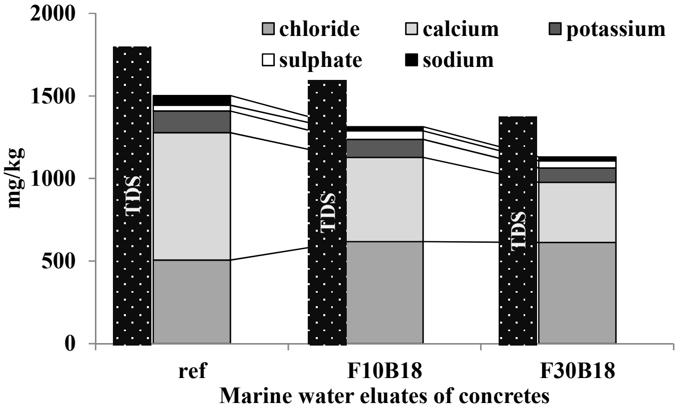


Figure 3.29 - Concentrations of TDS, sodium, sulfate, potassium, calcium and chloride on the marine eluates of the formulations with the codes ref, F10B18 and F30B18

3.2.3.3 Ecotoxicological characterization of eluates

Figure 3.30 shows the ecotoxicological levels of the eluates of concretes with the codes ref, F10B18 and F30B18 produced with the synthetic freshwater, regarding the organisms *D. magna* and *P. subcapitata.* Figure 3.31 shows the ecotoxicological levels of the eluates of concretes with the codes ref, F10B18 and F30B18 produced with the synthetic marine water, regarding the organisms *A. franciscana*, *V. fischeri*, and *P. tricornutum.*

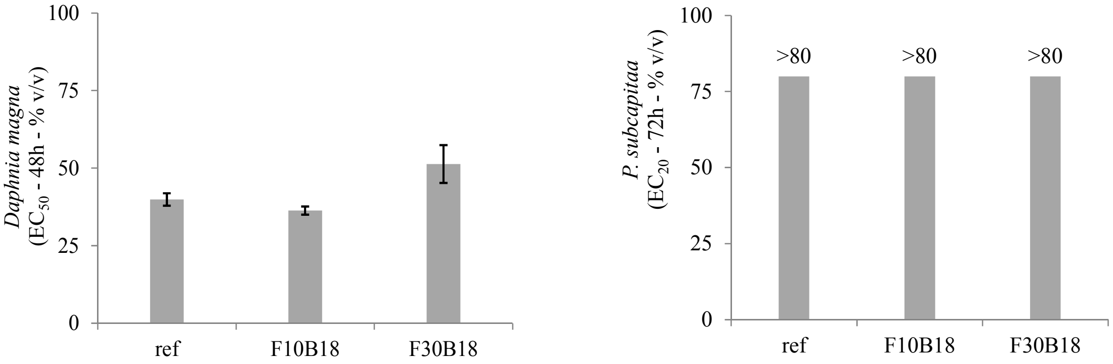


Figure 3.30 - Ecotoxicological levels of the freshwater eluates of the concretes with the codes ref, F10B18, and F30B18 to the microcrustacean *D. magna* and microalgae *P. subcapitata*

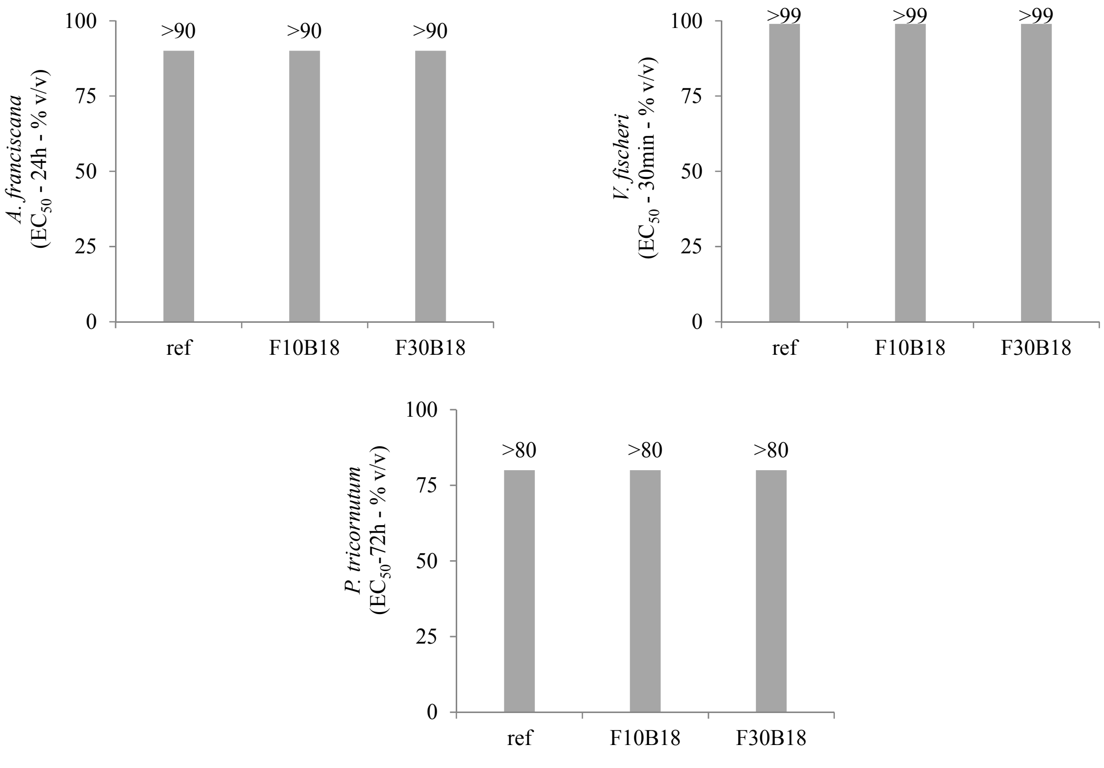


Figure 3.31 - Ecotoxicological levels of the marine eluates of the concretes ref, F10B18, and F30B18 to the organisms *A. franciscana*, *V. fischeri*, and *P. tricornutum*

The ecotoxicological levels were, generally, low to all of the biological indicators and to all of the concretes. The Effective Concentrations (ECxx) were higher than the highest concentration tested in each assay, except for the organism *D. magna*. One possible reason for the high sensitivity of this organism may be related to the concentration of salts (dissolved solids) in the eluates that have migrated from the concretes. The EC$_{50}$-48h of the concretes in which biomass ashes were used was similar (F10B18) to, or even higher (F30B18) than that observed for the reference material (ref), which indicates that no ecotoxicity was added to the concretes due to the use of biomass ashes. In a previous study performed by Barbosa et al. (2013) with the same biomass ashes, the ecotoxicological levels found for the as-received ashes were much higher than those found in the new concrete formulations (F10B18 and F30B18). This indicates that the incorporation of bottom and fly ashes in a concrete matrix has reduced their ecotoxicological levels.

According with the methodology indicated in CEMWE and adopted by Lapa et al. (2007), the formulations with the codes ref, F10B18 and F30B18 were classified as "without evidence of ecotoxicity," since both chemical and ecotoxicological characterizations have indicated concentrations of chemical species and ecotoxicological levels below the CEMWE limits.

3.2.4 Conclusions

Concrete formulations were produced by using biomass ashes as substitutes of cement and natural aggregates, without compromising their mechanical performance, the emission of chemical species, and the ecotoxicological properties, under marine and freshwater leaching conditions.

The concrete formulations prepared with biomass ashes have presented a range of values for compression strength from slightly higher to lower than those determined for the reference concrete. The formulations in which fly ashes were used to replace 10% of the cement (F10B0, F10B9, F10B18, and F10B36) have presented similar to slightly higher compressive strength values than those of the reference concrete. By opposition, the incorporation of 30% fly ashes has conducted to concretes with lower compressive strength values than that registered for the reference material. The substitution level of 18% of aggregates by bottom ashes (F10B18, F20B18, and F30B18) yielded for the highest compressive strength values among the new formulations of concretes.

The formulations selected for further chemical and ecotoxicological characterizations (ref, F10B18, and F30B18) have presented very low emission levels of chemical species in both marine and freshwater leaching scenarios. The new formulations F10B18 and F30B18 have presented emission levels similar to, or lower than those observed for the reference formulation. The ecotoxicological levels of the eluates produced by the new formulations of concretes were similar to, or even lower than that observed for the reference material.

3.3 Removal of phosphorus from wastewaters by biomass ashes

Based on the following paper:

R. Barbosa, N. Lapa, H. Lopes, A. Morujo, B. Mendes. Removal of phosphorus from wastewaters by biomass ashes. Water Science and Technology (accepted; In press)

IF (2012): 1.102; 5-year IF: 1.146

Water Science and Technology is indexed on Scopus, SCImago and WoS

ABSTRACT

Removal batch assays of phosphates from a synthetic wastewater (SWW) and a pulp and paper mill wastewater (PPWW) with two forestry biomass ashes were performed. The supernatants were not only chemically characterized but also the ecotoxicity was determined using two organisms: *Vibrio fischeri* and *Artemia franciscana*. The addition of fly and bottom ashes to the SWW in solid/liquid (S/L) ratios of 3.35 and 9.05 g/L, respectively, achieved removal percentages of phosphates >97% for both ashes. The addition of fly and bottom ashes to the PPWW in S/L ratios of 34.45 and 46.59 g/L, respectively, yield removal percentages of phosphates >90% for both ashes. According to the results of the Langmuir and Freundlich isotherms, the removal of phosphates from the SWW was mainly explained by surface removal mechanisms, while the removal from the PPWW was partially explained by multi-layer mechanisms. The supernatants resulting from the treatment of SWW and PPWW with both biomass ashes did not present acute ecotoxicity.

Keywords: Biomass ashes; ecotoxicity; pulp and paper mill wastewater; removal of phosphates

3.3.1 Introduction

Phosphorus (P) is an essential nutrient to biological activity in aquatic environments. However, the discharge of treated wastewaters containing P can stimulate the growth of photosynthetic algae and toxic cyanobacteria leading to eutrophication processes of natural water bodies and water contamination with toxins (Ugurlu and Salman, 1998; Douglas et al., 2004; Parsons and Berry; 2004; Lu et al., 2009; Xu et al., 2010; García-Albacete et al., 2012).

The EU established the concentrations of 1 and 2 mg P/L as the limit values for P discharges in the treated effluents of urban wastewater treatment plants (WWTP), depending on the number of inhabitants-equivalent attended by the WWTP. Nevertheless, some countries followed stricter limit-values (0.5 to 0.8 mg P/L) than those defined by EU to control eutrophication processes (Hussain et al., 2011; Sabir et al., 2011). This was based on the knowledge that a concentration as low as 1 mg P/L is high enough to cause eutrophication problems in natural water bodies.

Several chemical and biological treatment processes have been studied to remove P from wastewaters (Ugurlu and Salman, 1998; Douglas et al., 2004; Parsons and Berry; 2004; Yang et al., 2006; Wood et al., 2006; Pratt and Shilton, 2010), many of them chemical and other biological processes.

Caravelli et al. (2010) have studied the removal of P by ferric chloride in the presence of activated sludge. The authors have found that the presence of biomass did not affect the orthophosphate precipitation. However, a decrease of pH to values not compatible with the normal activity of activated sludge needed the addition of $NaHCO_3$, making more expensive the P-removal.

Al-Najjar et al. (2011) performed an interesting study on the role of microbial stringent response in excess intracellular accumulation of phosphorus in mixed consortia. The authors fed with synthetic wastewater four bench-scale sequencing batch reactors (SBRs) that were seeded with activated sludge. The SBRs were operated under either fully oxic or anoxic/oxic conditions. High percentages of phosphorus were removed (67-99%) in all four reactors. Nevertheless, it is unknown if the same behavior of the microbial consortia would be reached in real wastewaters. The effect of organic and hydraulic loads of real wastewaters is also unpredictable in the biological systems for P-removal.

In a very unusual researching topic, Boelee et al. (2011) have studied the nitrogen and phosphorus removal from municipal wastewater effluent using microalgal biofilms. The studies on microalgal films for nutrient removal from treated effluents are very scarce. Boelee et al. (2011) have cultivated microalgal biofilms in flow cells under different nutrient loads and continuous lighting. In this study a synthetic wastewater was also used. Authors have found a high uptake capacity for a load of 1.0 g NO_3^-- N/(m^2*d) and 0.13 g PO_4^{3-} - P/(m^2*d) under a light intensity of 230 mmol photons/(m^2*s). Once again, it was not studied for a real wastewater if the microalgal nutrient uptake would be similar to that observed for synthetic wastewater, and if the population would present a stable behavior over time.

The common aspects to all of the studies dealing with P-removal are the following: the chemical processes are highly efficient but very expensive, due to the costs of chemical reagents needed; biological processes are less expensive, but not as efficient as chemical processes, due to the unpredictable behavior of microorganisms involved in P-removal, namely when they are submitted to variations of chemical composition and hydraulic load of real wastewaters.

Among the group of chemical processes, the reuse of residue materials to remove P from wastewaters has been attempted in several works. This is an interesting issue of study, because of the high P-adsorption capability of some types of residues and also their low cost (Ugurlu and Salman, 1998; Douglas et al., 2004; Parsons and Berry; 2004; Lu et al., 2009).

Xiong et al. (2011) have studied the phosphate removal capability of freshwater mussel shells transformed into powder. The authors have concluded that a thermal treatment of 700ºC for 20 min would be necessary to enhance the phosphate removal capability of the mussel shell powders from 25% to 55%, at a pH value of 5.5. Despite of the interesting P-removal efficiencies, the thermal treatment would increase the cost of the final adsorption product. Nevertheless, the reuse of sub-products from thermal processes would avoid the need of thermal activation and consequently could decrease the final adsorbent cost.

Lu et al. (2009) have tested the phosphate removal mechanism from aqueous solution by using coal fly ashes. The major conclusions pointed out for a rapid phosphate removal: 68% to 96% of the maximum phosphate removal capability was reached in the first 5 minutes of contact time.

Xu et al. (2010) studied the phosphate removal from aqueous solutions by chemically activated coal fly ashes. The activation was performed by sulfuric acid. The authors have concluded that the activation of coal fly ashes significantly enhanced their phosphate immobilization capability, due to the increase of the specific surface area from 8.8 to 32.5 m^2/g after the treatment with sulfuric acid.

Regardless the effectiveness of coal ashes to remove phosphates from wastewaters, this coal combustion sub-product is normally composed by high concentrations of heavy metals (Ludwig et al., 2005), which can be transferred to the wastewater during the treatment. Although P concentration might be reduced to levels below the critical concentration for eutrophication, the dissolution of heavy metals from coal ashes in the wastewater can increase its ecotoxicity level and compromise its discharge in natural water bodies. There is a lack of discussion on this important issue in the bibliography.

In this framework, the use of ashes resulting from the combustion of forest biomass is much more interesting than coal ashes, due to the high concentrations of Ca, Al and Fe that can participate in phosphate removal from wastewaters. Moreover, the trace or even undetectable concentrations of heavy metals would not compromise the ecotoxicity level of the treated effluents (Mellbo et al., 2007).

The combustion technologies used to produce electricity from forest biomass also produce solid residues, namely fly and bottom ashes that must be recycled or disposed of properly (Reimann et al., 2008; Umamaheswaran and Batra, 2008; Ahmaruzzaman, 2010). The characteristics of biomass ashes are quite diverse from each other, depending on the type of biomass, soil and harvesting method used (Olanders and Steenari, 1995; Ahmaruzzaman, 2010; Singh et al., 2011). Furthermore, the same type of biomass can differ among itself due to biomass growth conditions, weather, storage and geographical origin.

The presence of several active metals that are usually used in chemical coagulation-flocculation treatments, such as Ca, Al and Fe (Grubb et al., 2000; Pengthamkeerati et al., 2008; Xu et al., 2010), makes biomass ashes a promising material for the removal of P from wastewaters.

Besides these aspects, the reuse of sub-products from thermal processes would be much more interesting, because they avoid the thermal activation pre-treatment. This aspect is quite important since other products that have been tested require a previous thermal activation before their use as efficient adsorbents, increasing the cost of the final adsorption product (Xiong et al., 2011).

The main objectives of this work were to (i) study the potential of biomass ashes to remove phosphates from both a SWW and a PPWW, and (ii) assess the ecotoxicity impact caused by the addition of these ashes to both wastewaters.

3.3.2 Materials and Methods

3.3.2.1 Origin and characterization of biomass ashes

Two types of biomass ashes were used in this study: fly and bottom ashes. They were collected in a biomass power plant that produces electricity by burning forestry residues (bark of eucalyptus and pine). The bottom ashes were collected in the bottom of the furnace and fly ashes was collected in the bag-house filters. In a previous work (Barbosa et al., 2013), both biomass ashes were characterized for (i) particle size distribution (ISO 3310-2, 1999), and (ii) chemical composition through an acidic digestion (USEPA Method 3051A, 2007).

3.3.2.2 Origin and characterization of wastewaters

A phosphate solution was used as the SWW. This was prepared as follows: $Na_2HPO_4.12H_2O$ (Sigma-Aldrich) at an initial concentration of 20±2 mg P/L (initial pH: 8.5±0.1).

A treated wastewater from a pulp and paper mill wastewater treatment plant (PPWWTP) was also used. Samples of the PPWW were collected in the discharge channel of the PPWWTP, just before the receiving water body (river estuary with a salted water environment). The PPWWTP includes the following treatment steps: neutralization, primary settling, high load activated sludge, and secondary settling.

Prior to the removal assays of phosphates, the PPWW was characterized to the following set of parameters: Total P (acidic digestion followed by colorimetry, method 4500; APHA/AWWA/WEF 2005), phosphates (colorimetric, method 4500; APHA/AWWA/WEF 2005), pH (electrometric, method 4500; APHA/AWWA/WEF, 2005); conductivity (electrometric; ISO 7888, 1985; color (spectrophotometric; method 2120 C; APHA/AWWA/WEF, 2005), Total Suspended Solids (TSS) (gravimetric; method 2540D; APHA/AWWA/WEF, 2005), Chemical Oxygen Demand (COD) (volumetric, method 5220 B; APHA/AWWA/WEF, 2005), Biochemical Oxygen Demand (BOD_5) (respirometric; method 5210 B; APHA/AWWA/WEF, 2005), Kjeldahl nitrogen (titrimetric; ISO 5663, 1984), ammonium (titrimetric; ISO 5664, 1984), nitrates and nitrites (ionic chromatography, method 4110; APHA/AWWA/WEF 2005), Ca (acidic digestion according with 3015A USEPA, followed by quantificaition by AAS nitrous oxide flame; ISO 7980, 2010), Al, Ba (acidic digestion according with 3015A USEPA, AAS nitrous oxide-acetylene flame, method 3111; APHA/AWWA/WEF, 2005), Fe, Sb (acidic digestion according with 3015A USEPA, AAS air-acetylene flame; APHA/AWWA/WEF, 2005).

3.3.2.3 Removal assays of phosphates

The removal assays of phosphates were conducted in triplicate under batch conditions, according to the following procedure (constant temperature of 20±2ºC):

(i) Aliquots of 500 mL of each wastewater were added to glass beakers;

(ii) Known amounts of fly and bottom ashes were added to each beaker (SWW: S/L ratios varying from 0.084 to 53.53 g/L for fly ashes, and from 0.57 to 72.39 g/L for bottom ashes; PPWW: S/L ratios varying from 0.013 to 34.45 g/L for fly ashes, and from 0.091 to 46.59 g/L for bottom ashes);

(iii) The mixtures were stirred in a Jar-test equipment for 1 min, at 100 rpm, followed by a slow stirring period of 15 min, at 40 rpm;

(iv) The mixtures were then settled for 30 min.

Figure 3.32 shows the phase (iv) of the settle down of the supernatants submitted to fly ashes treatment.

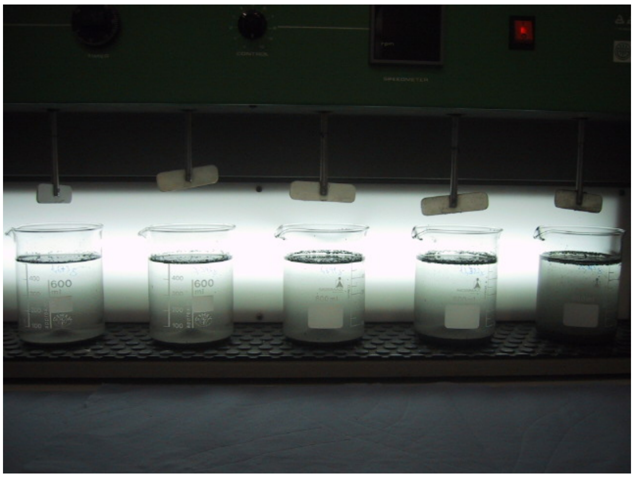


Figure 3.32 - Detail of the phase (iv) of the samples treated with fly ashes

The supernatants were filtered through a cellulose ester membrane of 0.45 µm porosity (Whatman, ref. 10401612). An aliquot of 100 mL of the filtered solutions was preserved for the quantification of phosphates (standard and method as referred before). An additional aliquot of 50 mL was preserved for the quantification of Al, Ba, Ca, Fe, and Sb (standards and methods as referred in sub-chapter 3.3.2.2). Al, Ca, and Fe were quantified because they are the predominant elements involved in the removal process of phosphates. Ba and Sb were quantified because they were the only metals detected in aqueous eluates of the biomass ashes (Barbosa et al., 2013).

A removal test of P was performed in a larger volume of the PPWW to allow for an extended characterization of two supernatants obtained with two different S/L ratios. The supernatants resulting from this enlarged test were characterized for total P, phosphates, pH, conductivity, color, TSS, COD, BOD_5, N-Kjeldahl, ammonium, nitrates, nitrites, Al, Ba, Ca, Fe, and Sb (standards and methods as referred in sub-chapter 3.3.2.2) as these are some of the chemical parameters that has to be controlled in the effluent of the PPWWTP.

3.3.2.4 Acute ecotoxicity of wastewaters and supernatants

The acute ecotoxicity of the SWW, PPWW and supernatants were assessed by using the following bioindicators: marine bioluminescent bacterium *Vibrio fischeri* (performed in a miniaturized system of Microtox® according with ISO 11348-3, 2007); salted water microcrustacean *Artemia franciscana* (performed in a miniaturized test kit from MicroBioTests Inc. according with ASTM E1440–91, 2004). Only marine organisms were used because the PPWW is directly discharged into a river estuary with salted water. The pH values of all samples were adjusted to 8.0±0.5 prior to the biological assays, because the effect of pH in the ecotoxicity was not intended to be analyzed.

3.3.2.5 Isotherms of Langmuir and Freundlich and statistical analysis

The data obtained in the removal assays of phosphates from the SWW and PPWW were modeled according to the isotherms of Langmuir (Eq. 3.2) and Freundlich (Eq. 3.3) (Santhosh et al., 2003):

$$C_e/Y_e = [1/(Q*b)]+C_e/Q \qquad \text{Eq. 3.2}$$

where C_e is the equilibrium concentration of the chemical species adsorbed (mg/L), Y_e is the mass of the chemical species adsorbed by unit mass of the adsorbent (mg/g), Q is the maximum amount of the chemical species adsorbed per unit mass of the adsorbent (mg/g), and b is the Langmuir's constant (L/mg). The Langmuir's isotherm is a mono-layer model, applicable to cases in which the adsorption occurs in the surface layer of the adsorbent;

$$\log Y_e = \log P + (1/n)^*\log C_e \qquad \text{Eq. 3.3}$$

where C_e and Y_e have the same meanings as defined above, and P and n are empirical constants (Freundlich's parameters) (dimensionless). If the value of n is greater than 1, then it must be concluded that a good adsorption of the adsorbate took place onto the adsorbent. The isotherms of Langmuir and Freundlich were adjusted to the experimental values with the minimum least-square method.

The statistical quality of the adjustments of both isotherms was tested by both the analysis of the determination coefficients (R^2) and F-test (two-sample for variances). In the F-test, the null hypothesis of the equality of the variances of experimental Y_e values ($\sigma_{exp,Ye}$) and modeled Y_e values ($\sigma_{mod,Ye}$) was tested (H_0: $\sigma_{exp,Ye} = \sigma_{mod,Ye}$). The experimental Y_e values were obtained in the removal assays of phosphates, and the modeled Y_e values were calculated by using the variables of the isotherms of Langmuir and Freundlich derived from the application of the mathematical models to the experimental values. The F-critical values were obtained for a significance level of 0.05.

3.3.3 Results and Discussion

3.3.3.1 Particle size distribution and chemical composition of biomass ashes

According to a previous work (Barbosa et al., 2013), fly ashes were mainly composed of particles with dimensions ranging from 20 to 200 µm (84.3% w/w db), while bottom ashes was predominantly composed of particles with sizes comprised between 200 and 4000 µm (78.3% w/w db). The data obtained in the size fractionation of ashes showed that fly ashes was mostly composed of fine particles, while the bottom ashes was mostly constituted of coarse particles. The chemical composition of the acidic digested samples of both fly and bottom ashes (Barbosa et al. 2013) revealed that alkali and alkaline-earth metals were the major elements in fly and bottom ashes (concentration and standard deviation in fly ashes): K = 17529±1372 mg/kg db, Na = 1953±269 mg/kg db, Ca = 43576±6103 mg/kg db, Mg = 22317±2128 mg/kg db, and Ba =

248±8 mg/kg db; concentration and standard deviation in bottom ashes: K = 3419±119 mg/kg db, Na = 283±15 mg/kg db, Ca = 14900±100 mg/kg db, Mg = 4627±432 mg/kg db, and Ba < 62.6 mg/kg db).

Fe and Al also showed high concentrations in both ashes (fly ashes: Fe = 17529±1372 mg/kg db, and Al = 27913±4298 mg/kg db; bottom ashes: Fe = 3560±340 mg/kg db, and Al = 3737±277 mg/kg db). Zn, Cr, Cu, As, Sb, and Se presented low or very low concentrations in both ashes (142±0.3 mg Zn/kg db in fly ashes and 30.3±2.4 mg Zn/kg db in bottom ashes; 48.6±3.7 mg Cr/kg db in fly ashes and <19.6 mg Cr/kg db in bottom ashes; 33.1±2.3 mg Cu/kg in fly ashes and <16.1 mg Cu/kg db in bottom ashes; 6.27±0.92 mg As/kg db in fly ashes and 0.80±0.02 mg As/kg in bottom ashes; 0.51±0.08 mg Sb/kg db in fly ashes and 0.19±0.02 mg Sb/kg in bottom ashes; 1.6±0.2 mg Se/kg in fly ashes 3.1±0.1 mg Se/kg db in bottom ashes). Mo, Ni, Cd, Hg, and Pb were below the respective QL (Mo < 41.1 mg/kg db in fly ashes <38.4 mg/kg db in bottom ashes; Ni <26.4 mg/kg db in fly ashes and <24.7 mg/kg db in bottom ashes; Cd 13.4 mg/kg db in fly ashes and <12.6 mg/kg db in bottom ashes; Hg <0.50 mg/kg db in fly ashes and <0.47 mg/kg db in bottom ashes; Pb <41.9 mg/kg db in fly ashes and <33.5 mg/kg db in bottom ashes).

3.3.3.2 Removal assays of phosphates from the SWW

Figure 3.33 shows the average removal efficiencies of phosphates and standard deviations obtained in the SWW as a function of the S/L ratios for both ashes.

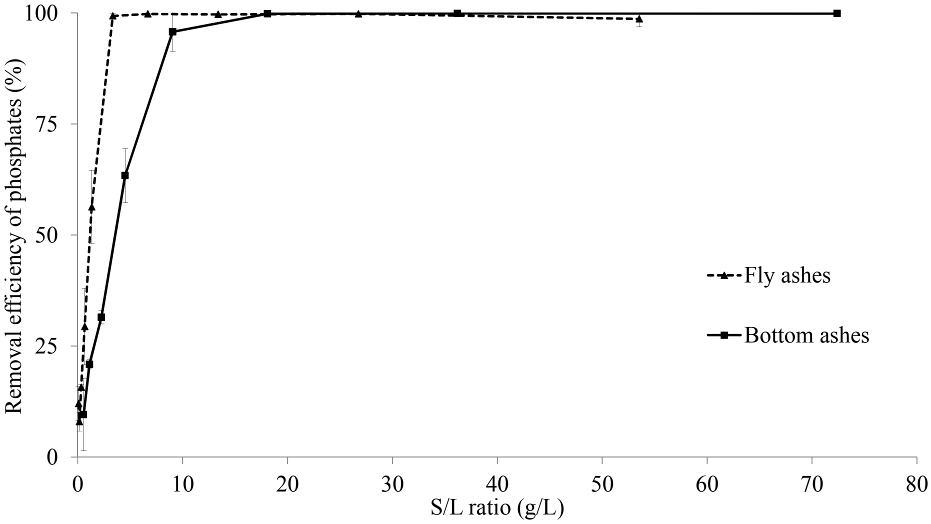


Figure 3.33 - Average removal efficiencies of phosphates obtained in the assays with the SWW as a function of the addition of biomass ashes

The removal percentages of phosphates for both biomass ashes increased rapidly with the increase of S/L ratios. The addition of 3.35 g/L of fly ashes to the SWW lead to a removal efficiency of phosphates of 99.3%, while the addition of 9.05 g/L of bottom ashes yield a removal percentage of only 97.6%.

Table 3.3 and Table 3.4 present the average concentrations of Ca, and Al in the supernatants obtained in the removal assays of phosphates from the SWW as a function of S/L ratios.

Table 3.3 - Al, and Ca content in the supernatants treated with fly ashes

S/L (g/L)	0.08	0.17	0.33	0.67	1.34	3.35	6.69	13.4	26.8	53.5
Al (mg/L)	0.73	0.75	0.75	0.85	0.96	1.11	2.64	4.90	5.71	6.97
Ca (mg/L)	0.84	0.61	0.98	0.51	0.67	5.11	56.1	62.3	105	157

Table 3.4 - Al, and Ca content in the supernatants treated with bottom ashes

S/L (g/L)	0.57	1.13	2.26	4.52	9.05	18.10	36.20	72.39
Al (mg/L)	0.34	0.34	0.34	0.34	0.41	1.52	2.26	2.34
Ca (mg/L)	0.45	0.02	0.02	0.53	2.33	27.66	92.09	108.79

The concentrations of Sb, Fe, and Ba (data not shown) in the supernatants were below the QL for all of the S/L ratios, except for Ba concerning the supernatant in which the maximum dosage of fly ashes was applied (Ba = 0.19 mg/L). The average concentrations of Ca in the supernatants rose with the increasing dosage of both biomass ashes. The average concentrations of Al in the supernatants also tended to increase with the increasing dosage of ashes. The concentrations of Al in the supernatants were high, especially for fly ashes, but all of them were much below the limit concentration defined by European and Portuguese legislations for treated wastewaters (10 mg/L). Also it is necessary to consider that these results were obtained in a synthetic wastewater; therefore, no other chemical substances were present in the liquid medium that can be involved in Al biding and removal, as it may occur in real wastewaters. Hence, the concentrations of Al tend to be higher in this wastewater.

Figure 3.34 shows the final pH values of SWW supernatants after the treatment with both biomass ashes. The SWW presented a low buffer capacity as the pH value significantly increased from about 8.5 to 11.0 for the low S/L ratios comprised in the range of 0.08 to 2.26 g/L for both biomass ashes. This significant increase in the pH values of supernatants also may contribute to the removal of phosphates from the SWW through precipitation, as the phosphates form insoluble salts at high pH values. In this context, it is interesting to note the similarity between the curves of the average removal efficiencies of phosphates (Figure 3.33) and the curves of the final pH values of supernatants (Figure 3.34) as a function of the S/L ratios of both biomass ashes.

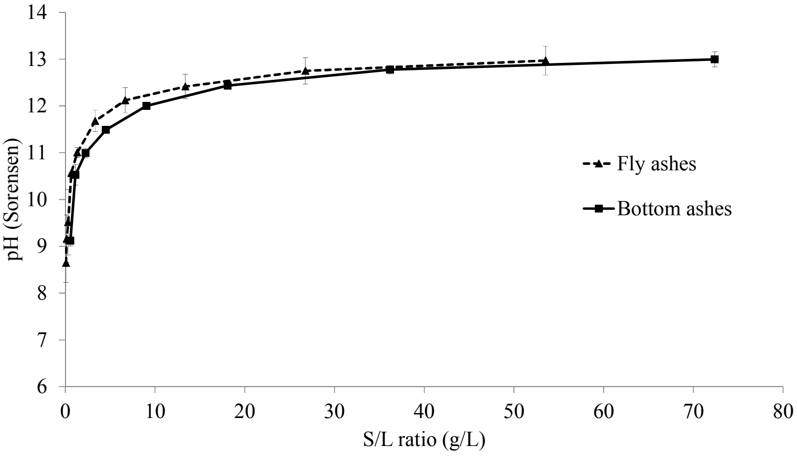


Figure 3.34 - Final pH values of the supernatants of the SWW after the treatment with fly and bottom ashes

3.3.3.3 Ecotoxicological levels of supernatants from the SWW

Figure 3.35 shows the ecotoxicological levels of SWW and the supernatants obtained after the treatment with bottom and fly ashes, for *V. fischeri* and *A. franciscana*.

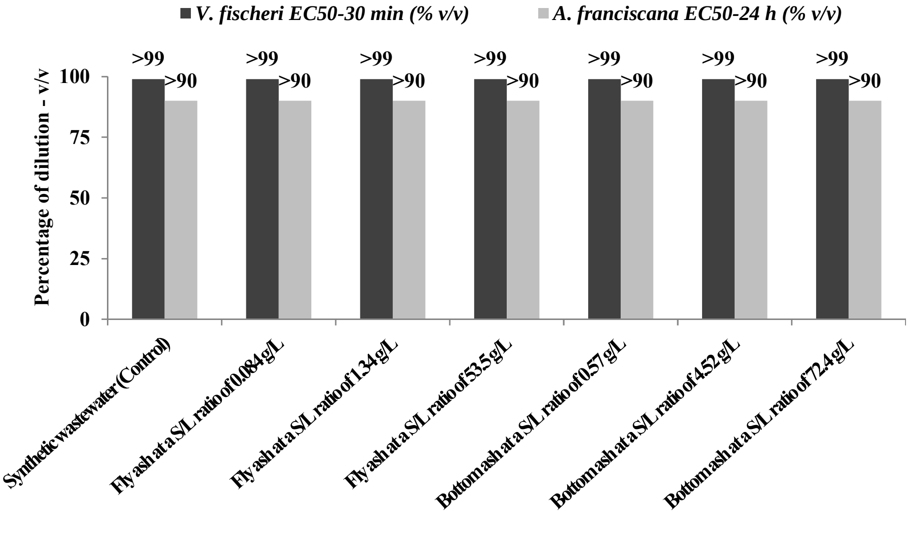


Figure 3.35 - Ecotoxicological levels of synthetic wastewater and of six supernatants obtained after the synthetic wastewater treatment with fly and bottom ashes.

The SWW and all supernatants did not show acute ecotoxicity for both bioindicators (EC_{50}-30 min >99% for *V. fischeri*, and EC_{50}-24 h >90% for *A. franciscana*). Therefore, it is possible to conclude that the addition of both fly and bottom ashes to the SWW had not promoted any level of acute ecotoxicity in the wastewaters.

3.3.3.4 Modeling the removal of phosphates from the SWW

Table 3.5 shows the parameters of the isotherms of Langmuir and Freundlich for the removal of phosphates from the SWW for both bottom and fly ashes.

The F-test shows that the variances of the modeled values were equal to the variances of the experimental values, for a significance level of 0.05, and for both isotherms. Therefore, both isotherms explained well the variance of the experimental data for both ashes. R^2 values were higher for bottom ashes than for fly ashes, indicating that the isotherms of Langmuir and Freundlich explained better the adsorption of phosphates onto the former ashes than onto the latter. Moreover, the R^2 values were higher for the Langmuir's isotherm than for the Freundlich's isotherm, meaning that the adsorption of phosphates onto the biomass ashes mainly occurred as a mono-layer mechanism, especially in the case of bottom ashes.

The Langmuir's isotherm indicated that the fly ashes showed a high adsorption capacity of phosphates with a *Q* value (12.9 mg/g) almost 4 times higher than the *Q* value for bottom ashes (3.4 mg/g). The Freundlich's isotherm pointed out for strong adsorption processes of the phosphates onto both bottom and fly ashes, as the *n* values were quite above 1.

Q values for coal fly ashes are reported to be in the range of 63.2 to 427 mg P/g (Li et al., 2006). The *Q* values for both ashes studied in the present work were lower than these values reported for coal fly ashes. Nevertheless, it is important to stress that the biomass ashes pose less ecotoxicity risk than coal fly ashes, as they contain trace or even undetectable concentrations of toxic metals.

Table 3.5 - Parameters of the isotherms of Langmuir and Freundlich, R^2, and F-test values for the removal tests of phosphates performed in the SWW (df: degrees of freedom; *p*: probability of F-critical to be higher or lower than F-ratio depending on the value of F-ratio to be higher or lower than 1, respectively; Null hypothesis: $\sigma_{exp,Ye} = \sigma_{mod,Ye}$)

Biomass ashes	SWW							
	Isotherm of Langmuir			F-test results				
	Q (mg/g)	*b* (L/mg)	R^2	F-ratio	df	*p*	F-critical one tail	Decision
Bottom ashes	3.4	2.08	0.976	0.741	7	0.352	0.264	Null hypothesis accepted
Fly ashes	12.9	0.40	0.704	2.26	9	0.120	3.18	Null hypothesis accepted

Biomass ashes	SWW							
	Isotherm of Freundlich			F-test results				
	n	*P*	R^2	F-ratio	df	*p*	F-critical one tail	Decision
Bottom ashes	3.5	1.59	0.843	0.863	7	0.426	0.264	Null hypothesis accepted
Fly ashes	2.7	3.94	0.581	2.93	9	0.063	3.18	Null hypothesis accepted

3.3.3.5 Chemical characterization of the crude PPWW

Figure 3.36 to Figure 3.39 show the data obtained in the chemical characterization of the PPWW before the treatment with biomass ashes (crude PPWW) Figure 3.36 to Figure 3.39 also show the chemical characterization after the treatment of PPWW with fly ashes (S/L ratio of 34.45 g/L), and bottom ashes (S/L ratio of 46.59 g/L). The data relative to the treated effluents is presented in the same Figures of the crude PPWW in order to be easier the treatment efficiency. The discussion related with the treated effluents will be discussed later.

The concentrations of N-kjeldhal, ammonium, nitrate, nitrite, Ba, Fe, and Sb in crude PPWW were below the QL (N-kjeldhal: < 7 mg N/L; ammonium: < 0.03 mg N/L; nitrate: < 0.68 mg N/L; nitrite: < 0.15 mg N/L; Ba: 0.16 mg Ba/L; Fe: < 0.06 mg Fe/L; Sb: < 0.3 µg/L).

The pH value was close to neutrality while the concentration of Ca was 36.6±1.3 mg/L. Total P was mainly constituted by phosphates, which were present in an average concentration (3.18±0.14 mg P/L) much lower than the concentration tested in the synthetic wastewater (20 mg P/L). The average chemical characterization is in agreement with several studies found in literature for the same type of wastewaters (for example, Devi et al., 2011).

The concentrations of TSS, BOD_5, COD, and the values for colour and conductivity were in agreement with several studies found in literature for the same type of wastewaters. Pokhrel and Viraraghavan (2004) determined similar concentrations of TSS (34 mg/L), BOD_5 (23 mg/L) and colour (4668 Hazen), as well as Devi et al. (2011) for TSS (27.5 mg/L), BOD_5 (27.5 mg/L) and COD (316.2 mg/L).

El-Bestawy et al. (2008) and Diniz et al. (2011) have reported values for COD of 552 mg/L and 392 mg/L, respectively, while Ugurlu and Karaoglu (2011) have obtained concentrations of BOD_5 of 25.5 mg/L and of COD of 426 mg/L. The Thematic European Network named Industrial Liquid Effluents - ILE (2006) have also reported concentrations of TSS of 36 mg/L), BOD_5 of 23 mg/L and COD of 384 mg/L for treated pulp and paper mill effluents. All these data are similar to the results obtained in the treated wastewater of pulp and paper mill studied in the present work.

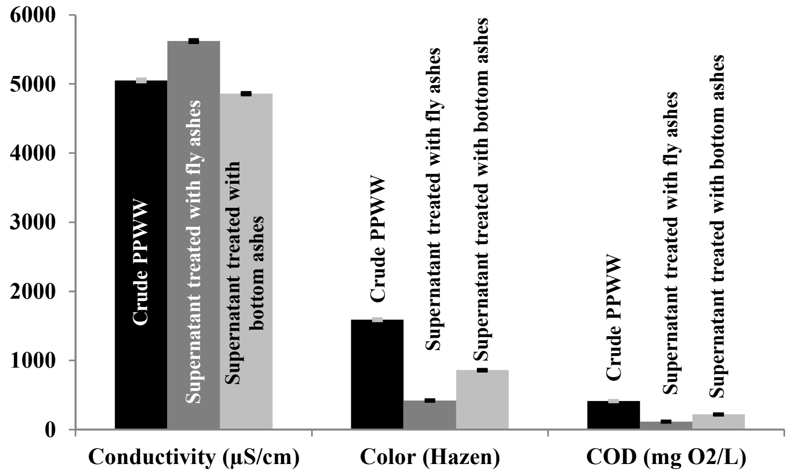


Figure 3.36 - Conductivity, color, and COD of the crude PPWW and extended characterization of two supernatants obtained after the treatment of the PPWW with fly ashes (S/L ratio = 34.45 g/L) and bottom ashes (S/L ratio = 46.59 g/L) (±SD;n=3)

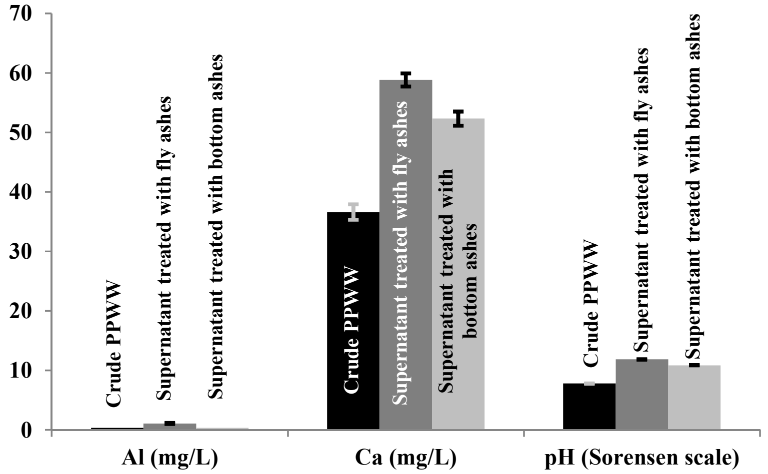


Figure 3.37 - Al, Ca, and pH of the crude PPWW and extended characterization of two supernatants obtained after the treatment of the PPWW with fly ashes (S/L ratio = 34.45 g/L) and bottom ashes (S/L ratio = 46.59 g/L) (±SD; n=3)

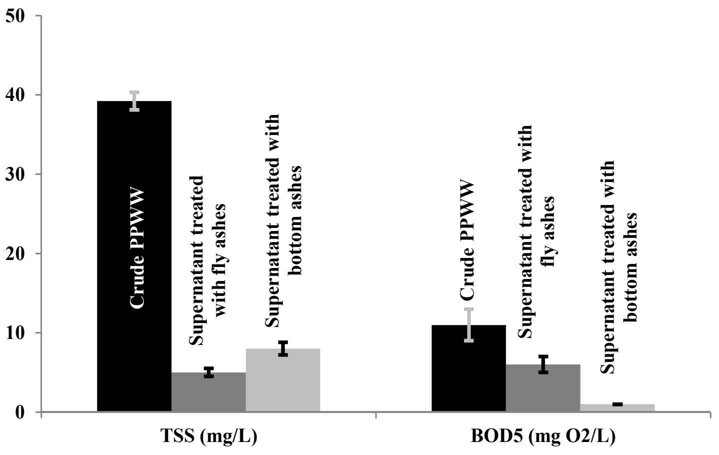


Figure 3.38 - TSS and BOD_5 of the crude PPWW and extended characterization of two supernatants obtained after the treatment of the PPWW with fly ashes (S/L ratio of 34.45 g/L) and bottom ashes (S/L ratio = 46.59 g/L) (±SD; n=3)

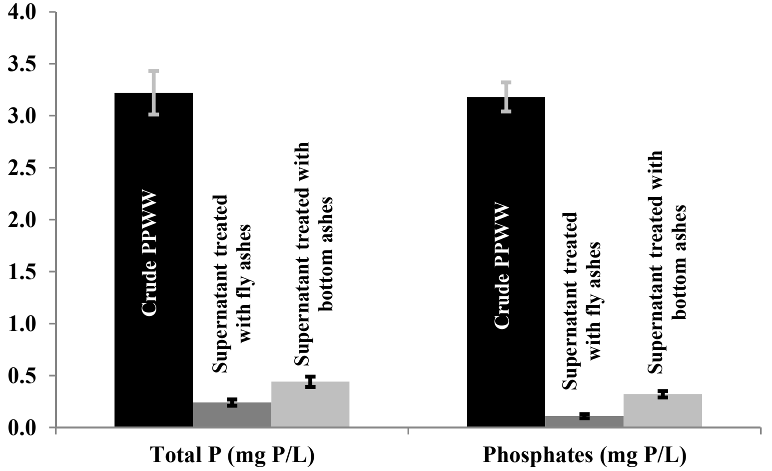


Figure 3.39 - Total P and phosphates of the crude PPWW and extended characterization of two supernatants obtained after the treatment of the PPWW with fly ashes (S/L ratio=34.45 g/L) and bottom ashes (S/L ratio= 46.59 g/L) (±SD;n=3)

3.3.3.6 Removal assays of phosphates from the PPWW

Figure 3.40 shows the removal efficiencies of phosphates and standard deviations for the PPWW as a function of the S/L ratios for both bottom and fly ashes.

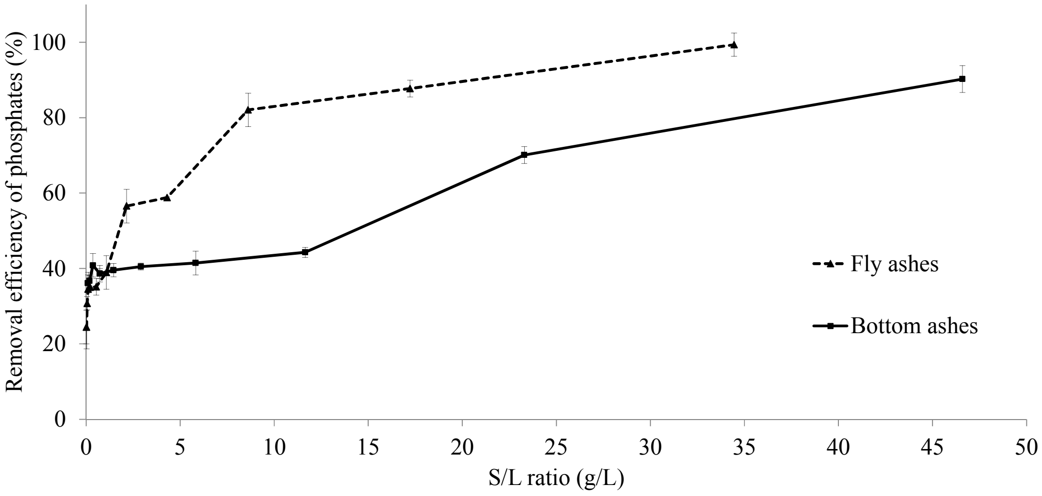


Figure 3.40 - Average removal efficiencies of phosphates obtained in the assays with the PPWW as a function of the addition of biomass ashes

The removal percentages were higher for the addition of fly ashes than for bottom ashes. The addition of 34.45 g/L of fly ashes yield to a removal percentage of 97.6%, while the addition of 46.59 g/L of bottom ashes only reached a removal percentage of 90.3%. The addition of fly ashes promoted a strong increase in the removal efficiencies of phosphates for the lowest S/L ratios, while the addition of bottom ashes only achieved high removal efficiencies for the highest S/L ratios (46.59 g/L).

The concentrations of Sb, Fe, Ba, and Al in the supernatants of the PPWW (results not shown) were below the respective QL (Sb ≤ 0.0003 mg/L, Fe ≤ 0.06 mg/L, Ba ≤ 0.16 mg/L, and Al ≤0.34 mg/L) for all of the dosages of both biomass ashes. The concentrations of Ca (results not shown) in the supernatants rose with the increase of S/L ratios of both fly and bottom ashes. The higher concentrations of Ca in the supernatants after the treatment with fly and bottom ashes were 58.0 and 50.0 mg/L, respectively.

Concerning Al, the behavior registered in the SWW was not repeated in the PPWW. The Al concentrations were low (≤0.34 mg/L, QL), demonstrating that Al might be removed from the liquid medium through other chemical substances present in a real wastewater.

Figure 3.41 presents the final pH values of PPWW supernatants after the treatment with both biomass ashes.

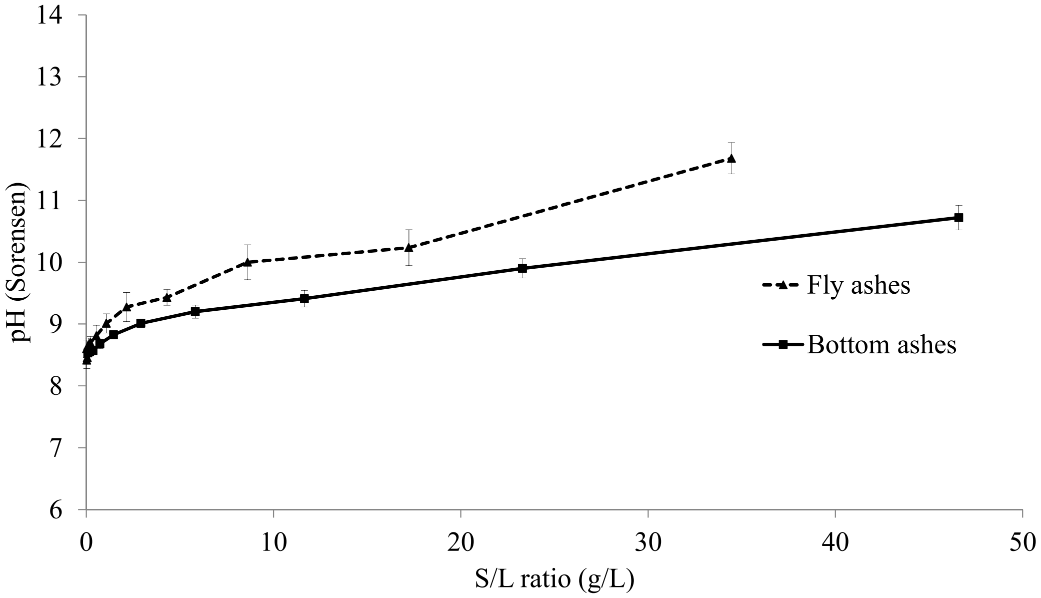


Figure 3.41 - . Final pH values of the supernatants of the PPWW after the treatment with fly and bottom ashes

The pH increase was not as intensive for the first S/L ratios as registered for the SWW supernatants, meaning that PPWW presented a high buffer capacity. The pH increase was more linear in PPWW supernatants and the highest pH values only were attained for the two highest S/L ratios tested (34.45 g/L for fly ashes, and 46.59 g/L for bottom ashes). Some similarity between the phosphate removal curves and pH curves was observed for PPWW supernatants, but not as strong as for SWW.

3.3.3.7 Extended chemical and ecotoxicological characterizations of supernatants from the PPWW

Based on the data obtained in the previous removal assays of phosphates from the PPWW, a dosage of fly ashes of 34.45 g/L and of bottom ashes of 46.59 g/L were selected for a removal assay conducted with a higher volume of PPWW. Figure 3.36 to Figure 3.39 show the concentrations of several chemical parameters determined in the two supernatants.

The addition of both biomass ashes to the PPWW enabled a significant reduction of Total P of 86.4% (to 0.44 mg P/L) when using bottom ashes and 92.5% (to 0.24 mg P/L) when using fly ashes. It was also observed a reduction in the concentration of phosphates in percentages ranging from 90.1 (to 0.32 mg P/L) when using bottom ashes to 96.5% (to 0.11 mg P/L) when using fly ashes. These results are very interesting if an additional decrease in P concentration will become necessary in future legislation. Furthermore, additional high reduction percentages in color, TSS, COD and BOD_5 were registered in the supernatants obtained after the treatment with both ashes.

The chemical element Al presented an increase in its concentration from the crude PPWW (<0.34 mg/L) to the supernatant treated with fly ashes (1.08 mg/L). This average concentration was below the limit concentration defined by the European and Portuguese legislations for treated wastewaters (10 mg/L). However, in countries in which this limit concentration is more restrictive, the S/L ratio of ashes added to the wastewaters also becomes a factor of concern in the treatment process, and eventually the bottom ashes can be considered more adequate to remove phosphates than fly ashes, as it caused no increase in Al concentration in the supernatant (Figure 3.36, Figure 3.37, Figure 3.38, and Figure 3.39).

Also the Al concentrations in the supernatants of the PPWW were much lower than those registered in the supernatants of SWW, for both biomass ashes. It is assumed that other chemical substances present in the PPWW were responsible for the Al removal during the treatment with both biomass ashes.

The pH increased significantly in the supernatants of the PPWW after the treatment with fly and bottom ashes (7.79 in PPWW; 11.86 in the supernatant of fly ashes; 10.86 in the supernatant of bottom ashes). This is due to the solubility of oxides existing in the ashes that produces strong hydroxides in the liquid medium. This can have two important consequences: firstly, the high pH values may be involved in the removal of phosphates as they form insoluble salts and precipitate under such high pH values; secondly, if this treatment system with biomass ashes would be implemented in a wastewater treatment plant, the supernatants should be submitted to a pH correction to a neutral value prior to their discharge in the environment, in order to avoid the pH change in the receiving aquatic ecosystem.

The ecotoxicological characterization carried out in the PPWW and in the two supernatants had not indicated ecotoxicity for both biological indicators (EC_{50}-30 min >99% for *V. fischeri*, and EC_{50}-24 h >90% for *A. franciscana*). Therefore, it is possible to conclude that the treatment of the PPWW with both fly and bottom ashes had not caused acute ecotoxicity in the supernatants.

3.3.3.8 Modeling the removal of phosphates from the PPWW

Table 3.6 presents a summary of the data obtained in the modeling process of the phosphate removal from PPWW through the isotherms of Langmuir and Freundlich.

Low fitness degrees of both isotherms to the experimental data were registered, although the highest values of R^2 for Freundlich's isotherm indicate for a removal process that partially occurred according to a multi-layer mechanism.

The results of the F-test supported the conclusion that the variances of the modeled data were not equal to the variances of the experimental data ($\sigma_{exp,Ye} \neq \sigma_{mod,Ye}$) for both isotherms and biomass ashes. Therefore, it is possible to conclude that the Langmuir's and Freundlich's isotherms did not explain adequately the removal process of phosphates from the PPWW, which can be explained by the following two reasons:

a) The process was not chiefly governed by adsorption mechanisms, but also by other mechanisms. The presence of Ca and Al in both biomass ashes and their high solubility in PPWW may indicate that coagulation-flocculation processes took place. Moreover, as both biomass ashes have promoted a high increase in the pH of the PPWW supernatants for values of

Table 3.6 - Parameters of the isotherms of Langmuir and Freundlich, R^2, and F-test values for the removal tests of phosphates performed in the PPWW (df: degrees of freedom; p: probability of F-critical to be higher or lower than F-ratio depending on the value of F-ratio to be higher or lower than 1, respectively; Null hypothesis: σexp,Ye = σmod,Ye)

Biomass ashes	PPWW							
	Isotherm of Langmuir			F-test results				
	Q (mg/g)	*b* (L/mg)	R^2	F-ratio	df	*p*	F-critical one tail	Decision
Bottom ashes	0.44	0.279	0.066	452	11	5.9E10^{-13}	2.82	Null hypothesis rejected
Fly ashes	1.73	0.293	0.206	209	11	3.9E10^{-11}	2.82	Null hypothesis rejected

Biomass ashes	PPWW							
	Isotherm of Freundlich			F-test results				
	n	*P*	R^2	F-ratio	df	*p*	F-critical one tail	Decision
Bottom ashes	0.62	0.378	0.355	104	11	1.8E10^{-9}	2.82	Null hypothesis rejected
Fly ashes	0.89	1.97	0.526	74.8	11	1.8E10^{-8}	2.82	Null hypothesis rejected

10.86 (bottom ashes) and 11.86 (fly ashes), it is possible that precipitation processes could also take part in the global removal process of phosphates;

b) Other substances present in the PPWW can compete with phosphates in the removal process considerably. As stated by Maurer and Boller (1999), the removal model is highly dependent on wastewater composition, such as dissolved solids, particulate solids, and phosphorus speciation, which are critical in PPWW.

3.3.4 Conclusions

Biomass ashes have presented a high capacity to remove phosphates from a SWW and PPWW and have not promoted any change in the ecotoxicity levels of the treated effluents. Nevertheless, fly ashes were more efficient in removing P than bottom ashes.

The removal of phosphates from the SWW was primarily governed by mono-layer mechanisms, while the removal of phosphates from the PPWW was partially explained by multi-layer mechanisms. Also precipitation probably occurred as a removal mechanism of phosphates, as both biomass ashes promoted a significant increase in the pH values of the supernatants of SWW and PPWW.

Globally, the use of biomass ashes, especially fly ashes, can be a promising methodology for removing phosphates from wastewaters, although further studies on the kinetics involved are needed.

3.4 Biomass fly ashes as low-cost chemical agents for Pb removal from synthetic and industrial wastewaters

Based on the following paper:

Rui Barbosa, Nuno Lapa, Helena Lopes, Annika Günther, Diogo Dias, Benilde Mendes (2013). Biomass fly ashes as low-cost chemical agents for Pb removal from synthetic and industrial wastewaters. Journal of Colloid and Interface Science. (Submitted; under review)

Journal of Colloid and Interface Science is indexed on Scopus and SCImago

ABSTRACT

The main aim of this work was to study the removal efficiency of Pb from synthetic and industrial wastewaters by using biomass fly ashes. The biomass fly ashes were produced in a biomass boiler of a pulp and paper industry. Three concentrations of Pb^{2+} were tested in the synthetic wastewater (1, 10 and 1000 mg Pb/L). Moreover, two different wastewaters were collected in an industrial wastewater treatment plant (IWWTP) of an industry of lead-acid batteries: (i) wastewater of the equalization tank, and (ii) IWWTP effluent. All the wastewaters were submitted to coagulation-flocculation tests with a wide range of biomass fly ashes dosage (expressed as Solid/Liquid – S/L – ratios). All supernatants were characterized for chemical and ecotoxicological parameters. The use of biomass fly ashes has reduced significantly the Pb concentration in the synthetic wastewater and in the wastewaters collected in the IWWTP. For example, the definitive coagulation-flocculation assays performed over the IWWTP effluent presented a very low concentration of Pb (0.35 mg/L) for the S/L ratio of 1.23 g/L. Globally, the ecotoxicological characterization of the supernatants resulting from the coagulation-flocculation assays of all wastewaters has indicated an overall reduction on the ecotoxicity of the crude wastewaters, due to the removal of Pb.

Keywords: Biomass fly ashes; Ecotoxicity; Industrial wastewaters; Lead-acid batteries; Pb.

3.4.1 Introduction

The most common sources of lead in the environment are Pb-base pigments in paints, Pb-containing pesticides, discarded batteries, shooting ranges or waterfowl hunting sites and plumbing installations or repair sites (Kadirvelu and Goel, 2007). Despite some efforts on the reduction of the use of lead in some industrial activities and in some manufactured products, there are still some industries that use lead as raw material. Since lead is a heavy metal which is toxic to humans and to other living beings (Povey, 2010; Islam et al., 2011; Shu et al., 2012; Needleman and Gee, 2013) it is extremely important to remove this pollutant from wastewater.

The precipitation of metals from wastewaters involves the conversion of the soluble metal salt to insoluble salts (Jankowski et al., 2006; Kumpiene et al., 2008). The precipitate formed can then be removed from the treated wastewater by sedimentation and/or filtration. This process usually needs a pH adjustment, followed by the addition of a chemical coagulant (Bayat, 2002a; Bayat 2002b; Allinor, 2007; Ahmaruzzaman, 2010; Al-Zboon et al., 2011). Typically, metals precipitate from the solution as hydroxides, sulfides or carbonates. Depending on the type of the process used, it may be produced a sludge with so high concentrations of metals that can be submitted to metal recovery (Meunier et al., 2002; Drogui et al., 2005). The classical wastewater treatment systems use ferric-chloride, ferric-sulfate and aluminum sulfate as coagulation reagents, but due to their high cost, the industrial sector has become to search for efficient and low cost chemical agents.

In this framework, several studies (Gupta and Torres, 1998; Rao et al., 2002; Cho et al., 2005; Jankowski et al., 2006; Alinnor, 2007; Malakootian et al., 2008; Al Zboon et al., 2011; Gonzalez et al., 2011a) have been performed related with wastewater treatment using fly ashes produced from the combustion of several fuels. However, none of these studies was focused neither on the treatment of wastewaters produced by industries of lead-acid batteries nor on the use of biomass fly ashes from forestry residues as chemical agent for metal removal.

Coal fly ashes have a high potential in the treatment of wastewater because of its chemical composition. This type of fly ashes has high content on alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon, which can participate on the removal of several elements (Jankowski et al., 2006; Kumpiene et al., 2008). Moreover, the physical properties of coal fly ashes, such as porosity, particle size distribution and surface area, make them also attractive for the treatment of wastewaters. The alkaline nature of fly ashes is also a good property since make them a good neutralizing agent of acid wastewaters (Bayat, 2002a; Bayat, 2002b).

Al Zboon et al. (2011) have produced a geopolymer from coal fly ashes and used it for the removal of Pb^{2+} from an aqueous wastewater. The authors have tested the effect of various parameters on lead adsorption, including geopolymer dosage, initial concentration, contact time, pH and temperature. Despite of the good results that were obtained, the assays performed were not applied to a real wastewater sample, but only to a synthetic one.

Gupta and Torres (1998) have evaluated the removal of heavy metals and the changes on the toxicity of an effluent of a municipal wastewater treatment plant by using coal fly ashes. After the treatment with fly ashes, a reduction in toxicity and in the concentrations of Cu, Pb, PO_4^{3-}, and NO_3^- were registered.

Cho et al. (2005) have investigated the possibility of using coal fly ashes as a chemical adsorbent. The authors have performed batch experiments to evaluate the removal of heavy metals from synthetic aqueous solutions by fly ashes. Adsorption studies were done at various pH values (3–10), at 25 ºC, and for heavy metal concentrations (Zn, Pb, Cd and Cu) of 10–400 mg/L using fly ashes dosages of 10, 20 and 40 g/L. The authors have concluded that coal fly ashes may promote good removal efficiencies unless the wastewater is strongly acidic.

Alinnor (2007) has evaluated the removal characteristics of Pb^{2+} and Cu^{2+} ions from aqueous solution by coal fly ashes under various conditions of contact time, pH and temperature (30 to 60ºC). The level of removal of these metals has generally increased with the increasing of pH values. In what concerns the effect of temperature, the highest removal rate of those metals was achieved at 40ºC. According to this author, the main mechanisms involved in the removal of Pb^{2+} and Cu^{2+} from solution were adsorption at the surface of the coal fly ashes and precipitation.

Malakootian et al. (2008) have evaluated the removal of heavy metals (Pb and Co) from an effluent produced by a paint industry. The effect of pH and dosages of wood ashes were tested. The highest Pb removal efficiency was of 96.1%, at pH 2, with a contact time of 3 h and 100 g/L wood ashes. The highest Co removal efficiency was of 99.0 %, at pH 2, with a contact time of 3 h and 100 g/L wood ashes.

Many other studies could be referred here. Nevertheless, to the author's knowledge, none of these studies was focused neither on the treatment of wastewaters from an industry of lead-acid batteries nor on the use of biomass fly ashes from forest residues as a chemical agent for Pb removal. In this framework, the main goal of this study was to assess the removal efficiency of Pb^{2+} from a synthetic wastewater containing the initial concentrations of 1, 10 and 1000 mg

Pb/L, and from two wastewaters of an industry of lead-acid batteries, by using biomass fly ashes from a biomass boiler of a pulp and paper industry.

3.4.2 Materials and Methods

3.4.2.1 Origin and characterization of biomass fly ashes

The biomass fly ashes were produced in a Portuguese biomass boiler of a pulp and paper industry that produces electricity by burning eucalyptus and pine bark in a BFBC. The fly ashes were collected in the hopper of the electrostatic precipitator. The BFBC uses sand as fluidizing agent. The ashes were stored in air-tight polypropylene containers, at 4±1ºC, in the absence of light. In a previous work, Barbosa et al. (2013) have characterized this biomass fly ashes for (i) chemical composition through an acidic digestion (USEPA Method 3051A, 2007), and (ii) leaching behavior (EN 12457-2, 2002).

3.4.2.2 Origin and characterization of wastewaters

3.4.2.2.1 Synthetic wastewater

Samples of the synthetic wastewater with three different initial concentrations of Pb^{2+} (1, 10, and 1000 mg Pb/L) were prepared by using $Pb(NO_3)_2$ (Panreac) and deionized water (<0.2 µmS/cm) (Elix 5, Millipore). The Pb^{2+} concentrations in the samples of the synthetic wastewater were determined by AAS, in air-acetylene flame (ISO 8288, 1986).

3.4.2.2.2 Industrial wastewaters

Two industrial wastewaters were collected in an IWWTP of a factory that produces lead-acid batteries.

The IWWTP is composed by: (i) a neutralization tank, in which the pH correction of the acidic wastewater is performed, (ii) an equalization tank, which receives the wastewater coming from the neutralization tank and the wastewater coming from the disassembling line of the lead-acid batteries, (iii) the coagulation-flocculation tank, which receives the wastewater of the equalization tank and in which the coagulation-flocculation agents are added, (iv) the lamellar sedimentation tank, which removes the solids of the wastewater coming from the coagulation-flocculation process, (v) the sand filter, which removes fine particles, and (vi) the discharge channel, which conducts the treated wastewater to the receiving water body.

One of the industrial wastewater samples was collected in the equalization tank of the IWWTP. The other sample was collected in the final discharge channel of the IWWTP. The samples were cooled to 4ºC during the transportation and preserved according to ISO 5667-3 (2003).

The industrial wastewaters were characterized for the following chemical species: pH (electrometric -method 4500; APHA/AWWA/WEF, 2005), SO_4^{2-} (Turbidimetric - method 4500 E; APHA/AWWA/WEF, 2005), F^- (SPADNS - method 4500 D, APHA/AWWA/WEF, 2005), Oil and grease (extraction using trichlorotrifluoroehtane as solvent followed by gravimetric method – adapted from method 5520, APHA/AWWA/WEF, 2005), COD (chemical oxidation with potassium dichromate 0.25N, at 160 ºC, in an acidic environment – H_2SO_4 98–99% v/v, in a Behr digester, and titration with ammonium ferrous sulphate 0.25N - method 5220 B; APHA/AWWA/WEF, 2005), Total Hardness (Titrimetric method with EDTA - method 2340; APHA/AWWA/WEF, 2005), Calcic Hardness (Titrimetric method with EDTA - method 2340, APHA/AWWA/WEF, 2005), Fe, Sb (AAS air-acetylene flame – method 3111; APHA/AWWA/WEF, 2005), Al, (AAS nitrous oxide-acetylene flame– method 3111; APHA/AWWA/WEF, 2005), Ca (AAS nitrous oxide-acetylene flame; ISO 7980, 2010), As (AAS air-acetylene flame; EN ISO 11969, 1996), and Pb (AAS air-acetylene flame; ISO 8288, 1986).

3.4.2.3 Coagulation-flocculation assays

Both synthetic and industrial wastewaters were submitted to coagulation-flocculation assays using the biomass fly ashes.

It was assumed that the removal of Pb^{2+} was dependent of the content of Ca, Fe and Al in the eluates. Therefore, it was calculated the sum of the number of moles of Ca, Al and Fe [$\sum(n\text{Ca}+n\text{Al}+n\text{Fe})$] present in the eluates produced during the leaching assay of fly ashes, and considered the number of moles of Pb to be removed in each assay [$\sum(n\text{Pb})$]. Each sample was submitted to the addition of different dosages of fly ashes, i.e. different [$\sum(n\text{Ca}+n\text{Al}+n\text{Fe})$]/[$\sum(n\text{Pb})$] ratios were applied. The dosages of fly ashes were defined as S/L ratios (g of ashes/L of wastewater).

The coagulation-flocculation tests were developed in a Jar-Test apparatus and comprised the following steps: 1) fast stirring step - 100 rpm, during 1 min; 2) slow stirring step - 40 rpm, during 15 min; 3) sedimentation step - 0 rpm, during 30 min; 4) filtration of the supernatants using an ester-cellulose membrane with a porosity of 0.45 μm (Whatman). The coagulation-flocculation tests were performed at a controlled temperature of 20±1ºC. Figure 3.42 shows the coagulation-flocculation test with synthetic wastewater and using forestry fly ashes as removal agent of pollutants.

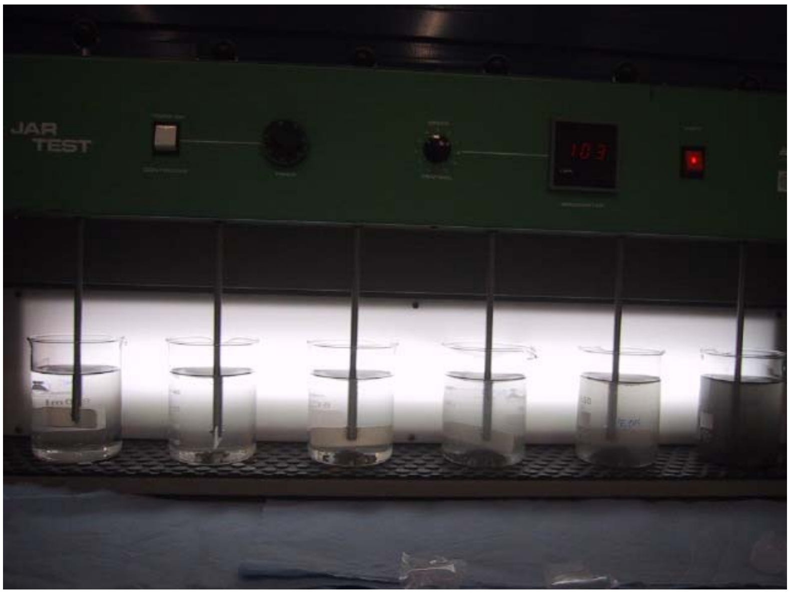


Figure 3.42 - Preparation of a coagulation-flocculation test with synthetic wastewater and using forestry fly ashes as removal agent of pollutants

3.4.2.4 Characterization of supernatants

3.4.2.4.1 Supernatants of the synthetic wastewater

After the coagulation-flocculation tests, the supernatants resulting from the treatment of the synthetic wastewater samples with biomass fly ashes were characterized for the following set of chemical parameters: pH, Pb, As, Sb, Ca, Fe, Al, F^-, SO_4^{2-}, total and calcic hardness (standards and methods were indicated in 3.4.2.2) and redox potential (Electrometric, method 2580 B, APHA/AWWA/WEF, 2005).

The ecotoxicological characterization using the biological indicators *Vibrio fischeri* (performed in a miniaturized system of Microtox® according with ISO 11348-3 2007) and *Artemia franciscana* (performed in a miniaturized test kit from MicroBioTests Inc. according with ASTM E1440–91 2004) was performed in four selected supernatants for each Pb^{2+}

concentration: the supernatant of the blank test (without ashes addition) and three supernatants obtained after the treatment with fly ashes in three different S/L ratios. The biological responses analyzed were the bioluminescence inhibition of *V. fischeri* and the mobility inhibition of *A. franciscana*. The pH values (standard and method were indicated previously) of the samples submitted to the ecotoxicological characterization were previously corrected to 8.0±0.3. TU were determined (TU = 100%/EC_{50}; EC_{50} means the Effective Concentration, expressed as %, that promotes a biological effect on 50% of the population of the organism tested).

3.4.2.4.2 Supernatants of the industrial wastewaters

In the case of the industrial wastewaters, the coagulation-flocculation tests were performed in two assays: preliminary and final assays. In the preliminary assay, the characterization of the supernatants included the determination of pH and Pb concentration. The final assay was performed with only three dosages of ashes selected from the preliminary assay: the blank test and two dosages of biomass fly ashes corresponding to two different S/L ratios. The final assay was performed with large volumes of the industrial wastewaters to allow a more complete characterization of the supernatants. The chemical characterization comprised the following chemical parameters: pH, sulfates, fluorides, oil and grease, COD, total and calcic hardness, Fe, Al, Ca, As, Sb and Pb (standards and methods were indicated in 3.4.2.2). The ecotoxicological characterization comprised the same biological indicators and methodologies as referred above.

3.4.2.4.3 Isotherms of Langmuir and Freundlich and statistical analysis

The data obtained in the removal assays of lead from the SWW and IWWTP were modeled according to the isotherms of Langmuir (Eq. 3.4) and Freundlich (Eq. 3.5) (Santhosh et al., 2003):

$$C_e/Y_e = [1/(Q*b)]+C_e/Q \qquad \text{Eq. 3.4}$$

where C_e is the equilibrium concentration of the chemical species (mg/L), Y_e is the mass of the chemical species adsorbed by unit mass of the adsorbent (mg/g), Q is the maximum amount of the chemical species adsorbed per unit mass of the adsorbent (mg/g), and b is the Langmuir's constant (L/mg). The Langmuir's isotherm is a mono-layer model, applicable to cases in which the adsorption occurs in the surface layer of the adsorbent;

$$\log Y_e = \log P + (1/n)^*\log C_e \qquad \text{Eq. 3.5}$$

where C_e and Y_e have the same meanings as defined above, and P and n are empirical constants (Freundlich's parameters) (dimensionless). If the value of n is greater than 1, then it must be concluded that a good adsorption of the adsorbate took place onto the adsorbent. The isotherms of Langmuir and Freundlich were adjusted to the experimental values with the minimum least-square method.

The statistical significance of the adjustments of isotherms was tested with the F-test (two-sample for variances). The null hypothesis of the equality of the variances of experimental Y_e values ($\sigma_{exp,Ye}$) and the modeled Y_e values ($\sigma_{mod,Ye}$) was tested (H_0: $\sigma_{exp,Ye} = \sigma_{mod,Ye}$). The experimental Y_e values were obtained in the removal assays of Pb, and the modeled Y_e values were calculated by using the variables of the isotherms of Langmuir and Freundlich derived from the application of the mathematical models to the experimental values. The F-ratio (F-calculated), was determined by dividing $\sigma_{exp,Ye}$ for $\sigma_{mod,Ye}$. The F-critical values were obtained for a significance level of 0.05. Under these circumstances, if the F-ratio is lower than 1, then the null hypothesis is accepted if the F-critical value is lower than the F-ratio value, for a probability of p. If the F-ratio is higher than 1, then the null hypothesis is accepted if the F-critical value is higher than the F-ratio value, for a probability of p.

3.4.3 Results and Discussion

3.4.3.1 Bulk content and leaching behavior of biomass fly ashes

As published in a previous work (Barbosa et al., 2013), the bulk content showed that the biomass fly ashes was mainly composed by alkali and earth-alkali elements (K = 17529±1372 mg/kg db, Na = 1953±269 mg/kg db, Ca = 43576±6103 mg/kg db, Mg = 22317±2128 mg/kg db, and Ba = 248±8 mg/kg db). Fe and Al also were present in high concentrations (Fe = 17529±1372 mg/kg db, and Al = 27913±4298 mg/kg db). Nevertheless, the leaching rates of these elements were quite distinct among them. The leaching rates of Ca and Na were about 17% of the bulk content, whereas the leaching rate of K was only about 6%. Mg presented a very low leaching rate (<0.001% of the bulk content).

Zn, Cu, and Cr showed concentrations in the fly ashes of 142±1 mg/kg db, 33.1±2.3 mg/kg db and 48.6±3.7 mg/kg db, respectively. The percentage of Cr in the hexavalent state was quite low

(1.4% of total Cr). The elements Cd, Ni, Mo, Pb and Hg presented concentrations below the quantification limits (QL).

Singh et al. (2011) performed a broad characterization of different fly ashes. In what concerns the biomass fly ashes, these authors have reported similar concentrations of Hg (<0.1 mg/kg), Mo (10 mg/kg), Zn (161 mg/kg), Pb (26 mg/kg), Ba (376 mg/kg) and Cr (61 mg/kg) to those determined in the present study.

3.4.3.2 Synthetic wastewater

3.4.3.2.1 Chemical characterization of the supernatants

Table 3.7 shows the chemical characterization of the supernatants resulting from the coagulation-flocculation assays of the synthetic wastewater with an initial concentration of 1 mg Pb/L.

The redox potential has decreased with the increase of the S/L ratio. The low redox potentials in the highest S/L ratios (>0.8 g/L) reveal the presence of strong oxidized species in fly ashes that were able to reduce the chemical species present in the synthetic wastewater, producing supernatants with oxidizing potentials lower than +100 mV.

The release of sulfates and fluorides has not followed any pattern during the coagulation-flocculation tests. Considering that these elements are easily soluble in water and therefore easily releasable from fly ashes, probably their partial precipitation with cations took place.

The increase of the S/L ratio also caused the increase of the total and calcic hardness, which may indicate an increase of the concentration of carbonates in the solution. These anions may participate in the removal of several cations, namely divalent metals (Jankowski et al., 2006; Kumpiene et al., 2008; Jianguo et al., 2009; Gonzalez et al., 2011a; van Caneghem et al., 2012).

Figure 3.43 shows the Pb concentration in the supernatants of the synthetic wastewater with an initial concentration of 1 mg Pb/L.

Table 3.7 - Chemical characterization of the supernatants resulting from the coagulation-flocculation assays of the synthetic wastewater with an initial concentration of 1 mg Pb/L and different S/L ratios of the biomass fly ashes (n=2; ±SD; n.a.: SD not applicable)

Parameter	Unit	S/L ratios (g/L)								
		0.00	0.03	0.05	0.10	0.20	0.40	0.80	1.20	1.61
pH	Sorensen	4.64±0.62	4.95±0.13	4.73±0.38	6.73±0.35	8.01±1.42	10.32±0.22	10.78±0.16	11.00±0.04	11.21±0.07
Redox	mV	+255±4	+270±28	+288±5	+205±37	+206±39	+127±47	+79.9±30	+81.2±7	+54.4±6
SO_4^{2-}	mg/L	<3.0(n.a.)	8.5±0.7	4.5±1.11	7.5±1.2	5.0±1.5	8.5±2.1	15.5±2.2	6.0±0.1	9.0±0.5
F^-	mg/L	<0.05(n.a.)	0.48±0.04	0.48±0.04	0.38±0.11	0.68±0.32	0.45<0.01	0.53±0.04	0.53±0.04	0.58±0.32
Total Hardness	mg $CaCO_3$/L	2.5±0.7	3.5±0.7	2.8±0.4	5.3±1.1	7.5±1.4	13.3±0.4	24.0<0.1	35.3±1.1	37.8±5.3
Calcic Hardness	mg $CaCO_3$/L	0.5(<0.1)	0.75±0.2	0.75±0.2	3.8±0.5	5.3±0.4	11.5(<0.1)	21.5(<0.1)	32.0±1.4	32.5±8.5
Fe	mg/L	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)
Al	mg/L	<0.34(n.a)	<0.34(n.a.)	<0.34(n.a)	<0.34(n.a)	<0.34(n.a)	<0.34(n.a)	0.47±0.07	0.92±0.01	1.32±0.19
Ca	mg/L	<0.015(n.a.)	<0.015(n.a.)	<0.015(n.a)	0.72±0.03	0.77±0.03	0.89±0.03	4.46±0.32	4.57±0.20	4.75±0.11
Sb	µg/L	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	0.35±0.03
As	µg/L	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)

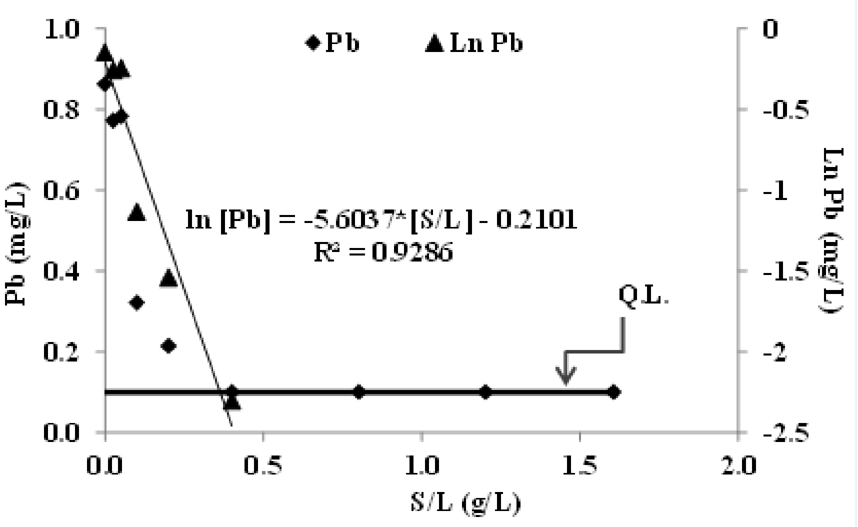


Figure 3.43 - Pb concentration and Ln (Pb) in the supernatants of the synthetic wastewater (1 mg Pb/L) as a function of the S/L ratio of biomass fly ashes used in the coagulation-flocculation assay

The concentration of Pb has decreased with the increase of S/L ratio. Above the S/L ratio of 0.4 g/L, the Pb concentration was below the QL (0.1 mg Pb/L). The data suggest that the optimal dosage of fly ashes, i.e. the lowest ashes dosage that promoted the highest removal rate of Pb, was 400 mg fly ashes/mg Pb [calculated through the following expression: 400 mg fly ashes/L / (1 mg Pb/L)]. A good linear response between Ln[Pb] and S/L ratio was observed, suggesting that a first-order kinetic was governing the Pb removal.

The increase of Pb removal as a function of the S/L ratio increase may be due to both the higher amount of fly ashes available and the increase of pH values when the dosages of fly ashes rose. According to Qiu et al. (2008), Pb^{2+} is present in solution mainly as $PbOH^{+}$ and $Pb_3(OH)_4^{2+}$ for pH values higher than 8.85. These Pb hydroxides may precipitate in the presence of cations, namely Ca and P (Coutand et al., 2008; Dybowska et al., 2009). As shown in Table 3.7, at least Ca was present in the liquid medium after the treatment with fly ashes which suggests that this metal might be involved in the precipitation of Pb.

Table 3.8 shows the chemical characterization of the supernatants resulting from the coagulation-flocculation assays of the synthetic wastewater with an initial concentration of 10 mg Pb/L.

Table 3.8 - Chemical characterization of the supernatants resulting from the coagulation-flocculation assays of the synthetic wastewater with an initial concentration of 10 mg Pb/L and different S/L ratios of the biomass fly ashes (n=2; ±SD; n.a.: SD not applicable)

Parameter	Unit	S/L ratios (g/L)								
		0.00	0.25	0.50	1.0	2.0	4.0	8.0	12.0	16.0
pH	Sorensen	5.71±0.58	7.57±0.16	10.22±0.49	10.51±0.66	11.27±0.04	11.55±0.14	11.93±0.01	12.10±0.08	12.35±0.20
Redox	mV	+196±16	+208±21	+135±1	+143±81	+83.8±25.3	+49.3±11.5	+15.8±0.6	+0.3±0.6	-8.7±3.3
SO_4^{2-}	mg/L	<3.0(n.a.)	4.5±1.5	7.5±0.7	5.0±1.4	16.0±1.4	29.0±1.4	49.0(<0.1)	57.0±4.2	73.0(<0.1)
F^-	mg/L	<3.0(n.a)	0.35±0.07	0.45±0.14	0.60±0.14	0.58±0.04	0.63±0.11	0.63±0.04	1.13±0.04	1.33±0.04
Total Hardness	mg $CaCO_3$/L	2.3±0.4	8.8±0.4	20.0±2.1	28.0±1.4	44.0±15.6	63.8±7.4	156±38	235±8	264±40
Calcic Hardness	mg $CaCO_3$/L	0.50(<0.01)	6.3±0.3	14.8±2.5	24.5±3.5	37.8±15.9	51.0±7.8	131±23	214±1	246±56
Fe	mg/L	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)
Al	mg/L	<0.34(n.a.)	<0.34(n.a.)	<0.34(n.a.)	<0.34(n.a.)	0.98(±0.01)	2.92±0.28	5.21±0.50	7.14±0.69	8.12±0.74
Ca	mg/L	<0.02(n.a.)	0.95±0.03	1.1±0.1	2.7±1.0	5.4±0.1	11.0±0.3	11.1±0.4	43.9±0.7	46.8±2
Sb	µg/L	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	0.32(n.a.)	0.68(n.a.)	0.80(n.a.)	0.62(n.a.)
As	µg/L	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)

As it was observed in the wastewater with an initial concentration of 1 mg Pb/L, the pH has increased and the redox potential has decreased with the increase of the S/L ratio. The concentrations of Ca and Al have increased with the increase of the S/L ratio, and the concentrations of Fe were below the QL for all the S/L ratios. The increase of the S/L ratio has also promoted the increase of the total and calcic hardness, which may indicate an increase in the concentration of carbonates. As discussed above, the increase in hardness may be positively involved in the removal of Pb.

Figure 3.44 shows the Pb concentration in the supernatants of the synthetic wastewater (initial concentration of Pb: 10 mg/L) as a function of the S/L ratio.

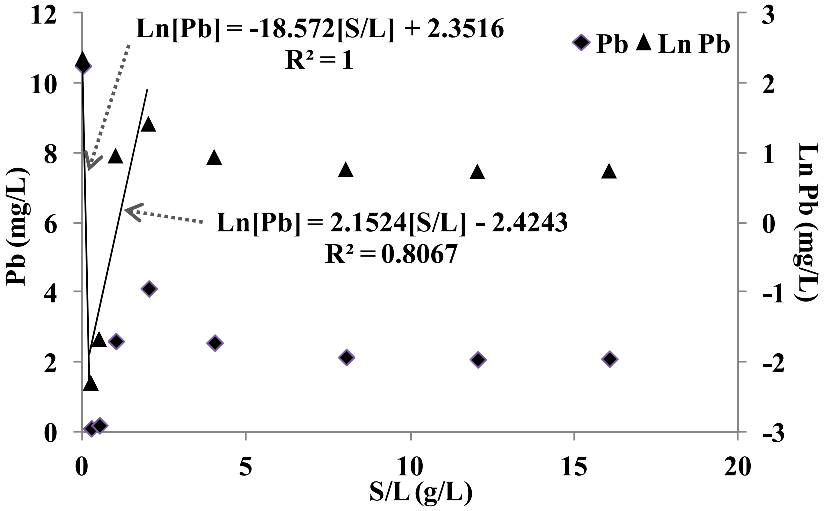


Figure 3.44 - Pb concentration and Ln (Pb) in the supernatants of the synthetic wastewater (10 mg Pb/L) as a function of the S/L ratio of biomass fly ashes used in the coagulation-flocculation assay

Two linear regressions are shown in Figure 3.44. The first one considers the S/L ratios of 0.0 and 0.25 g/L. The concentration of Pb has decreased significantly in these first S/L ratios, in which a pH of 7.57 was reached. The second linear regression comprises the S/L ratios of 0.25 to 2.0 g/L. For the S/L ratios higher than 0.25 g/L, an increase in the Pb concentrations was registered. As Pb is an amphoteric element, it presents a solubility increase in the form of $Pb(OH)_3$ for high pH values (Chandler et al., 1997; Ecke, 2003; Bouvet et al., 2007). This fact and the high pH values in the supernatants of the higher S/L ratios may explain the partial re-solubilization of Pb.

The results suggest that the optimal dosage of fly ashes is between 25 to 50 mg/mg Pb (calculated as indicated previously). This ratio is 8 to 16-fold lower than that observed for the synthetic wastewater with an initial concentration of 1 mg Pb/L. The highest removal percentages of Pb for the S/L ratios of 0.25 g/L (>99%) and 0.50 g/L (98%) may be due to the adequate pH values (7.6 and 10.2) for Pb removal (Table 3.8). These results are in agreement with those reported by other authors as for example Cho et al. (2005), Mousavi and Seyedi (2010), and Mousavi et al. (2010).

Table 3.9 shows the chemical characterization of the supernatants resulting from the coagulation-flocculation assays of the synthetic wastewater with an initial concentration of 1000 mg Pb/L.

Once again, the pH values have increased and the redox potential has decreased with the increase of the S/L ratio. The concentrations of As, Sb and Fe were below the QL. The concentrations of Ca, Al, sulfates, fluorides, and total and calcic hardness have increased with the increase of the S/L ratio. As discussed previously, this indicates an increase of the concentrations of anions that may be involved in Pb removal.

Figure 3.45 shows the Pb concentrations in the supernatants of the synthetic wastewater with an initial concentration of 1000 mg Pb/L as a function of the S/L ratio.

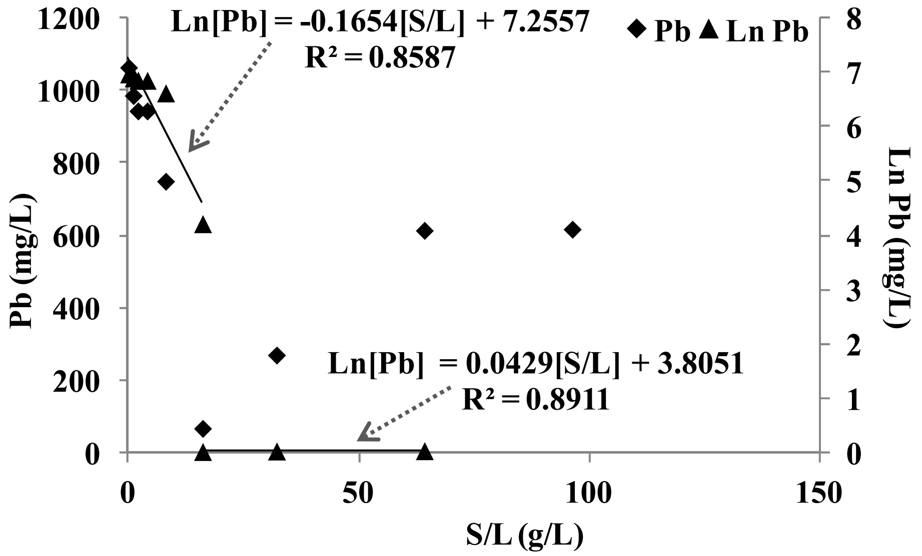


Figure 3.45 - Pb concentration and Ln Pb in the supernatants of the synthetic wastewater (1000 mg Pb/L) as a function of the S/L ratio of biomass fly ashes used in the coagulation-flocculation assay

Table 3.9 - Chemical characterization of the supernatants resulting from the coagulation-flocculation assays of the synthetic wastewater with an initial concentration of 1000 mg Pb/L and different S/L ratios of the biomass fly ashes (n=2; ±SD; n.a.: not applicable)

Parameter	Unit	S/L ratios (g/L)								
		0.00	1.00	2.01	4.01	8.02	16.0	32.1	64.2	96.3
pH	Sorensen	5.16±0.46	6.66±0.03	6.91±0.01	7.11±0.08	7.77±0.15	11.66±0.04	12.31±0.11	12.77±0.05	13.04±0.09
Redox	mV	+205.1±1.1	+201±15	+203±9	+199±13	+178±2.8	+46±18.4	-8.7±0.3	-45.9±0.6	-65.3±0.7
SO_4^{2-}	mg/L	<3.0(n.a)	<3.0(n.a)	<3.0(n.a.)	<3.0(n.a)	20.0±1.4	86.5±1.4	112(<1)	140±4	230(<1)
F^-	mg/L	<3.0(n.a)	0.5±0.1	0.48±0.11	0.65±0.07	0.95<0.01	0.98±0.04	1.10±0.07	1.18±0.11	1.25±0.07
Total Hardness	mg $CaCO_3$/L	280±7	318±32	305±7	300±21	323±4	320±7	593±103	1158±53	1880±78
Calcic Hardness	mg $CaCO_3$/L	260±7	253±11	243±11	273±4	308±11	293±4	563±124	1063±11	1778±4
Fe	mg/L	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)
Al	mg/L	<0.34(n.a.)	<0.34(n.a.)	<0.34(n.a.)	<0.34(n.a.)	<0.34(n.a.)	2.61±0.24	3.45±0.10	<0.34(n.a.)	<0.34(n.a.)
Ca	mg/L	<0.015(n.a.)	17.1±5.7	55.0±15.0	68.0±15.0	122±13.2	148±28	263±41	656±36	836±68
Sb	µg/L	<0.3(n.a.)	<0.3(n.a.)	<0.3 (n.a.)	<0.3 (n.a.)	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)	<0.3(n.a.)
As	µg/L	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)

Once again, a relationship between the removal of Pb and the pH values of the supernatants was observed. The removal efficiencies seemed to increase with the increase of the pH from slightly acidic to slightly alkaline values. Nevertheless, with the increase of the pH value to extreme alkaline conditions (>12), the Pb removal efficiency has decreased. The concentration of Pb has decreased up to the L/S ratio of 16.0 g/L, where the lowest concentration was determined (67.7 mg Pb/L). Above the S/L ratio of 16.0 g/L, the concentration of Pb have increased to 614 mg/L (S/L ratio = 64.2 g/L) probably due to the solubility increase of Pb under extreme alkaline conditions.

The experimental data suggest that for an initial concentration of 1000 mg Pb/L, the optimal dosage of fly ashes for the removal of Pb is about 16.0 g/L. This is equivalent to the addition of about 16 mg fly ashes/mg Pb, which is 25 and 2.5-fold lower than that observed for the synthetic wastewater with the initial concentrations of 1 mg Pb/L and 10 mg Pb/L, respectively. Globally, it is possible to conclude that the removal efficiency of Pb increased with the increase of the initial concentration of Pb in the synthetic wastewater.

Figure 3.46 shows the concentration of Pb as function of pH of the SWW supernatants containing initial concentrations of 1, 10, and 1000 mg Pb/L.

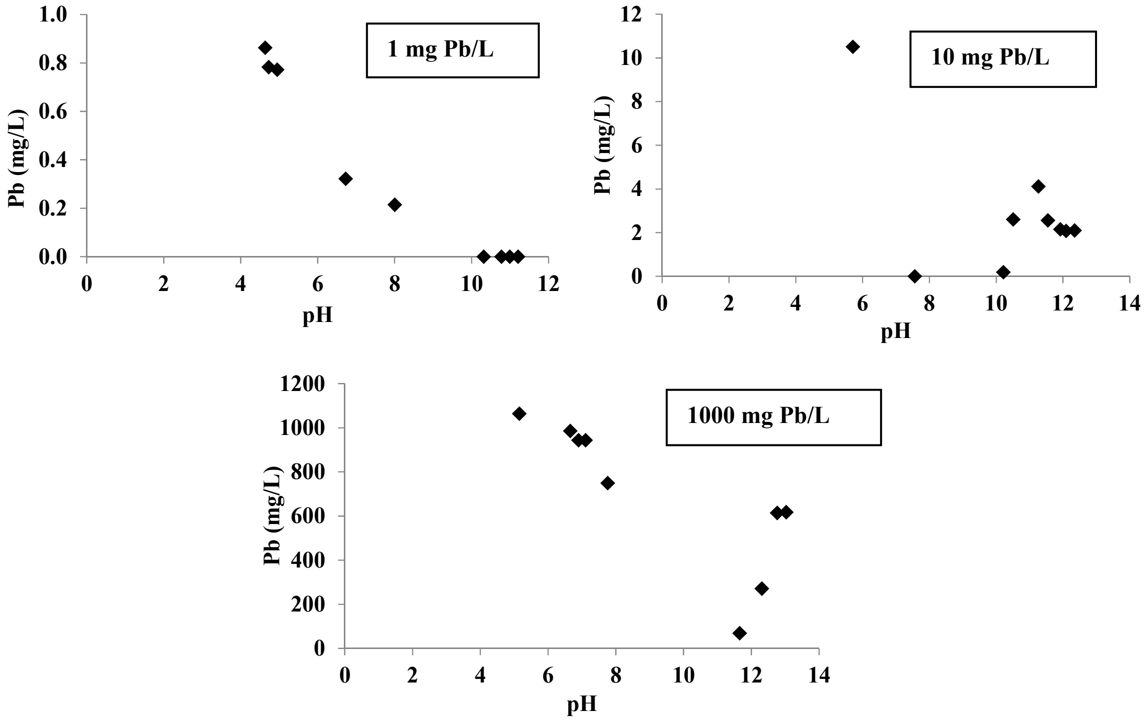


Figure 3.46 - Pb concentration as function of the pH of the supernatants of the SWW containing initial concentrations of 1, 10, and 1000 mg Pb/L

As indicated previously, Pb behaves as an amphoteric element. This means that the solubilization of Pb increases at extreme pH values and decreases at pH values close to neutrality. According to Figure 3.46, a reduction in the concentration of Pb in the supernatants was observed for pH values ranging between 8 and 10. Based on this analysis, it can be assumed that the removal mechanism for the removal of Pb from solution is probably associated with precipitation.

3.4.3.2.2 Isotherms of Langmuir and Freundlich and statistical analysis

Table 3.11 shows the parameters of the isotherms of Langmuir and Freundlich for the removal of Pb from the SWW by fly ashes. The R^2 values were generally low, which indicates a low level of adjustment of the isotherms to the experimental data. This fact may indicate that the removal of Pb was eventually performed by precipitation instead of adsorption onto the surface of the fly ashes.

3.4.3.2.3 Ecotoxicological characterization of the supernatants

Table 3.10 shows the experimental data obtained in the ecotoxicological characterization of the supernatants of the synthetic wastewater.

Table 3.10 - Ecotoxicological characterization of some supernatants of the synthetic wastewater (n=2; ±SD; n.a.: SD not applicable)

Synthetic wastewater	S/L ratios (g/L)	*V. fischeri* (EC_{50}–30 min,% v/v)	*A. franciscana* (EC_{50}–24 h,%v/v)
1 mg Pb/L	0.00	24.3±0.1	>90(n.a.)
	0.05	57.3±5.2	>90(n.a.)
	0.20	34.9±2.9	>90(n.a.)
	1.61	61.4±7.2	>90(n.a.)
10 mg Pb/L	0.00	4.4±1.4	>90(n.a.)
	0.50	40.6±5.9	>90(n.a.)
	2.01	14.0±2.9	>90(n.a.)
	16.0	50.9±5.2	>90(n.a.)
1000 mg Pb/L	0.00	<1(n.a.)	66.5±8.5
	2.01	<1(n.a.)	74.6±6.9
	16.0	43.2±3.9	>90(n.a.)
	96.3	1.3±0.3	>90(n.a.)

Table 3.11 - Parameters of the isotherms of Langmuir and Freundlich, R^2, and F-test values for the removal tests of lead performed in the SWW (df: degrees of freedom; p: probability of F-critical to be higher or lower than F-ratio depending on the value of F-ratio to be higher or lower than 1, respectively; Null hypothesis: σexp,Ye = σmod,Ye)

Effluent	Synthetic wastewater							
	Isotherm of Langmuir			F-test results				
	Q (mg/g)	*b* (L/mg)	R^2	F-ratio	df	*p*	F-critical one tail	Decision
1 mg Pb/L	1.73	-6.45	0.031	0.653	3	0.367	0.108	Null hypothesis accepted
10 mg Pb/L	2.55	0.54	0.824	518	7	$5.82*10^{-9}$	3.787	Null hypothesis rejected
1000 mg Pb/L	96.8	0.00032	0.012	12.1	7	0.0019	3.787	Null hypothesis rejected

Effluent	Synthetic wastewater							
	Isotherm of Freundlich			F-test results				
	n	*P*	R^2	F-ratio	df	*p*	F-critical one tail	Decision
1 mg Pb/L	2.36	0.45	0.333	2.076	3	0.108	9.277	Null hypothesis accepted
10 mg Pb/L	1.271	0.276	0.005	2.142	6	0.188	4.284	Null hypothesis accepted
1000 mg Pb/L	7.194	0.016	0.224	$1.137*10^{-41}$	7	0.000	0.264	Null hypothesis rejected

The micro-crustacean *A. franciscana* was less sensitive than the bioluminescent bacteria *V. fischeri*, which may be explained by the different trophic levels that these organisms occupy in the marine ecosystems. For *V. fischeri*, the ecotoxicity levels significantly decreased with the use of biomass fly ashes to remove Pb, as the EC_{50}-30 min values were higher in the supernatants obtained after the treatment with fly ashes.

Figure 3.47 shows the relationship between the final Pb concentration in each supernatant after the coagulation-flocculation assays and the TU determined for *V. fischeri*.

It was not observed any relationship between Pb concentration and TU for the SWW with an initial concentration of 1 mg Pb/L. This may be related with the low final concentrations of Pb in these supernatants. On the contrary, strong relationships between Pb concentration in the supernatants and TU values were registered for the SWW with initial concentrations of 10 and 1000 mg Pb/L. By treating the SWW with biomass fly ashes it was possible to reduce the TU values in factors of 25 (initial concentration of 10 mg Pb/L) and 100 (initial concentration of 1000 mg Pb/L).

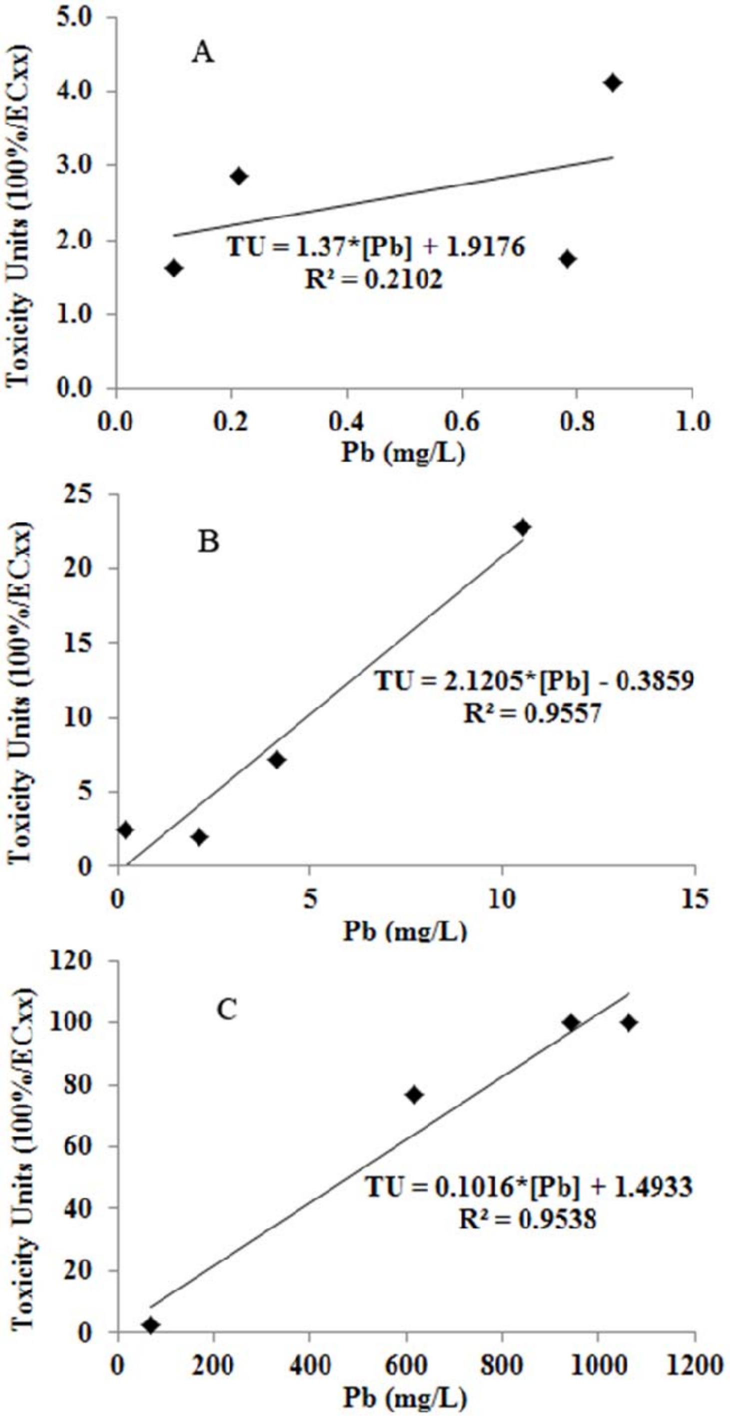


Figure 3.47 - Relationships between TU, based on *V. fischeri* assays, of the supernatants of the SWW and their final Pb concentrations (A: wastewater containing an initial concentration of 1 mg Pb/L; B: wastewater containing an initial concentration of 10 mg Pb/L; C: wastewater containing an initial concentration of 1000 mg Pb/L)

3.4.3.3 Industrial wastewaters

3.4.3.3.1 Chemical characterization of raw wastewaters

Table 3.12 shows the chemical characterization of the raw industrial wastewaters and the discharge limit-values defined for the treated effluent of the IWWTP.

Table 3.12 - Chemical characterization of the raw industrial wastewater collected in the equalization tank and in the discharge channel of the treated wastewater of the IWWTP (n=2; ±SD) and discharge limit-values

Parameter	Unit	Equalization tank	IWWTP treated effluent	IWWTP discharge limit-value
pH	Sorensen	6.80±0.10	7.2±0.10	5.5-9.5
COD	mg O_2/L	28.6±2.4	16.8±4.8	1500
Total Suspend Solids (TSS)	mg/L	15.0±1.3	5.0±0.8	1000
Sulfates	mg/L	330±28	430±49	1000
Oil and grease	mg/L	3.00±0.25	4.40±0.39	100
Total Pb	mg/L	2.42±0.34	1.02±0.18	1.0
Dissolved Pb	mg/L	0.14±0.01	0.94±0.01	Not defined

Both industrial wastewaters have presented pH values close to the neutrality, which reflects the correction of the pH to 6.0-6.5 that takes place before the equalization tank. The concentration of sulfates was a little higher in the IWWTP effluent, which can be due to the composition of the reagents used in the coagulation-flocculation process.

Pb was mainly bonded to suspended solids in the sample collected from the equalization tank (total Pb: 2.42 mg Pb/L; dissolved Pb: 0.14 mg/L). In the treated effluent of the IWWTP, Pb was essentially dissolved (total Pb: 1.02 mg Pb/L; dissolved Pb: 0.94 mg/L).

3.4.3.3.2 Preliminary coagulation-flocculation assays

Figure 3.48 shows the Pb concentrations and pH values of the supernatants resulting from the coagulation-flocculation assays with the wastewater collected in the equalization tank.

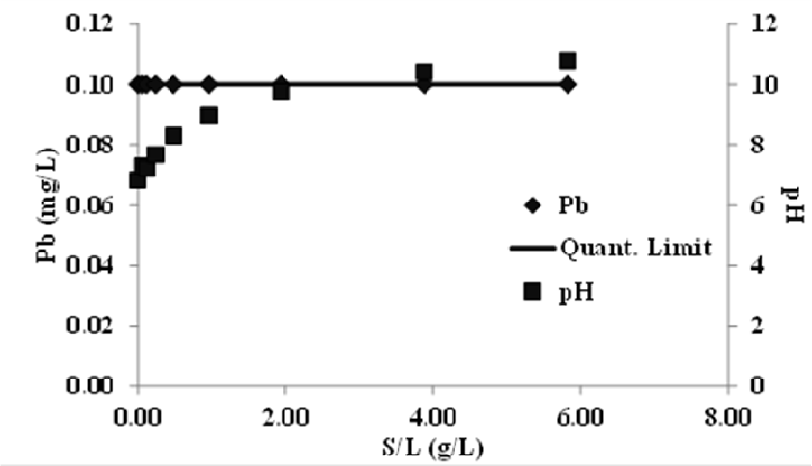


Figure 3.48 - Pb concentrations and pH values of the supernatants resulting from the preliminary coagulation-flocculation assay with the wastewater collected in the equalization tank as a function of the S/L ratio

Pb concentrations were below the QL for all the S/L ratios. The pH values ranged between 6.8 and 10.8. Consequently, the dissolved Pb present in the raw wastewater has probably precipitated, while the Pb associated to suspended solids kept bonded to solids being removed with them.

Figure 3.49 shows the Pb concentrations and the pH values of the supernatants resulting from the coagulation-flocculation assays with the IWWTP treated effluent.

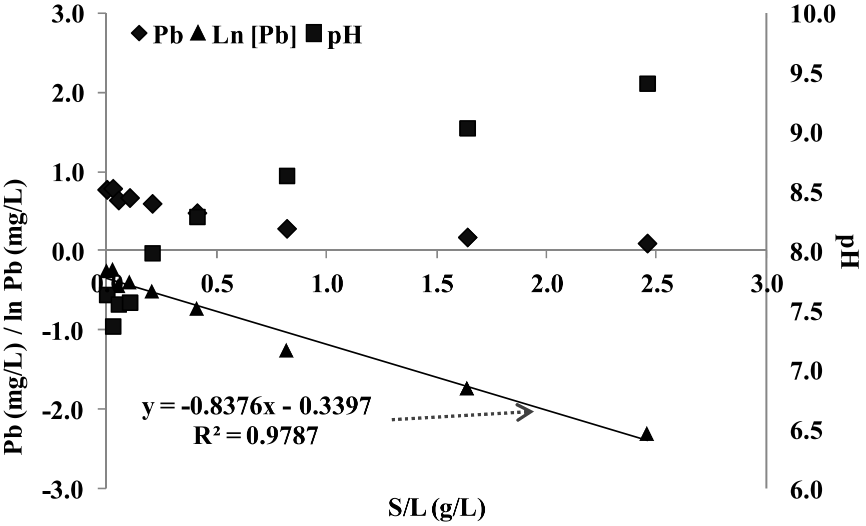


Figure 3.49 - Pb concentrations and pH values of the supernatants obtained in the preliminary coagulation-flocculation assay of the IWWTP treated effluent as function of the S/L ratio

The pH values ranged between 7.6 and 9.4, which were within the optimal range for Pb precipitation. A significant reduction in the Pb concentrations of Pb with the increase of S/L ratio was registered. The highest S/L ratio promoted the reduction of Pb concentration to less than the QL (0.1 mg Pb/L), which is equivalent to a removal rate higher than 87%.

Table 3.13 shows the results of the isotherms of Langmuir and Freundlich, R^2, and F-test values for the removal tests performed in the treated effluent of the IWWTP. The sample collected in the equalization tank was not submitted to these tests since the concentrations of Pb were below the QL.

Table 3.13 - Isotherms of Langmuir and Freundlich, R^2, and F-test values for the removal tests of Pb performed in the treated effluent of the IWWTP (df: degrees of freedom; p: probability of F-critical to be higher or lower than F-ratio depending on the value of F-ratio to be higher or lower than 1, respectively; Null hypothesis: σexp,Ye = σmod,Ye)

Isotherm of Langmuir			F-test results				
Q (mg/g)	*b* (L/mg)	R^2	F-ratio	df	*p*	F-critical one tail	Decision
3.67	0.674	0.460	4.16	6	0.053	4.28	Null hypothesis accepted
Isotherm of Freundlich			F-test results				
n	*P*	R^2	F-ratio	df	*p*	F-critical one tail	Decision
0.90	3.25	0.669	3.08	7	0.080	3.79	Null hypothesis accepted

The adjustment of both isotherms was weak as the R^2 values were low. The removal of Pb may have occurred by precipitation since the pH of the eluates has ranged between 8 to 10, which according to Chandler et al. (1997) is the range in which Pb shows the lowest solubility.

3.4.3.3.3 Definitive coagulation-flocculation assays

Table 3.14 shows the chemical characterization of the supernatants resulting from the definitive coagulation-flocculation assays carried out in the wastewater of the equalization tank.

The addition of fly ashes has increased the concentration of sulfates and pH values. Nevertheless, these parameters were still within the limit-values defined in the discharge license (Table 3.12). The concentrations of fluorides, total and calcic hardness, Al, Ca, and Sb also have moderately increased. In the S/L ratios of 0.03 and 2.91 g/L, removal rates of Pb of 22% (0.70 mg Pb/L) and >89% (<0.1 mg Pb/L) were determined, respectively. It is possible to conclude that the addition of biomass fly ashes has efficiently removed Pb from the equalization tank wastewater.

Table 3.14 - Chemical characterization of the supernatants resulting from the definitive coagulation-flocculation assay of the wastewater collected in the equalization tank (n=2; ±SD; n.a.: SD not applicable)

Parameter	Units	S/L ratios (g/L)		
		0.00	0.03	2.91
pH	Sorensen	6.76±0.19	6.72±0.13	9.48±0.06
Sulfates	mg SO_4^{2-}/L	152±19	152±11	180±7
Fluorides	mg F^-/L	1.35±0.21	1.43±0.04	16.5±2.1
Oil and grease	mg/L	1.85±0.46	1.65±0.36	1.10±0.19
COD	mg O_2/L	25.0±7.1	20.0(<0.1)	15.0±7.1
Total Hardness	mg $CaCO_3$/L	2.30(<0.01)	2.40(<0.01)	3.50(<0.01)
Calcic Hardness	mg $CaCO_3$/L	1.50(<0.01)	1.60(<0.01)	2.70(<0.01)
Fe	mg/L	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)
Al	mg/L	<0.34(n.a.)	<0.34(n.a.)	0.38±0.01
Ca	mg/L	22.0±5.8	21.2±1.8	40.3±3.3
As	µg/L	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)
Sb	µg/L	<0.30(n.a.)	<0.30(n.a.)	0.74±0.08
Pb	mg/L	0.90±0.02	0.71±0.03	<0.10(n.a.)

Table 3.15 shows the data obtained in the ecotoxicological characterization of the supernatants obtained from the definitive coagulation-flocculation assays performed in the equalization tank wastewater.

Table 3.15 - Ecotoxicological characterization of the supernatants obtained from the definitive coagulation-flocculation assay of the industrial wastewater collected in the equalization tank (n=2; ±SD; n.a.: SD not applicable)

Parameter	Units	S/L ratios of the biomass fly ashes (g/L)		
		0.00	0.03	2.91
V. fischeri	EC_{50} 30min - % v/v	84.2±3.3	73.9±3.1	>99(n.a.)
A. franciscana	EC_{50} 24h - % v/v	>90(n.a.)	>90(n.a.)	>90(n.a.)

A reduction in the ecotoxicological levels was observed for the biological indicator *V. fischeri* for the highest S/L ratio (2.91 g/L), which can probably be attributed to the reduction of the Pb concentration.

Table 3.16 shows the chemical characterization of the supernatants obtained in the definitive coagulation-flocculation assay performed with the IWWTP treated effluent.

The tendencies registered for sulfates, pH, fluorides, total and calcic hardness, Ca, and Sb were the same as for the supernatants of the definitive coagulation-flocculation assay of the equalization tank wastewater. In the S/L ratios of 0.01 and 1.23 g/L, removal percentages of 6.4% (0.88 mg Pb/L) and 62.8% (0.35 mg Pb/L) were determined, respectively. Again, the biomass fly ashes were an efficient agent to remove Pb from the IWWTP treated effluent. The treatment of the IWWTP effluent with biomass fly ashes would allow the Company to accomplish the limit-values defined in the discharge license and even much more restrictive limit-values.

Table 3.16 - Chemical characterization of the supernatants resulting from the definitive coagulation-flocculation assays of the IWWTP treated effluent (n=2; ±SD; n.a.: SD not applicable)

Parameter	Units	S/L ratios (g/L)			IWWTP discharge limit-value
		0.00	0.01	1.23	
pH	Sorensen	7.01±0.02	6.69±0.33	8.41±0.04	5.5-9.5
Sulfates	mg SO_4^{2-}/L	395±7	415±35	465±35	1000
Fluorides	mg F^-/L	5.75±1.06	6.25±1.06	6.00(<0.01)	Not defined
Oil and Grease	mg/L	2.10±0.46	2.15±0.21	2.10±0.36	100
COD	mg O_2/L	20.0(<0.1)	20.0(<0.1)	15.0±1.5	1500
Total Hardness	mg $CaCO_3$/L	2.40±0.07	2.38±0.04	3.30±0.07	Not defined
Calcic Hardness	mg $CaCO_3$/L	1.63±0.11	1.68±0.04	2.45±0.07	Not defined
Fe	mg/L	<0.06(n.a.)	<0.06(n.a.)	<0.06(n.a.)	Not defined
Al	mg/L	<0.34(n.a.)	<0.34(n.a.)	<0.34(n.a.)	Not defined
Ca	mg/L	17.6±3.2	26.7±0.9	30.0±1.6	Not defined
As	µg/L	<2.0(n.a.)	<2.0(n.a.)	<2.0(n.a.)	Not defined
Sb	µg/L	<0.30(n.a.)	<0.30(n.a.)	0.45±0.09	Not defined
Pb	mg/L	0.94±0.02	0.88±0.02	0.35±0.03	Total Pb: 1.0 mg/L; Dissolved Pb: not defined

Table 3.17 shows the ecotoxicological characterization of the supernatants obtained from the definitive coagulation-flocculation assays of the IWWTP treated effluent.

Table 3.17 - Ecotoxicological characterization to the supernatants obtained from the definitive coagulation-flocculation assay of the industrial wastewater treated effluent (n=2; n.a.: SD not applicable)

Parameter	Units	S/L ratios (g/L)		
		0.00	0.01	1.23
V. fischeri	EC_{50} 30min - % v/v	>99(n.a.)	>99(n.a.)	>99(n.a.)
A. franciscana	EC_{50} 24h - % v/v	>90(n.a.)	>90(n.a.)	>90(n.a.)

No significant ecotoxicological levels were determined for both biological indicators and for all the S/L ratios, including the control test (S/L = 0.00 g/L). It is therefore possible to conclude that the biomass fly ashes have not caused any acute ecotoxicity level in the supernatants of the IWWTP treated effluent.

3.4.4 Conclusions

The biomass fly ashes have reduced significantly the Pb concentration in the SWW and in the industrial wastewaters of the Company of lead-acid batteries.

In the SWW, with an initial Pb concentration of 1 mg/L, an increase of the removal rate of Pb up to the S/L ratio of 0.40 g/L was registered. For the S/L ratios above 0.40 g/L, the concentration of Pb was below the QL. When the initial concentration of Pb of 10 mg/L was tested, the highest removal rate was attained for the S/L ratio of 0.25 g/L. For the S/L ratios above 0.25 g/L, an increase of the Pb concentrations was determined due to the re-solubilisation of Pb caused by the pH increase. For the initial concentration of 1000 mg Pb/L, an increase of the Pb removal rate up to the S/L ratio of 16 g/L was determined (67.7 mg Pb/L). For the S/L ratios above 16 g/L, an increase of the concentration of Pb in solution was determined to about 615 mg Pb/L, due again to the pH increase.

The ecotoxicological characterization of the supernatants of the SWW resulting from the coagulation-flocculation assays indicates an overall reduction of the ecotoxicity level of the wastewater.

In what concerns the sample collected in the equalization tank of the IWWTP, the Pb concentrations of the samples resulting from the definitive coagulation-flocculation assay were very low for the S/L ratio of 0.03 g/L and below the QL for the S/L ratio of 2.91 g/L. The definitive coagulation-flocculation assays performed on the IWWTP treated effluent showed a decrease in Pb concentrations with the increase of the S/L ratio. A very low concentration of Pb (0.35 mg/L) was achieved in the S/L ratio of 1.23 g/L.

The ecotoxicological characterization of the supernatants resulting from the coagulation-flocculation assays of the industrial wastewaters has indicated an overall reduction of the ecotoxicity of the equalization tank wastewater, and undetectable levels of ecotoxicity for the IWWTP treated effluent.

Generally, the isotherms of Langmuir and Freundlich have not adjusted to the experimental data. This means that the adsorption ob Pb to fly ashes was not the main removal mechanism of

Pb. The removal of Pb was probably governed by precipitation processes, due to changes in the pH of the supernatants.

Globally, it is possible to conclude that the use of biomass fly ashes efficiently removed Pb from all the wastewaters studied. This technique may allow the industry to accomplish the current limit values established for the IWWTP effluent and even more restrictive limits.

4 General Conclusions and Future Work

4.1 General Conclusions

4.1.1 Management and valorization of ashes from co-combustion processes

In sub-chapter 2.1, the chemical and ecotoxicological behaviors of ashes produced in a lab-scale fluidized-bed reactor (LNEG, Portugal) were assessed. This study contributed for the understanding of ashes properties produced in extreme level of substitution of coal by a residue used as alternative fuel – MBM.

The substitution of coal by MBM produced ashes with a higher content of heavy metals than that produced in the combustion of coal. Nevertheless, the leaching rates of metals were generally reduced and similar among the same type of ashes, i.e., the ashes collected in the same points of the combustor. The highest chemical toxicity levels were determined in the ashes produced during the mono-combustion of MBM (0.82 µmol/L for bottom ashes; 1.51 µmol/L for 1st cyclone ashes; 1.04 µmol/L for 2nd cyclone ashes); this was essentially due to the concentrations of Cr and CrVI in the eluates of MBM ashes.

The responses of the biological indicators used to test the ecotoxicity levels of ashes from the mono-combustion and co-combustion assays were generally low, indicating that the organisms were not highly sensitive to the concentrations of chemical species released from the ashes to the eluates. The biological responses of the biological indicators were probably associated with the pH of the eluates. Nevertheless, it is necessary to develop more studies in order to identify the factors that effectively contributed to the ecotoxicity levels of some ashes eluates.

In sub-chapter 2.2, some properties of the ashes produced in an industrial fluidized-bed power plant (Duisburg power plant, Germany) working under mono-combustion and co-combustion conditions were studied. MBM and sewage sludge (SS) were used as alternative co-fuels and have partially replaced coal in an energy basis.

Generally, the use of co-fuels has not promoted significant changes in the leaching behavior of the ashes. Similar chemical and ecotoxicological properties of the eluates of ashes collected in the same points of the combustor and produced during different combustion regimes were obtained.

It was possible to stabilize adequately the fly ashes produced in combustion and co-combustion tests. All stabilized/solidified materials achieved a good degree of mechanical solidification, being characterized by medium to high compressive strength values. The compressive strength values have ranged from 28 to 40 MPa (for mortars produced with coal fly ashes), and 25 to 39 MPa (for mortars produced with coal, SS and MBM fly ashes).

The compressive strength values of concretes produced with the mixture of bottom and circulating ashes were in the range of low to medium values. The compressive strength values have ranged from 12 to 22 MPa (for concretes produced with coal ashes) and 13 to 24 MPa (for concretes produced with coal, SS and MBM ashes). Based on the Dutch BMD, some of the concretes developed could be used in real environmental conditions with limited moistening and without insulation, or with permanent moistening and with insulation.

Therefore, it is possible to conclude that the use of SS and MBM as co-fuels in the same conditions as described in sub-chapter 2.2 does not promote significant changes in the chemical and ecotoxicological properties of fly, bottom and circulating ashes. Moreover, fly ashes produced can be stabilized/solidified adequately in cement mortar matrices, and bottom and circulating ashes can be used successfully as raw materials to prepare concretes for civil engineering works.

4.1.2 Management and valorization of biomass ashes from the combustion of forestry residues

Sub-chapter 3.1 was devoted to the study of physical, chemical and ecotoxicological properties of biomass ashes and of their particle size fractions. In this work, biomass ashes were considered to be the bottom and fly ashes that are produced in biomass power plants during the combustion of forestry residues.

It was concluded that bottom and fly ashes were mainly composed by earth and alkali-earth metals and silica compounds. The concentrations of heavy metals and metalloids were found to be vestigial or below the quantification limits. The highest concentrations of metals and metalloids were found in the lowest particle size fractions of both bottom and fly ashes. It was not observed any releasing pattern from the particle size fractions, except for fly ashes in which the releasing rate of some earth and alkali-earth metals seemed to increase with the decrease of particle size fractions.

The freshwater organisms revealed more sensitivity than the marine organisms to the ecotoxicity levels of eluates of bottom and fly ashes and of their particle size fractions. This was attributed to the adaptation of marine organisms to high salinity values present in the eluates of ashes and of their particle size fractions. The largest particle size fractions of bottom ashes (4000-10000 µm and >10000 µm) have presented lower ecotoxicity levels than all the other particle size fractions, which can be attributed to the higher concentrations of metals and metalloids in the lowest particle size fractions.

The valorization of biomass ashes as raw materials for the production of concretes was successfully performed in sub-chapter 3.2. Several new concrete formulations were prepared, as well as a reference concrete. The concretes produced with biomass ashes were submitted to compressive strength tests and to two types of leaching tests: one simulating freshwater leaching conditions and the other one simulating marine leaching conditions.

The formulations in which fly ashes replaced 10% of cement have presented similar to slightly higher compressive strength values (29 to 32.6 MPa) than the average value for the reference concrete (32.2 MPa). On the contrary, the incorporation of 30% fly ashes has conducted to concretes with lower compressive strength values (23.8 to 28 MPa) than the average value registered for the reference concrete.

The formulations selected for further chemical and ecotoxicological characterizations have presented very low emissions of chemical species in both marine and freshwater leaching conditions. Actually, the new formulations have presented chemical emissions similar to or even lower than those observed for the reference concrete.

Also, the ecotoxicological levels of the eluates of new concretes were similar to or even lower than that observed for the reference concrete. The eluate produced by the reference material has promoted an EC_{50}-48h for *D. magna* of 39.9%, while the concretes produced by the new materials promoted an EC_{50}-48h for *D. magna* of 36.3% (F10B18) and 51.3% (F30B18). The other organisms have not revealed sensitive to the ecotoxicity levels of the eluates.

As a global conclusion, it is possible to state that biomass ashes were successfully used as substitutes of cement and natural aggregates in concretes, without compromising their mechanical performance, the emission of chemical species, and the ecotoxicological levels determined under both marine and freshwater leaching conditions.

Sub-chapter 3.3 was devoted to the removal of P, mainly in the form of phosphates, from wastewaters by using biomass ashes as chemical agents. P is a nutrient commonly present in treated wastewaters in concentrations around 1 mg P/L. Even when present in concentrations as high as 1 mg P/L, it may still cause eutrophication problems in the receiving water bodies. The study on P removal was performed over synthetic and industrial wastewaters by using biomass ashes (bottom and fly ashes).

Biomass ashes have presented a high capacity to remove phosphates from both SWW and PPWW. Also they have not promoted any change in the ecotoxicity levels of the treated effluents. Fly ashes were more efficient in removing phosphates than bottom ashes.

The removal of phosphates from the SWW was primarily governed by mono-layer mechanisms, while the removal of phosphates from the PPWW was explained by both multi-layer mechanisms and precipitation through pH change of the liquid medium.

A similar valorization pathway of biomass ashes was tried in the sub-chapter 3.4, but here only biomass fly ashes were used in the removal of the heavy metal Pb from wastewaters. Fly ashes were chosen because in the previous sub-chapter they proved to be the most efficient material in removing P. Fly ashes were used as chemical agent to remove Pb from a SWW and two industrial wastewaters produced in a plant of lead-acid batteries.

In the SWW with an initial Pb concentration of 1 mg/L, an increase of the Pb removal rate up to the S/L ratio of 0.40 g/L was observed. For S/L ratios higher than 0.40 g/L, Pb concentration was below the quantification limit. When an initial Pb concentration of 10 mg/L was tested, the highest removal rate was attained for the S/L ratio of 0.25 g/L. For S/L ratios higher than this, an increase of the Pb concentrations was determined, due to the re-solubilization of Pb caused by the high pH value that was achieved in the eluates (between 7.6 and 11.3). For the initial concentration of 1000 mg Pb/L, the lowest concentration of Pb in the treated effluents was observed for the S/L ratio of 16 g/L (67.7 mg Pb/L).

The ecotoxicological characterization of the supernatants of the SWW resulting from the Pb removal assays indicates an overall reduction of the ecotoxicity level of the wastewater. This is linked to the high Pb removal efficiency as this was the only toxic element present in the SWW.

In what concerns the wastewater that was collected in the equalization tank of the IWWTP, Pb concentrations in the supernatants resulting from the definitive coagulation-flocculation assay were very low for the S/L ratio of 0.03 g/L (Pb = 0.71 mg Pb/L), and below the quantification limit for the S/L ratio of 2.91 g/L (Pb < 0.10 mg Pb/L). The definitive coagulation-flocculation assays performed on the effluent of the IWWTP showed a decrease in Pb concentrations with the increase of the S/L ratio. A very low concentration of Pb (0.35 mg/L) was achieved in the S/L ratio of 1.23 g/L.

The ecotoxicological characterization of the supernatants resulting from the Pb removal assays performed over the wastewaters collected in the IWWTP has indicated an overall reduction of the ecotoxicity.

The Langmuir and Freundlich isotherms have not adjusted well to the experimental data, since the determination coefficients (R^2) were low. The removal of Pb from the studied wastewaters was chiefly governed by precipitation mechanisms, due to pH increase up to values of 8 to 10.

Globally, it is possible to conclude that the biomass fly ashes have promoted the Pb removal from all the wastewaters studied. This treatment process may allow the industry to accomplish the current limit values of 1 mg Pb/L, and even more restrictive limits (0.35 mg Pb/L, considering the results of the definitive test).

Finally, this thesis shows that the ashes produced during the co-combustion of coal, MBM and SS in fluidized-bed combustors and the ashes produced during the combustion of forestry residues in a bubbling fluidized bed combustor can be used in new valorization pathways, namely, the production of mortars and concretes, and the removal of pollutants from liquid media. These alternative routes of valorization may avoid the extensive use of these ashes in cement production and forestland application, and the disposal in landfills. New potential valorization routes are now opened with the present thesis.

4.2 Future Work

It is necessary to perform other assays in order to understand more deeply the properties of the ashes. It would be important to perform a scanning electron microscopy of ashes, since it can add valuable information related with the microstructure of ashes. The knowledge of the microstructure of ashes may help to understand the leaching behavior of some compounds in leaching tests, and the adsorption of pollutants from liquid media when ashes are used as chemical agent for the removal of contaminants.

There are a set of organic compounds which may lead to negative environmental impacts. In the thesis this characterization was not performed. Therefore, it would be important to perform an organic characterization of the eluates, namely in what concerns dioxins and furans, which can act as toxic compounds at very low concentrations and for long periods of exposure (chronic toxicity).

It is also important to submit the materials to other types of leaching tests. In laboratory leaching tests it is important to assess the chemical and ecotoxicological behavior of the ashes when the liquid to solid ratio is low, because the release of some pollutants from the ashes can be more marked at low solid to liquid ratios.

Besides the laboratory leaching tests, it is necessary to submit the concretes to leaching tests under real scenarios. In real environments, the mobilization of compounds from the ashes to eluates may be different than that observed in the leaching assays used in the present thesis. Therefore, the next steps of future works can be to submit the concretes to real marine and freshwater environments. This would allow to study, in real conditions, the environmental impacts of the use of concretes containing ashes. The following questions would be answered or at least partially answered: a) Can the concretes be used as artificial reefs? b) What are the impacts in aquatic flora and fauna? c) What are the long term effects on the concrete structure?

The ashes produced by the combustion of forestry residues have less content of heavy metals than the ashes resulting from the combustion of fossil fuels, such as coal, MBM and SS. Therefore it is possible to think about their use in applications that are not advisable for the ashes produced by the combustion of coal and residues, such as those involving the contact with environmental compartments (treatment of wastewaters, contaminated soils, among other applications). In this framework, it could be interesting to develop other assays to test their efficiency under different conditions of work, namely i) the removal of pollutants in continuous conditions, for example through column systems; and ii) in large scale (pilot and industrial facilities). Besides these conditions, it would be important to test a set of parameters in order to maximize the removal of pollutants, namely the contact time of the ashes with the wastewater, the effect of pH in the removal efficiency, among other factors, to be possible to define the removal kinetics, the best operation conditions that yield the highest removal rates, and the mechanisms governing the removal of pollutants.

References

Abbasi, T., Abbasi, S.A., 2010. Biomass energy and the environmental impacts associated with its production and utilization. Renew. Sustain. Energy Rev. 14, 919–937.

Abdullahi, M., 2006. Characteristics of wood ashes/OPC concrete. Leonardo Electron. J. Pract. Technol. 8, 9-6.

Acma, H.H., 2003. Combustion characteristics of different biomass materials. Energy Convers. Manag. 44, 155–162.

AFNOR X31-211, 2000. Caractérisation des déchets - Essai de lixiviation d'un déchet solide initialement massif ou généré par un procédé de solidification.

Aguiar del Toro, M., Calmano, W., Ecke, H., 2009. Wet extraction of heavy metals and chloride from MSWI and straw combustion fly ashes. Waste Manag. 29, 2494–2499.

Ahmaruzzaman, M., 2010. A review on the utilization of fly ash. Prog. Energy Combust. Sci. 36, 327–363.

Alinnor, I.J., 2007. Adsorption of heavy metal ions from aqueous solution by fly ash. Fuel 86, 853–857.

Al-Kassir, A., Gañán-Gómez, J., Mohamad, A.A., Cuerda-Correa, E.M., 2010. A study of energy production from cork residues: Sawdust, sandpaper dust and triturated wood. Energy 35, 382-386.

Allison, J.D., Brown, D.S., 1991. Novo-gradac, K.J., MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.11, Databases and Version 3.0 User's Manual. US EPA, Athens.

Al-Najjar, M.M., Coats, E.R., Loge, F.J., 2011. The role of the microbial stringent response in excess intracellular accumulation of phosphorous in mixed consortia fed synthetic wastewater. Water Res. 45, 5038-5046.

Alonso-Santurde, R., Coz, A., Quijorna, N., Viguri, J. R., Andrés, A., 2010. Valorization of Foundry Sand in Clay Bricks at Industrial Scale. J. Ind. Ecol. 14, 217-230.

Alvarez, R., Callén, M.S., Clemente, C., Gómez-Limón, D., López, J.M., Mastral, A.M., Murillo, R., 2004a. Soil, Water, and Air Environmental Impact from Tire Rubber/Coal Fluidized-Bed Cocombustion, Energy Fuels 18 1633-1639.

Alvarez, R., Callén M.S., Clemente, C., Díaz-Bautista, M.A., López, J.M., Mastral, A.M., Murillo, R., 2004b. Slagging in Fluidized Bed Combustion of Rubber Tire. Inorganic Component Evolution. Ind. Eng. Chem. Res. 43, 7762-7767.

Al-Zboon, K., Al-Harahsheh, M.S., Hani, F.B., 2011. Fly ash-based geopolymer for Pb removal from aqueous solution. J. Hazard. Mater. 188, 414–421.

APHA/AWWA/WEF, 2005. Standard Methods for the Examination of Water and Wastewater.

Arias, B., Pevida, C., Rubiera, F., Pis, J.J., 2008. Effect of biomass blending on coal ignition and burnout during oxy-fuel combustion. Fuel 87, 2753–2759.

ASTM D3172, 2007. Standard Practice for Proximate Analysis of Coal and Coke.

ASTM D3173, 2008. Standard Test Method for Moisture in the Analysis Sample of Coal and Coke.

ASTM D3174, 2004. Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal.

ASTM D3175, 2007. Standard Test Method for Volatile Matter in the Analysis Sample of Coal and Coke.

ASTM D3177-02, 2007. Standard Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke.

ASTM D4208-02, 2007. Standard Test Method for Total Chlorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method.

ASTM D5016, 2008. Standard Test Method for Total Sulfur in Coal and Coke Combustion Residues Using a High-Temperature Tube Furnace Combustion Method with Infrared Absorption.

ASTM D5373, 2008. Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal.

ASTM D5865, 2010. Standard Test Method for Gross Calorific Value of Coal and Coke.

ASTM D7573, 2009, Standard Test Method for Total Carbon and Organic Carbon in Water by High Temperature Catalytic Combustion and Infrared Detection.

ASTM E1440-91, 2004. Standard Guide for Acute Toxicity Test with the *Rotifer Brachionus*.

Aydın, S., Yazıcı, H., Yiğiter, H., Baradan, B., 2007. Sulfuric acid resistance of high-volume fly ash concrete. Build. Environ. 42, 717–721.

Ban, C.C., Ramli, M., 2011. The implementation of wood waste ash as a partial cement replacement material in the production of structural grade concrete and mortar: an overview. Resour. Conserv. Recyl. 55, 669–685.

Barber, T.R., Lutes, C.C., Doorn, M.R.J., Fuchsman, P.C., Timmenga, H.J., Crouch, R.L., 2003. Aquatic ecological risks due to cyanide releases from biomass burning. Chemosphere 50, 343–348.

Barbosa, R., 2005. Caracterização química e ecotoxicológica de escórias e cinzas resultantes da co-combustão de lamas e carvão, MSc thesis submitted to UNL/FCT, Lisbon, Portugal.

Barbosa, R., Dias, D., Lapa, N., Lopes, H., Mendes, B., 2013. Chemical and ecotoxicological properties of size fractionated biomass ashes. Fuel Process. Technol 109, 124-132.

Barbosa, R., Lapa N., Lopes H., Gulyurtlu I., Mendes, B., 2011. Stabilization/solidification of fly ashes and concrete production from bottom and circulating ashes produced in a power plant working under mono and co-combustion conditions. Waste Manag. 31, 2009-2019.

Barbosa, R., Lapa, N., Boavida, D., Lopes, H., Gulyurtlu, I., Mendes, B., 2009. Co-combustion of coal and sewage sludge: chemical and ecotoxicological properties of ashes. J. Hazard. Mater., 170, 902-909.

Baxter, L., 2005. Biomass–coal co-combustion: opportunity for affordable renewable energy. Fuel 84, 1295–1302.

Bayat, B., 2002a. Comparative study of adsorption properties of Turkish fly ashes. II. The case of chromium(VI) and cadmium(II). J Hazard. Mater. 95, 275-290.

Bayat, B., 2002b. Comparative study of adsorption properties of Turkish fly ashes. I. The case of nickel(II), copper(II) and zinc(II). J Hazard. Mater. 95, 251–273.

Beck, J., Brandenstein, J., Unterberger, S., Hein, K.R.G., 2004. Effects of sewage sludge and meat and bone meal co-combustion on SCR catalysts. Appl. Catal. B: Environ. 49, 15–25.

Bjurstöm, H., Herbert, R., Ribbing, C., Tham., G., 2012. Using ash in a sustainable society: Swedish R&D case, in: Cossu, R., Salieri, V., Bisinella, V., CISA Publishers, ISBN 9788862650014, pp. 278-288.

Boelee, N.C., Temmink, C., Janssen, M., Buisman, C.J.N., Wijffels, R.H., 2011. Nitrogen and phosphorus removal from municipal wastewater effluent using microalgal biofilms. Water Res. 45, 5925-5933.

Bouvet, M., François, D., Schwartz, C., 2007. Road soil retention of Pb leached from MSWI bottom ash. Waste Manag. 27, 840–849.

Callén, M., Marañón, E., Mastral, A., Murillo, R., Salgado, P., Sastre, H., 1998. Ecotoxicological Assessment of Ashes and Particulate Matter from Fluidized Bed Combustion of Coal. Ecotoxicol. Environ. Saf. 41, 59-61.

Camerani, M.C., Steenari, B.M., Sharma, R., Beckett, R., 2002. Cd speciation in biomass fly ash particles after size separation by centrifugal SPLITT. Fuel 81, 1739-1753.

Cappai, G., Cara, S., Muntoni, A., Piredda, M., 2012. Application of accelerated carbonation on MSW combustion APC residues for metal immobilization and CO_2 sequestration. J. Hazard. Mater. 207-208, 159-164.

Caravelli, A.H., Contrerasa, E.M., Zaritzkya, N.E., 2010. Phosphorous removal in batch systems using ferric chloride in the presence of activated sludges. J. Hazard. Mater. 177, 199-208.

CELPA-Associação da Indústria Papeleira, 2012. 2011 - Boletim Estatístico – Indústria Papeleira Portuguesa, ISSN 1645-4154.

CEN/TS 14774, 2009. Technical specification: Solid biofuels - Determination of moisture content - Oven dry method.

CEN/TS 14775, 2004. Technical specification: Solid biofuels - Methods for determination of ash content.

CEN/TS 14918, 2005. Technical specification: Solid biofuels - Methods for the determination of calorific value.

CEN/TS 15104, 2005. Technical specification: Solid biofuels - determination of total content of carbon, hydrogen and nitrogen - instrumental methods.

CEN/TS 15148, 2005. Technical specification: Solid biofuels - Method for the determination of the content of volatile matter.

CEN/TS 15289, 2006. Technical specification: Solid biofuels - Determination of total content of sulphur and chlorine.

Centro da Biomassa para a Energia, 2007. Atlas da biomassa florestal residual produzida em Portugal Continental, 44 pp.

Chaala, A., Roy, C., 2003. Recycling of meat and bone meal animal feed by vacuum pyrolysis. Environ. Sci. Technol. 37, 4517–4522.

Chai, J.-C., Onitsuka, K., Hayashi, S., 2009. Cr (VI) concentration from batch contact/tank leaching and column percolation test using fly ash with additives. J. Hazard. Mater. 166, 67–73.

Chandler, A. Eighmy, T., Hartlén, J., Hjelmar, O., Kosson, D., Sawell, S., van der Sloot, H., Vehlow, J., 1997. Municipal solid waste incineration residues., in: Stud. Environ. Sci. 67, Elsevier Science, Amsterdam, Netherlands.

Chirenje, T., Rivero, C., Ma, L.Q., 2002. Leaching of As and Cr in wood-ash-amended soil columns. Soil Sediment Contam. 11, 359-375.

Cho, H., Oh, D., Kim, K., 2005. A study on removal characteristics of heavy metals from aqueous solution by fly ash. J. Hazard. Mater. B127, 187-195.

Conesa, J.A., Fullana, A., Font, R., 2003. Thermal decomposition of meat and bone meal. J. Anal. Appl. Pyrolysis 70, 619–630.

Conesa, J.A., Fullana, A., Font, R., 2005. Dioxin production during the thermal treatment of meat and bone meal residues. Chemosphere 59, 85–90.

Cornelis, G., Anette Johnson, C., van Gerven, T., Vandecasteele, C., 2008. Leaching mechanisms of oxyanionic metalloid and metal species in alkaline solid wastes: A review. Appl. Geochem. 23, 955–976.

Cornelis, G., Van Gerven, C., Vandecasteele, T., 2006. Antimony leaching from uncarbonated and carbonated MSWI bottom ash. J. Hazard. Mater. 137, 1284-1292.

Cossu, R., Salieri, V., Bisinella, V., 2012. Introduction: The Urban Mining concept, Urban Mining: A global cycle approach to resource recovery from solid waste, in: Cossu, R., Salieri, V., Bisinella, V., CISA Publishers, ISBN 9788862650014, pp. 13-20.

Council of the European Communities, 1986. Council Directive 86/278/EEC on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Official Journal of the European Communities L181/6.

Council of the European Communities, 1991. Council Directive 91/271/EEC concerning waste water treatment. Official Journal of the European Communities L135/40.

Council of the European Communities, 1991. Council Directive 91/689/EEC on hazardous waste. Official Journal of the European Communities L377.

Council of the European Union, 2002. Council Decision 2003/33/EC establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC. Official Journal of the European Communities L11/27.

Coutand, M., Cyr, M., Clastres, P., 2011. Quantification of uncertainty of experimental measurement in leaching test on cement-based materials. J. Environ. Manag. 92, 2494-2503.

Coutand, M., Cyr, M., Deydier, E., Guilet, R., Clastres, P., 2008. Characteristics of industrial and laboratory meat and bone meal ashes and their potential applications. J. Hazard. Mater. 150, 522-532.

Coutand, M., Deydier, E., Cyr, M., Mouchet, F., Gauthier, L., Guilet, R., Bernues Savaete, L., Cren, S., Clastres, P., 2009. Evaluation of laboratory and industrial meat and bone meal combustion residue as cadmium immobilizing material for remediation of polluted aqueous solutions: “Chemical and ecotoxicological studies”. J. Hazard. Mater. 166, 945–953.

Cummins, E.J., McDonnell, K.P., Ward, S.M., 2006. Dispersion modelling and measurement of emissions from the co-combustion of meat and bone meal with peat in a fluidised bed. Bioresour. Technol. 97, 903–913.

Cyr, M., Coutand, M., Clastres, P., 2007. Technological and environmental behavior of sewage sludge ash (SSA) in cement-based materials. Cem. Concr. Res. 37, 1278–1289.

Cyr, M., Ludmann, C., 2006. Low risk meat and bone meal (MBM) bottom ash in mortars as sand replacement. Cem. Concr. Res. 36, 469 – 480.

Dahl, O., Nurmesniemi, H., Pöykiö, R., Watkins, G., 2009. Comparison of the characteristics of bottom ash and fly ash from a medium-size (32 MW) municipal district heating plant incinerating forest residues and peat in a fluidized-bed boiler. Fuel Process. Technol. 90, 871-878.

Dahl, O., Nurmesniemi, H., Pöykiö, R., Watkins, G., 2010. Heavy metal concentrations in bottom ash and fly ash fractions from a large-sized (246 MW) fluidized bed boiler with respect to their Finnish forest fertilizer limit values. Fuel Process. Technol. 91, 1634-1639.

Davis, R.D., 1995. Legislative developments and sewage sludge disposal strategy in Europe. Proc. of the Symp. on Sewage Sludge Disposal, Prague, Rhenipal and Dirk (ed.), European Holdings Limited, England.

Deleebeeck, N.M.E., Schamphelaere, K.A.C. de, Heijerick, D.G., Bossuyt, B.T.A., Janssen, C.R., 2008. The acute toxicity of nickel to Daphnia magna: Predictive capacity of bioavailability models in artificial and natural waters. Ecotoxicol. Environ. Saf. 70, 67–78.

Devi, N.L., Yadav, I.C., Shihua, Q.I., Singh, S., Belagali, S.L., 2011. Physicochemical characteristics of paper industry effluents - a case study of South India Paper Mill (SIPM). Environ. Monit. Assess. 177, 23-33.

Diniz, M.S., Pereira, R., Freitas, A.C., Rocha-Santos, T.A.P., Castro, L., Peres, I., Duarte, A.C., 2011. Evaluation of the sub-lethal toxicity of bleached kraft pulp mill effluent to *Carassius auratus* and *Dicentrarchus labrax*. Water, Air, Soil Pollut. 217, 35-45.

Donatello, S., Cheeseman, C.R., 2013. Recycling and recovery routes for incinerated sewage sludge ash (ISSA): A review. Waste Manag. (In Press)

Donatello, S., Tyrer, M., Cheeseman, C.R., 2010. Comparison of test methods to assess pozzolanic activity. Cem. Concr. Compos. 32, 121-127.

Douglas, G.B., Robb, M.S., Coad, D.N., Ford, P.W., 2004. A review of solid phase adsorbents for the removal of phosphorus from natural and wastewaters, in: Phosphorous in environmental technologies – principles and application, E. Valsami-Jones (ed.), IWA, UK, pp. 291-320.

Drogui, P., Blais, J.-F., Mercier, G., 2005. Hybrid process for heavy metal removal from wastewater sludge. Water Environ. Resear. 77, 372-380.

Dybowska, A., Manning, D.A.C., Collins, M.J., Wess, T., Woodgate, S., Valsami-Jonesa, E., 2009. An evaluation of the reactivity of synthetic and natural apatites in the presence of aqueous metals. Sci. Total Environ. 407, 2953–2965.

Ecke, H., 2003. Sequestration of metals in carbonated municipal solid waste incineration (MSWI) fly ash. Waste Manag. 23, 631–640.

Eco Logic, Institute for European Environmental Policy, 2009. Report on the implementation of the Sewage Sludge Directive 86/278/EEC. (Report available on http://ec.europa.eu/environment/waste/reporting/pdf/Sewage%20sludge_Directive.pdf)

El-Bestawy, E.. El-Sokkary, I.., Hussein, H., Abu Keela, A.F., 2008. Pollution control in pulp and paper industrial effluents using integrated chemical–biological treatment sequences. J. Ind. Microbiol. Biotechnol. 35, 1517-1529.

Elinwa. A.U., Mahmood Y.A., 2002. Ash from timber waste as cement replacement material. Cem. Concr. Compos. 24, 219-222.

Elled, A.-L., Åmand, L.-E., Leckner, B., Andersson, B.-Å., 2007. The fate of trace elements in fluidised bed combustion of sewage sludge and wood. Fuel 86, 843–852.

EN 12457-2, 2002. Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction).

EN 13656, 2002. Characterization of waste - Microwave assisted digestion with hydrofluoric (HF), nitric (HNO_3) and hydrochloric (HCI) acid mixture for subsequent determination of elements.

EN 197-1, 2011. Cement. Part 1: Composition, specifications and conformity criteria for common cements.

EN 450-1, 2012. Fly ash for concrete. Part 1: Definitions, specifications and conformity criteria.

EN ISO 11969, 1996. Water quality - Determination of arsenic -- Atomic absorption spectrometric method (hydride technique).

Esteves, T.C., Rajamma, R., Soares, D., Silva, A.S., Ferreira, V.M., Labrincha, J.A., 2012. Use of biomass fly ash for mitigation of alkali-silica reaction of cement mortars. Constr. Build. Mater. 26, 687–693.

European Commission, 1998. Directive 98/15/EC amending Council Directive 91/271/EEC with respect to certain requirements established in Annex I. Official Journal of the European Communities L67/29.

European Commission, 2001. Disposal and recycling routes for sewage sludge. DG Environment – B/2, Part 1–4, October 2001.

European Commission, 2006a. Report from the Commission to the Council and the European Parliament on the implementation of community waste legislation – Directive 86/278/EEC on sewage sludge – for the period 2001–2003, COM(2006) 406 final, SEC(2006) 972, Brussels, 19.7.2006.

European Commission, 2006b. Integrated Pollution Prevention and Control - Reference Document on Best Available Techniques for Large Combustion Plants.

European Commission, 2011. Regulation 142/2011 implementing Regulation (EC) 1069/2009 of the European Parliament and of the Council. Official Journal of the European Union L54/1.

European Commission, 2013. http://ec.europa.eu/environment/waste/sludge/index.htm (assessed in May-2013).

European Parliament and Council, 2008. Directive 2008/1/EC concerning integrated pollution prevention and control. Official Journal of the European Union L 24/8.

European Parliament and Council, 2009. Directive 2009/28/EC on the promotion of the use of energy from renewable sources. Official Journal of the European Union L 140/16.

European Parliament and Council, 2009. Regulation 1069/2009 laying down health rules as regards animal by-products and derived products not intended for human consumption. Official Journal of the European Union L 300/1.

Felekoglu, B., 2007. Effects of PSD and surface morphology of micro-aggregates on admixture requirement and mechanical performance of micro-concrete. Cem. Concr. Compos. 29, 481–489.

Folgueras, M. B., Díaz, R. M., Xiberta, J., Prieto, I., 2003. Volatilisation of trace elements for coal–sewage sludge blends during their combustion. Fuel 82, 1939-1948.

Fonts, I., Gea, G., Azuara, M., Ábrego, J., Arauzo, J., 2012. Sewage sludge pyrolysis for liquid production: A review. Renew. Sustain. Energy Rev. 16, 2781-2805.

French Ministry of Environment, Directorate for Prevention Pollution and Risk Control, Products and Division of Wastes, 1998. Proposal for a criterion and evaluation methods of waste ecotocixity (CEMWE), Paris.

Fruergaard, T., Astrup, T., Ekvall, T., 2009. Energy use and recovery in waste management and implications for accounting of greenhouse gases and global warming contributions. Waste Manag. Res. 27, 724-737.

Fryda L., Panopoulos, K., Vourliotis, P., Kakaras, E., Pavlidou, E., 2007. Meat and bone meal as secondary fuel in fluidized bed combustion. Proc. Combust. Inst. 31, 2829–2837.

García-Albacete, M., Martín, A., Cartagena, M.C., 2012. Fractionation of phosphorus biowastes: characterisation and environmental risk. Waste Manage. 32, 1061-1068.

Ghirardinia, A.V., Girardini, M., Marchetto, D., Pantani, C., 2009. Microtox® solid phase test: Effect of diluents used in toxicity test, Ecotoxicol. Environ. Saf. 72, 851–861.

Gonzalez, A., Moreno, N., Navia, R., Querol, X., 2011a. Development of a non-conventional sorbent from fly ash and its potential use in acid wastewater neutralization and heavy metal removal. Chem. Eng. J. 166, 896-905.

González, J.F., Ledesma, B., Alkassir, A., 2011b. González, J., Study of the influence of the composition of several biomass pellets on the drying process. Biomass Bioenergy 35, 4399-4406.

Goumans, J.J.J.M., van der Sloot, H.A., Aalbers, T.G., 1994. Environmental aspects of construction with waste materials. Proc. Int. Conf. Environ. Implic. Construc. Mater. Technol. Dev. Elsevier (Eds.), Maastricht, The Netherlands, pp. 988.

Grubb, D.G., Guimaraes, M.S., Valencia, R., 2000. Phosphate immobilization using an acidic type F fly ash. J. Hazard. Mater. 76, 217–236.

Gulyurtlu, I., Abelha, P., Lopes, H., Crujeira, A., Cabrita, I., 2007. Considerations on valorization of biomass origin materials in co-combustion with coal in fluidized beds. Third Int. Conf. Clean Coal Technol. Future, 15-17 May, Sardinia, Italy.

Gulyurtlu, I., Boavida, D., Abelha, P., Lopes, M.H., Cabrita, I., 2005. Co-combustion of coal and meat and bone meal. Fuel 84, 2137–2148.

Gulyurtlu, I., Monteiro, A.P., 1991. Descriptive memory of the fluidized bed LF30, LNETI/DEC, Lisbon, Portugal.

Gupta, G., Torres, N., 1998. Use of fly ash in reducing toxicity of and heavy metals in wastewater effluent. J. Hazard. Mater. 57, 243-248.

Ha, T.H., Muralidharan, S., Bae, J.H., Ha, Y.-C., Lee, H.G., Park, K.W., Kim, D.K., 2007. Accelerated short-term techniques to evaluate the corrosion performance of steel in fly ash blended concrete. Build. Environ. 42, 78-85.

Heikkinen, J.M., Venneker, B.C.H., di Nola, G., de Jong, W., Spliethoff, H.,2008. CFD simulation and experimental validation of co-combustion of chicken litter and MBM with pulverized coal in a flow reactor. Fuel Process. Technol. 89, 874–889.

Hussain, S., Aziz, H. A., Isa, M. H., Ahmad, A., Van Leeuwen, J., Zou, L., Beecham, S., Umar, M., 2011. Orthophosphate removal from domestic wastewater using limestone and granular activated carbon. Desalination 271, 265-272.

IAWG, 1997, Municipal Solid Waste Incinerator Residues. Elsevier (Eds.), The Netherlands.

ILE, 2006. A Guide Book on the Treatment of Effluents from the Mining/Metallurgy, Paper, Plating and Textile Industries. INASMET-Tecnalia (ed.), San Sebastián, Spain.

Ingerslev, M., Skov, S., Sevel, L., Pedersen, L.B., 2011. Element budgets of forest biomass combustion and ash fertilisation - A Danish case-study. Biomass Bioenergy 35, 2697 – 2704.

Islam, E., Liu, D., Li, T., Yang, X., Jin, X., Khan, M.A., Mahmood, Q., Hayat, Y., Imtiaz, M., 2011. Effect of Pb toxicity on the growth and physiology of two ecotypes of *Elsholtzia argyi* and its alleviation by Zn. Environ. Toxicol. 26, 403-416

ISO 10253, 2006. Water quality -- Marine algal growth inhibition test with *Skeletonema costatum* and *Phaeodactylum tricornutum*.

ISO 11348-3, 2007. Water quality -- Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (Luminescent bacteria test) -- Part 3: Method using freeze-dried bacteria.

ISO 3310-2, 1999. Test sieves - Technical requirements and testing - Part 2: Test sieves of perforated metal plate.

ISO 5663, 1984. Water quality - Determination of Kjeldahl nitrogen - Method after mineralization with selenium.

ISO 5664, 1984. Water quality - Determination of ammonium - Distillation and titration method.

ISO 5666/1, 1983. Water quality - Determination of total mercury by flameless atomic absorption spectrometry - Part 1: Method after digestion with permanganate-peroxodisulfate.

ISO 5667-3, 2003. Water quality - Sampling - Part 3: Guidance on the preservation and handling of water samples.

ISO 6341, 1996. Water quality - Determination of the inhibition of the mobility of *Daphnia magna* Straus (Cladocera, Crustacea) - Acute toxicity test.

ISO 6439, 1990. Water quality - Determination of phenol index - 4-Aminoantipyrine spectrometric methods after distillation.

ISO 7888, 1985. Water quality - Determination of electrical conductivity.

ISO 7980, 2010. Water quality - Determination of calcium and magnesium - Atomic absorption spectrometric method.

ISO 8288, 1986. Water quality - Determination of cobalt, nickel, copper, zinc, cadmium and lead - Flame atomic absorption spectrometric methods.

ISO 8692, 2004. Water quality - Freshwater algal growth inhibition test with unicellular green algae.

ISO 9174, 2009. Water quality - Determination of chromium - Atomic absorption spectrometric methods.

ISO 9297, 1989. Water quality - Determination of chloride - Silver nitrate titration with chromate indicator (Mohr's method).

ISO 9964-1, 1993. Water quality -- Determination of sodium and potassium -- Part 1: Determination of sodium by atomic absorption spectrometry.

ISO 9964-2, 1993. Water quality -- Determination of sodium and potassium -- Part 2: Determination of potassium by atomic absorption spectrometry.

ISO 9965, 1993. Water quality -- Determination of selenium -- Atomic absorption spectrometric method (hydride technique).

ISWA. 1995. Handling, treatment and disposal of sludge in Europe. Situation report 1 - an overview. ISWA, Working Group on Sewage and Water Works.

Izquierdo, M., Moreno, N., Font, O., Querol, X., Alvarez, E., Antenucci, D., Nugteren, H., Luna, Y., Fernández-Pereira, C., 2008. Influence of the co-firing on the leaching of trace pollutants from coal fly ash. Fuel 87, 1958-1966.

Jankowski, J., Ward C.R., French, D., Groves, S., 2006. Development of a non-conventional sorbent from fly ash and its potential use in acid wastewater neutralization and heavy metal removal. Fuel 85, 243–256.

Jianguo, J., Maozhe, C., Yan, Z., Xin, X., 2009. Pb stabilization in fresh fly ash from municipal solid waste incinerator using accelerated carbonation technology. J. Hazard. Mater. 161, 1046-1051.

Jiao, F., Cheng, Y., Zhang, L., Yamada, N., Sato, A., Ninomiy, Y., 2011. Effects of HCl, SO_2 and H_2O in flue gas on the condensation behavior of Pb and Cd vapors in the cooling section of municipal solid waste incineration. Proc. Combust. Inst. 33, 2787–2793.

Jing, C., Liu, S., Korfiatis, P., Meng, X., 2006. Leaching behavior of Cr(III) in stabilized/solidified soil. Chemosphere 64, 379–385.

Johnson, A., Catalan, L.J.J., Kinrade, S.D., 2010. Characterization and evaluation of fly-ash from co-combustion of lignite and wood pellets for use as cement admixture. Fuel 89, 3042–3050.

Jones, D.R., 1995. The leaching of major and trace elements from coal ash. in: D.J. Swaine and F. Goodarzi (Eds.), Environmental aspects of trace elements in coal, Kluwer Academic Publishing, Dordrecht, pp. 221–262.

Kadirvelu, K., Goel, J., 2007. Hazardous materials and wastewater – Treatment, removal and analysis. Ed. Allison Lewisnky - Nova Science Publishers Inc, New York.

Kalembkiewicz, J., Chmielarz, U., 2012. Ashes from co-combustion of coal and biomass: New industrial wastes. Resour. Conserv. Recyl. 69, 109-121.

Kang, S.-W., Seo, J., Han, J., Lee, J.-S., Jung, J., 2011. A comparative study of toxicity identification using Daphnia magna and Tigriopus japonicus: Implications of establishing effluent discharge limits in Korea. Mar. Pollut. Bulletin 63, 370-375.

Kelessidis, A., Stasinakis, A.S., 2012. Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries. Waste Manag. 32, 1186–1195.

Kent, D.B., Puls, R.W., Ford, R.G., 2007. Chromium. Environmental Protection Agency, EPA/600/R-07/140.

Khan, A.A., Jong, W., Jansens, P.J., Spliethof, H., 2009. Biomass combustion in fluidized bed boilers: Potential problems and remedies. Fuel Process. Technol. 90, 21-50.

Klemm, W.A., 1998. Ettringite and oxyanion-substitited ettringites – Their characterization and applications in the fixation of heavy metals: a synthesis of the literature. Portland Cement Assoc., ISBN 0-89312-192-4.

Komjarova, I., Blust, R., 2009. Effect of Na, Ca and pH on simultaneous uptake of Cd, Cu, Ni, Pb, and Zn in the water flea *Daphnia magna* measured using stable isotopes. Aquat. Toxicol. 94, 81–86.

Kookos, I.K., Pontikes, Y., Angelopoulos, G.N., Lyberatos, G. G., 2011. Classical and alternative fuel mix optimization in cement production using mathematical programming. Fuel 90, 1277-1284.

Koukouzas, N., Ketikidis, C., Itskos, G., 2011. Heavy metal characterization of CFB-derived coal fly ash. Fuel Process. Technol. 92, 441–446.

Kumpiene, J., Lagerkvist, A., Maurice, C., 2008. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments – A review. Waste Manag. 28, 215-225.

Lapa, N., Barbosa, R., Lopes, M.H., Mendes, B., Abelha, P., Gulyurtlu, I., Santos Oliveira, J., 2007. Chemical and ecotoxicological characterization of ashes obtained from sewage sludge combustion in a fluidised-bed reactor. J. Hazard. Mater. 147, 175–183.

Lapa, N., Barbosa, R., Mendes, B., 2012. Intrinsic properties of new materials for civil engineering works based on the reuse of MSWI bottom ashes: Chemical and ecotoxicological assessment, Urban Mining: A global cycle approach to resource recovery from solid waste. Ed. Cossu, R., Salieri, V., Bisinella, V., CISA Publishers, 13-20.

Lapa, N., Barbosa, R., Morais, J., Mendes, B. Méhu, J., Oliveira, J.F.S., 2002. Ecotoxicological assessment of leachates from MSWI bottom ashes. Waste Manag. 22, 583–593.

Leckner, B., Åmand, L.-E., Lücke, K., Werther, J., 2004. Gaseous emissions from co-combustion of sewage sludge and coal/wood in a fluidized bed., Fuel 83, 477-486.

Li, Y., Liu, C., Luan, Z., Peng, X., Zhu, C., Chen, Z., Zhongguo Zhanga, Fan, J., Jia, Z., 2006. Phosphate removal from aqueous solutions using raw and activated red mud and fly ash. J. Hazard. Mater. 137, 374-383.

Lin, H., Ma, X., 2012. Simulation of co-incineration of sewage sludge with municipal solid waste in a grate furnace incinerator. Waste Manag. 32, 561-567.

Lindberg, D., Backman, R., Chartrand, P., Hupa, M., 2013. Towards a comprehensive thermodynamic database for ash-forming elements in biomass and waste combustion - Current situation and future developments. Fuel Process. Technol 105, 129-141.

Lopes, H., Gulyurtlu, I., Abelha, P., Crujeira, T., Salema, D., Freire, M., Pereira, R., Cabrita, I., 2009. Particulate and PCDD/F emissions from coal co-firing with solid biofuels in a bubbling fluidised bed reactor. Fuel 88, 2373–2384.

Lopes, I., Gonçalves, F., Soares, A.M.V.M., Ribeiro, R., 1999. Discriminating the ecotoxicity due to metals and to low pH in acid mine drainage, Ecotoxicol. Environ. Saf. 44, 207-214.

Lopes, M. H., Abelha, P., Santos Oliveira, J.F., Cabrita, I., Gulyurtlu, I., 2005. Heavy metals behavior during monocombustion and co-combustion of sewage sludge. Environ. Eng. Sci. 22, 205-220.

Lopes, M.H., Abelha, P., Lapa, N., Oliveira, J.S., Cabrita, I., Gulyurtlu, I., 2003. The behaviour of ashes and heavy metals during the co-combustion of sewage sludges in a fluidised bed. Waste Manag. 23, 859-870.

López-Antón, M.A., Días-Somoano, M., Cuesta, A.F., Riesco, A.R.., Martínez-Tarazona, M.R., 2008. Speciation of Cr and its leachability in coal by-products from spanish coal combustion plants. J. Environ. Monit. 10, 778-781.

Lu, S.G., Bai, S.Q., Zhu, L., Shan, H.D., 2009. Removal mechanism of phosphate from aqueous solution by fly ash. J. Hazard. Mater. 161, 95–101.

Ludwig, B., Khanna, P., Prenzel, J., Beese, F., 2005. Heavy metal release from different ashes during serial batch tests using water and acid. Waste Manage. 25, 1055-1066.

Mahieux, P.-Y., Aubert, J.-E., Cyr, M., Coutand, M., Husson, B., 2010. Quantitative mineralogical composition of complex mineral wastes – contribution of the Rietveld method. Waste Manage. 30, 378–388.

Mahuli, S., Agnihotri, R., Chauk, S., Ghosh-Dastidar, A., Fan, L.S., 1997. Mechanism of arsenic sorption by hydrated lime. Environ. Sci. Technol. 31, 3226–3231.

Malakootian, M., Almasi, A., Hossaini, H., 2008. Pb and Co removal from paint industries effluent using wood ash. Int. J. Environ. Sci. Tech. 5, 217-222.

Mandre, M., Pärn, H., Klõšeiko, J., Ingerslev, M., Stupak, I., Kört, M., Paasrand, K., 2010. Use of biofuel ashes for fertilisation of Betula pendula seedlings on nutrient-poor peat soil. Biomass Bienergy 34, 1384-1392.

Mao, X., Guo, X., Chang, Y., Peng, Y., 2005. Improving air quality in large cities by substituting natural gas for coal in China: changing idea and incentive policy implications. Energy Policy 33, 307–318.

Marion, A.-M., Lanève, M., Grauw, A., 2005. Study of the leaching behaviour of paving concretes: quantification of heavy metal content in leachates issued from tank test using demineralized water. Cem. Concr. Res. 35, 951–957.

Maschio, S., Tonello, G., Piani, L., Furlani, E., 2011. Fly and bottom ashes from biomass combustion as cement replacing components in mortars production: Rheological behaviour of the pastes and materials compression strength. Chemosphere 85, 666–671.

Maurer, M., Boller, M., 1999. Modelling of phosphorus precipitation in wastewater treatment plants with enhanced biological phosphorus removal. Water Sci. Technol. 39, 147-163.

McCubbina, D., Sovacool, B.K., 2013. Quantifying the health and environmental benefits of wind power to natural gas. Energy Policy 53, 429–441.

McDonnell, K., Cummins, E.J., Fagan, C.C., Orjala, M., 2010. Co-Fuelling of Peat with Meat and Bone Meal in a Pilot Scale Bubbling Bed Reactor. Energies 3, 1369-1382.

Melchers, R.E., Li, C.Q., 2009. Reinforcement corrosion initiation and activation times in concrete structures exposed to severe marine environments. Cem. Concr. Res.39, 1068-1076.

Mellbo, P., Sarenbo, S., Stalnacke, O., Claesson, T., 2007. Leaching of wood ash products aimed for spreading in forest floors – influence of method and L/S ratio. Waste Manag. 28, 2235-2244.

Meunier, N., Blais, J.F., Lounès, M., Tyagi, R.D., Sasseville, J.L., 2002. Different options for metal recovery after sludge decontamination at the Montreal Urban Community wastewater treatment plant. Water Sci Technol. 6, 33-41.

Milieu Ltd., WRc, Risk & Policy Analysts Ltd (RPA), 2010. Environmental, economic and social impacts of the use of sewage sludge on land. Final Report, Part III: Project Interim Reports, DG-ENV.G.4/ETU/2008/0076r, 10.2.2010. (Report available on http://ec.europa.eu/environment/waste/sludge/pdf/part_iii_report.pdf)

Miller, B.B., Kandiyoti, R., Dugwell, D.R., 2004. Trace element behavior during co-combustion of Sewage Sludge with Polish Coal, Energy Fuels. 18, 1093-1103.

Miller, S.F., Miller, B.G., 2007. The occurrence of inorganic elements in various biofuels and its effect on ash chemistry and behavior and use in combustion products. Fuel Process. Technol. 88, 1155–1164.

Miravet, R., López-Sánchez, J.F., Rubio, R., 2006. Leachability and analytical speciation of antimony in coal fly ash. Anal. Chim. Acta 576, 200–206.

Mizuno, S., Nakayama, K., Kawachi, T., Kojima, Y., Watanabe, F., Matsuda, H., Takada, M., 2006. Enhancement of chloride volatilization of Zn, Pb and Cu from molten fly ash under reduced pressure. Kagaku Kogaku Ronbunshu 32, 99-102.

Modolo, R.C.E., Ferreira, V.M., Tarelho, L.A., Labrincha, J.A., Senff, L., Silva, L., 2013. Mortar formulations with bottom ash from biomass combustion. Constr. Build. Mater. 45, 275-281.

Morais, J., Barbosa, R., Lapa, N., Mendes, B., Gulyurtlu I., 2011. Environmental and socio-economic assessment of co-combustion of coal, biomass and non-hazardous wastes in a Power Plant. Resour. Conserv. Recycl. 55, 1109-1118.

Morais, J., Lapa, N., Barbosa, R., Santos, A., Mendes, B., Santos Oliveira, J.F., 2008. Environmental and socio-economic assessment of co-combustion of coal, biomass and non-hazardous wastes in a full scale power plant. in: Proceedings of the International Conference and Exhibition on Bioenergy: Bioenergy: Challenges and Opportunities, April 6th – 9th, Universidade do Minho, Guimarães, Portugal.

Mousavi, H.Z., Hosseynifar, A., Jahed, V., Dehghani, S.A.M., 2010. Removal of Lead from Aqueous Solution using Waste Tire Rubber Ash as an Adsorbent. Braz. J. Chem. Eng. 27, 79-87.

Mousavi, H.Z., Seyedi, S.R., 2010. Kinetic and Equilibrium Studies on the Removal of Pb(II) from Aqueous Solution using Nettle Ash. J. Chil. Chem. Soc. 55, 307-311.

Nakayama, K., Dalibor, K., Sakai, K. Kubota, M., Matsuda, H., 2008. Effect of unburned carbon on lead, zinc, and copper recovery from molten fly ash by chloride-induced volatilization. J Mater. Cycles Waste Manag. 10, 102–109.

Narukawa, T., Takatsu, A., Chiba, K., Riley, K. W., French, D.H., 2005. Investigation on chemical species of arsenic, selenium and antimony in fly ash from coal fuel thermal power stations. J . Environ. Monit. 7, 1342–1348.

Nawy, E., 2008. Concrete Construction Engineering Handbook. 2nd Ed. New York: Taylor & Francis Group.

Needleman, H., Gee, D., 2013. Lead in petrol 'makes the mind give way' - Lessons from health hazards (from http://www.eea.europa.eu/publications/late-lessons-2/late-lessons-chapters/late-lessons-ii-chapter-3 (assessed on July 2013).

NEN 7343, 1995. Leaching Characteristics of Building and Solid Waste Material, Leaching Tests, Determination of the Leaching of Inorganic Components from Granular Materials with the Column Test.

NEN 7345, 1995. Leaching Characteristics Of Solid Earthy And Stony Building And Waste Materials - Leaching Tests - Determination Of The Leaching Of Inorganic Components From Buildings And Monolitic Waste Materials With The Diffusion Test.

NF T90-043, 1988. Essais des eaux - Dosage du chrome (VI) - Méthode par spectrométrie d'absorption moléculaire.

NP EN 12390-3, 2011. Testing hardened concrete. Part 3: Compressive strength of test specimens.

Nurmesniemi, H., Pöykiö, R., Kuokkanen, T., Rämö, J., 2008. Chemical sequential extraction of heavy metals and sulphur in bottom ash and in fly ash from a pulp and paper mill complex. Waste Manag. Res. 26, 389-399.

Obernberger, I., Biedermann, F., Widmann, W., Riedl, R., 1997. Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions. Biomass Bioenergy 12, 211-224.

Obernberger, I., Thek, G., 2008. Combustion and gasification of solid biomass for heat and power production in Europe – state of the art and relevant future developments. Proc of the 8th European Conference on Industrial Furnaces and Boilers, Portugal, Cenertec. ISBN 978-972-99309-3-5.

Olanders, B., Steenari, B., 1995. Characterization of ashes from wood and straw. Biomass Bioenergy 8, 105-115.

Otsuka, N., 2008. A thermodynamic approach on vapor-condensation of corrosive salts from flue gas on boiler tubes in waste incinerators. Corrosion Science 50, 1627–1636.

Pack, S.W., Jung, M.S., Song, H.W, Kim, S.H., Ann. K.Y., 2010. Prediction of time dependent chloride transport in concrete structures exposed to a marine environment. Cem. Concr. Res. 40, 302-312.

Paisley, L.G., Hostrup-Pedersen, J., 2005. A quantitative assessment of the BSE risk associated with fly ash and slag from the incineration of meat-and-bone meal in a gas-fired power plant in Denmark. Prev. Vet. Med. 68, 263–275.

Pantoleontos, G., Basinas, P., Skodras, G., Grammelis, P., Pintér, J.D., Topis, S., Sakellaropoulos, G.P., 2009. A global optimization study on the devolatilisation kinetics of coal, biomass and waste fuels. Fuel Process. Technol. 90, 762–769.

Paoletti, F., 2002. Behaviour of oxyanions forming heavy metals in municipal solid waste incineration. Ph.D. Thesis, Univ. Stuttgart, Germany.

Paoletti, F., Sirini, P., Seifert, H., Vehlow, J., 2001. Fate of antimony in municipal solid waste incineration. Chemosphere 42, 533–543.

Papadimitriou, C.A., Haritou, I., Samaras, P., Zouboulis, A.I., 2008. Evaluation of leaching and ecotoxicological properties of sewage sludge-fly ash mixtures. Environ. Res. 106, 340-348.

Park, E.J., Jo, H.J., Jung, J., 2009. Combined effects of pH, hardness and dissolved organic carbon on acute metal toxicity to *Daphnia magna*. J. Ind. Eng. Chem. 15, 82-85.

Parsons, S. A., and Berry, T., 2004. Chemical phosphorus removal, in: Phosphorous in environmental technologies – principles and application, E. Valsami-Jones (ed.), IWA, UK, pp. 260-271.

Patrão, G., 2010. A experiência pioneira da EDP Produção – Bioeléctrica, S.A. na central termoeléctrica de biomassa florestal residual de Mortágua, 4ª Conferência Nacional de Avaliação de Impactes, UTAD, 20-22 Outubro 2010.

Payá, J., Monzá, J., Borrachero, M.V., Amahjour, F., Girbés, I., Velázquez, S., Ordóñez, L.M., 2002. Advantages in the use of fly ashes in cements containing pozzolanic combustion residues: silica fume, sewage sludge ash, spent fluidized bed catalyst and rice husk ash. J. Chem. Technol. Biotechnol. 77, 331-335.

Pels, J.R., de Nie, D.S., Kiel, J.H.A., 2005. Utilization of ashes from biomass combustion and gasification. in: Proc 14th European biomass conference and exhibition, Paris, p. 3–9.

Pengthamkeerati, P., Satapanajaru, T., Chularuengoaksorn, P., 2008. Chemical modification of coal fly ash for the removal of phosphate from aqueous solution. Fuel 87, 2469-2476.

Perkins, R.B., 2000. Solubility and thermodynamic properties of ettringite, its chromium analogs and calcium aluminium monochromate ($3CaO*Al_2O_3*CaCrO_4*nH_2O$). Ph.D. Thesis, Portland State Univ.

Pokhrel, D., Viraraghavan, T., 2004. Treatment of pulp and paper mill wastewater - a review. Sci. Total Environ. 333, 37-58.

Polettini, A., Pomi, R., Trinci, L., Muntoni, A., Mastro, S.L., 2004. Engineering and environmental properties of thermally treated mixtures containing MSWI fly ash and low-cost additives. Chemosphere 56, 901–910.

Povey, D., 2010. Lead Poisoning: The Truth Behind Consumer Products and Legislation. The Ed. Anne Roberts. LEAD Group Inc.

Poykio, R., Nurmesniemi, H., Keiski, R.L., 2009. Total and size fractionated concentrations of metals in combustion ash from forest residues and peat. Proc. Eston. Acad. Sci. 58, 247-254.

Pratt, C., Shilton, A. 2010. Active slag filters—simple and sustainable phosphorus removal from wastewater using steel industry byproduct. Water Sci. Technol. 62, 1713-1718.

Prochnow, A., Heiermann, M., Plöchl, M., Amon, T., Hobbs, P.J., 2009. Bioenergy from permanent grassland – A review: 2. Combustion. Bioresour. Technol. 100, 4945–4954.

Qiu, Y., Cheng, H., Xua, C., Daniel Sheng, G., 2008. Surface characteristics of crop-residue-derived black carbon and lead(II) adsorption. Water Resear. 42, 567-574.

Quina, M.J., Bordado, J.C.M., Quinta-Ferreira, R.M., 2009. The influence of pH on the leaching behaviour of inorganic components from municipal solid waste APC residues. Waste Manag. 29, 2483-2493.

Rajamma, R., Ball, R.J., Tarelho, L.A.C., Allen, G.C., Labrincha, J.A., Ferreira, V.M., 2009. Characterisation and use of biomass fly ash in cement-based materials. J. Hazard. Mater. 172, 1049–1060.

Rao, M., Parwate, A.V., Bhole, A.G., 2002. Removal of Cr^{6+} and Ni^{2+} from aqueous solution using bagasse and fly ash. Waste Manag. 22, 821-830

Reddy, M.S., Basha, S., Joshi, H.V., Jha, B., 2005. Evaluation of the emission characteristics of trace metals from coal and fuel oil fired power plants and their fate during combustion. J. Hazard. Mater. 123, 242-249.

Reemtsma, T., Mehrtens, J., 1997. Determination of polycyclic aromatic hydrocarbon (PAH) leaching from contaminated soil by a column test with on-line solid phase extraction. Chemosphere 35, 2491-2501.

Reimann, C., Ottesen, R. T., Andersson, M., Arnoldussen, A., Koller, F., Englmaier, P., 2008. Element levels in birch and spruce wood ashes - green energy?. Sci. Total Environ. 393, 191-197.

Richers, U., Scheurer, W., Seifert, H., Hein, K.R.G., 2002. Present status and perspectives of co-combustion in German power plants. Forschungszentrum Karlsruhem, Institute for Technical Chemistry, Karlsruhe, Germany, ISSN 0947-8620.

Rourke, F.O., Boyle, F., Reynolds, A., 2009. Renewable energy resources and technologies applicable to Ireland. Renew. Sustain. Energy Rev. 13, 1975–1984.

Rule, K.L., Comber, S.D.W., Ross, D., 2006. Thornton, A., Makropoulos, C.K., Rautiu, R., Diffuse sources of heavy metals entering an urban wastewater catchment. Chemosphere 63, 64–72.

Sabir, H., Aziz, A.H., Isa, M.H., Ahmad, A., Van Leeuwen, J., Zou, L., Beecham, S., Umar, M., 2011. Orthophosphate removal from domestic wastewater using limestone and granular activated carbon. Desalination 271, 265-272.

Saffarzadeh, A., Shimaoka, T., Wei, Y., Gardner, K.H., Musselman, C.N., 2011. Impacts of natural weathering on the transformation/neoformation processes in landfilled MSWI bottom ash: A geoenvironmental perspective. Waste Manag. 31, 2440–2454.

Sami, M., Annamalai, K., Wooldridge, M., 2001. Co-firing of coal and biomass fuel blends. Prog. Energy Combust. Sci. 27, 171–214.

Santhosh, G., Venkatachalam, S., Ninan, K.N., Sadhana, R., Alwan, S., Abarna, V., Joseph, M.A., 2003. Adsorption of ammonium dinitramide (ADN) from aqueous solutions: 1. Adsorption on powdered activated charcoal. J. Hazard. Mater. 98, 117-126.

Sarabèr, A., Haasnoot, K., 2012. Recycling of biomass ashes in The Netherlands. Ash Utilisation 2012 - Ashes in a Sustainable Society. January 25th – 27th, Stockholm, Sweden.

Sarkar, A., Rano, R., 2007. Water Holding Capacities of Fly Ashes: Effect of Size Fractionation, Energy Sources. Part A. Recov., Util. Environment. Eff. 29, 471-482.

Sata, V., Tangpagasit, J., Jaturapitakkul, C., Chindaprasirt, P., 2012. Effect of W/B ratios on pozzolanic reaction of biomass ashes in Portland cement matrix. Cement & Concrete Compos. 34, 94-100.

Schäfer, S., Bonn, B., 2002. Hydrolysis of HCN as an important in nitrogen oxide formation in fluidised combustion. Part II. Heteregenous reactions involving limestone. Fuel 81, 1641-1646.

Senneca, O., 2008. Characterisation of meat and bone mill for coal co-firing. Fuel 87, 3262–3270.

Shao, Y., Wang, J., Xu, C., Zhu, J., Preto, F., Tourigny, G., Badour, C., Li, H., 2011. An experimental and modeling study of ash deposition behaviour for co-firing peat with lignite. Applied Energy. 88, 2635-2640.

Shu, X., Yin, L., Zhang, Q., Wang, W., 2012. Effect of Pb toxicity on leaf growth, antioxidant enzyme activities, and photosynthesis in cuttings and seedlings of *Jatropha curcas* L. Environ. Sci. Pollut. Res. Int. 19, 893-902.

Singh, S., Ram, L.C., Masto, R.E., Verma, S.K., 2011. A comparative evaluation of minerals and trace elements in the ashes from lignite, coal refuse, and biomass fired power plants. Int. J. Coal Geol. 87, 112–120.

Singhal, A., Tewari, V.K., Prakash, S., 2008. Utilization of treated spent liquor sludge with fly ash in cement and concrete. Build. Environ. 43, 991-998.

Skodras, G., Grammelis, P., Basinas, P., 2007. Pyrolysis and combustion behaviour of coal–MBM blends. Bioresour. Technol. 98, 1-8.

Spinosa, L., 2011. Wastewater Sludge: A Global Overview of the Current Status and Future Prospects (second ed.), 978-1-84-339388-7IWA Publishing, UK pp. 11–15.

Spliethoff, H., 2010. Power Generation from Solid Fuels, Springer, ISBN 978-3-642-02855-7.

Stark, J., 2011. Recent advances in the field of cement hydration and microstructure analysis. Cem. Concr. Res. 41, 666-678.

Steenari, B.M., Schelander, S., Lindqvist, O., 1999a. Chemical and leaching characteristics of ash from combustion of coal, peat and wood in a 12 MW CFB - a comparative study. Fuel Energy 78, 249–258.

Steenari, B.M., Karlsson, L.G., Lindqvist, O., 1999b. Evaluation of the leaching characteristics of wood ash and the influence of ash agglomeration. Biomass Bioenergy 16, 119-136.

Sterling, R.O., Helble, J.J., 2003. Reaction of arsenic vapor species with fly ash compounds: kinetics and speciation of the reaction with calcium silicates. Chemosphere 51, 1111–1119.

Stiernström, S., Hemström, K., Wik, O., Carlsson, G., Bengtsson, B.-E., Breitholtz, M., 2011. An ecotoxicological approach for hazard identification of energy ash. Waste Manag. 31, 342–352.

Sun, L.-S., Abanades, S., Lu, J.D., Flamant, G., Gauthier, D., 2004. Volatilization of heavy metals during incineration of municipal solid wastes. J. Environ. Sci. (IOS Press) 16, 635-639.

Tkaczewska, E., Mróz, R., Łój, G., 2012. Coal–biomass fly ashes for cement production of CEM II/A-V 42.5R. Constr. Build. Mater. 28, 633-639.

Tortosa Masiá, A.A., Buhre, B.J.P., Gupta, R.P., Wall, T.F., 2007. Characterising ash of biomass and waste. Fuel Process. Technol. 88, 1071–1081.

Travar, I., Lidelöw, S., Andreas, L., Tham, G. Lagerkvist, A., 2009. Assessing the environmental impact of ashes used in a landfill cover construction. Waste Manag. 29, 1336-1346.

Tsiridis, V., Samaras, P., Kungolos, A., Sakellaropoulos, G.P., 2006. Application of leaching tests for toxicity evaluation of coal fly ash. Environ. Toxicol. 21, 409-416.

Ugurlu, A., Salman, B., 1998. Phosphorus removal by fly ash. Environ. Int. 24, 911–918.

Ugurlu, M., Karaoglu, M.H., 2011. Adsorption of ammonium from an aqueous solution by fly ash and sepiolite: Isotherm, kinetic and thermodynamic analysis. Microporous Mesoporous Mater. 139, 173–178.

Umamaheswaran, K., Batra, V.S., 2008. Physico-chemical characterisation of Indian biomass ashes. Fuel 87, 628-638.

United States Department of Transportation – Federal Highway Transportation, 2012. User Guidelines for Waste and Byproduct Materials in Pavement Construction. Publication Number: FHWA-RD-97-148.

United States Department of Transportation - Federal Highway, and Technology, 2001. The Effects of Higher Strength and Associated Concrete Properties on Pavement Performance. Publication number FHWA-RD-00-161, Georgetown Pike.

USEPA Method 3015A, 2007. Microwave assisted acid digestion of aqueous samples. Revision 1.

USEPA Method 3051A, 2007. Microwave assisted acid digestion of sediments, sludgesm soils, and oils. Revision 1.

USEPA Method 7196A, 1992. Chromium, Hexavalent (colorimetric). Revision 1.

Üstün, G.E., 2009. Occurrence and removal of metals in urban wastewater treatment plants. J. Hazard. Mater. 172, 833-838.

Vamvuka, D., Pitharoulis, M., Alevizos, G., Repouskou, E., Pentari, D., 2009. Ash effects during combustion of lignite/biomass blends in fluidized bed. Renew. Energy 34, 2662–2671.

van Caneghem, J., Brems, A., Lievens, P., Block, C., Billen, P., Vermeulen, I., Dewil, R., Baeyens, J., Vandecasteele, C., 2012. Fluidized bed waste incinerators: Design, operational and environmental issues. Prog. Energy Combust. Sci.

van de Velden, M., Dewil, R., Baeyens, J., Josson, L., Lanssens, P., 2008. The distribution of heavy metals during fluidized bed combustion of sludge (FBSC). J. Hazard. Mater. 151, 96–102.

van der Sloot, H.A., Kosson, D.S., Hjelmar, O., 2001. Characteristics, treatment and utilization of residues from municipal solid waste incineration. Waste Manag. 21, 753–765.

van Eijk, R.J., Obernberger, I., Supancic, K., 2012. Options for increased utilization of ash from biomass combustion and co-firing. IEA Bioenergy Task 32 - Deliverable D4, 30102040-PGR/R&E 11-2142.

van Loo, S., Koppejan, J., 2008. The handbook of biomass combustion and co-firing. London: Sterling (VA) Earthscan.

Vassilev, S.V., Baxter, D., Andersen, L.K., Vassilev, C.G., 2013. An overview of the composition and application of biomass ash.: Part 2. Potential utilisation, technological and ecological advantages and challenges. Fuel 105, 19-39.

Venkatesh, A., Jaramillo, P., Griffin, W.M., Matthews, H.S., 2012. Implications of near-term coal power plant retirement for SO_2 and NO_X and life cycle GHG emissions. Environ. Sci. Technol. 46, 9838-9845.

Wagland, S.T., Kilgallon, P., Coveney, R., Garg, A., Smith, R., Longhurst, P.J., Pollard, S.J.T., Simms, N., 2011. Comparison of coal/solid recovered fuel (SRF) with coal/refuse derived fuel (RDF) in a fluidised bed reactor. Waste Manag. 31, 1176-1183.

Wang, G., Shen, L., Sheng, C., 2012. Characterization of biomass ashes from power plants firing agricultural residues. Energy Fuels 26, 102–111.

Wang, S., Baxter, L., 2007. Comprehensive study of biomass fly ash in concrete: strength, microscopy, kinetics and durability. Fuel Process. Technol. 88, 1165–1170.

Wang, S., Miller, A., Llamazos, E., Fonseca, F., Baxter, L., 2008a. Biomass fly ash in concrete: Mixture proportioning and mechanical properties. Fuel 87, 365-371.

Wang, W., Qin, Y., Song, D., Wang, K., 2008b. Column leaching of coal and its combustion residues, Shizuishan. China. Int. J. Coal Geol. 75, 81-87.

Wang, S., Baxter, L., Fonseca, F., 2008c. Biomass fly ash in concrete: SEM, EDX and ESEM analysis. Fuel 87, 372–379.

Ward, C.R., French, D., Riley, K., Stephenson, L., Farrel, O., Li, Z., 2011. Element leachability from a coal stockpile and associated coastal sand deposits. Fuel Process. Technol., 92, 817–824.

Werther, J., Ogada, T., 1999. Sewage sludge combustion. Prog. Energy Combust. Sci. 26, 1-27.

Wieck-Hansen, K., Overgaard, P., Larsen, O.H., 2000. Cofiring coal and straw in a 150 MWe power boiler experiences. Biomass Bioenergy 19, 395–409.

Wood, K., Wood, G., Prokop, D., Lewyille, F., 2006. Phosphorus removal using novel crystallisation technology. Water Sci. Technol. 53, 169-175.

World Health Organization (Water Sanitation and Health), 2003. Molybdenum in Drinking-water - Background document for development of WHO Guidelines for Drinking-water Quality, WHO/SDE/WSH/03.04/11.

World Health Organization (Water Sanitation and Health), 2004. Barium in drinking-water; Background document for development of WHO Guidelines for Drinking-water Quality, WHO/SDE/WSH/03.04/76.

Wzorek, M., 2012. Characterisation of the properties of alternative fuels containing sewage sludge. Fuel Process. Technol. 104, 80-89.

Xiong, J., Qin, Y., Islam, E., Yue, M., Wang, W., 2011. Phosphate removal from solution using powdered freshwater mussel shells. Desalination 276, 317-321.

Xu, K., Deng, T., Liu, J., Peng, W., 2010. Study on the phosphate removal from aqueous solution using modified fly ash. Fuel 89, 3668-3674.

Yang, Y., Tomlinson, D., Kennedy, S., Zhao, Y.Q., 2006. Dewatered alum sludge: a potential adsorbent for phosphorus removal. Water Sci. Technol. 54, 207-213.

Yuan, X., Huang, H., Zeng G., Li, H., Wanga, J., Zhou, C., Zhu, H., Pei, X., Liu Z., Liu, Z., 2011. Total concentrations and chemical speciation of heavy metals in liquefaction residues of sewage sludge. Bioresour. Technol., 102, 4104–4110.

Zheng, Y., Jensen, P.A., Jensen, A.D., Sander, B., Junker, H., 2007. Ash transformation during co-firing coal and straw. Fuel 86, 1008–1020.