OLENA LYGINA

WASTE RECOVERY INTO ACTIVATED CARBON FOR WATER PURIFICATION FROM HEAVY METALS

Lisboa, Portugal

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WASTE RECOVERY INTO ACTIVATED CARBON FOR WATER PURIFICATION FROM HEAVY METALS

OLENA LYGINA

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I would like to dedicate this thesis to my loving family- my son, my husband, parents, my grandmother and grandparents of my husband, to whom I owe my unconditional love and friendship

To invent, you need a good imagination and a pile of junk.

Thomas Edison

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To you my son! This work would not be possible without your smiles!

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Preface

The PhD work was carried out as a part of one national and two international programs in a close collaboration with six R&D centres from Portugal and Ukraine, namely

(1) Research on *co-mingle waste co-processing* was accomplish at Donetsk State University of Economic and Trade, Department of Chemistry under supervision of Prof. Alexandr Dmitruk. Work was carried out in the frame of the Ukrainian Program of National Academy of Science of Ukraine, Ministry of Science and Education as a PhD Fellowship.

(2) Research on *treatability study of wastewater purification from heavy metals* was accomplish at Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologia, REQUIMTE, Departamento de Química under supervision of Prof. Isabel Fonseca. The reserach was carried out in the frame of NATO "Science for Peace" Programme, project SfP 977984 as project student's research training.

(3) Two research trainings on *Eco-design co-mingle waste recovery concept in its triple dimension (waste recycling, recover and reuse)* and on *Eco-efficiency co-mingle waste re-used concept demonstration within electrodialytic soil remediation* were accomplished at INETI - Instituto Nacional de Engenharia, Tecnologia e Inovação under supervision of Prof. Ibrahim Gulyurtlu and Universidade Nova de Lisboa, UNL/FCT, CENSE, Dept. Ciências e Engenharia do Ambiente under supervision of Prof. Alexandra Ribeiro. The work was carried out in the frame of the INTAS -European Community International Association for the promotion of co-operation with scientists from the New Independent States of the former Soviet Union Program as a personal the INTAS Young Scientist Fellowship N^0 06-1000014-5820.

(4) Research on *activated carbon design and manufacture* was carried in *a lab scale* at Institute of Physical Organic and Coal Chemistry of National Academy of Science of Ukraine under supervision of Dr. Leonid Galushko, and in *a pilot-scale* at Joint Stock Company "Electrod" from Donetsk, Ukraine, under supervision of Eng. Sergiy Mikhajlyuk. The work was carried out in the frame of NATO "Science for Peace" Programme, project SfP 977984 as a project student's industrial training.

The thesis is divided in seven *CHAPTERS. Chapter 1* and *7* correspond to the introduction and conclusions, respectively. The structure of the research, the achievements and the conclusions are divided in three major sections:

- The study of the co-thermolysis process of the solid and liquid carbon-containing residues (*Chapters 2* and *3*);
- The study of the co-mingled waste recovery into environmentally friendly secondary porous solid products (*Chapter 4*);
- The study of 3d transition metals adsorption by activated carbons from co-mingled waste (*Chapters 5* and *6*).

The main core of the *Chapters 2, 3, 4, 5* and *7* is based on 6 published scientific papers in refereed journals and conference presentations, namely:

Chapter 2

E. S. Lygina, A. F. Dmitruk, S. B. Lyubchik, L. Ya. Galushko and V. F. Tret'yakov. Thermodynamic Study of the Thermal Degradation of Solid and Liquid Organic Carbon-Containing Products. *Solid Fuel Chemistry*, **2009**, Vol. 43, pp. N 3, pp. 177-192.

E. S. Lygina, A. F. Dmitruk, S. B. Lyubchik, L. Ya. Galushko and V. F. Tret'yakov. Thermal Degradation of Solid and Liquid Organic Carbon-Containing Products *Chemistry of Solid Fuels*, **2009,** N 3, pp. 58-74. (in Rus).

Chapter 3

E. S. Lygina, A. F. Dmitruk, S. B. Lyubchik and V. F. Tret'yakov. Application of thermogravimetry to the analysis of thermodestruction of co-mingled solid and liquid waste materials. *Solid Fuel Chemistry*, **2009**, Vol. 43, pp. N 4, pp. 247-266.

E. S. Lygina, A. F. Dmitruk, S. B. Lyubchik and V. F. Tret'yakov. New Approach to the Thermogravimetry Data Analysis of the Co-mingled Solid and Liquid Organic Waste Thertmodestruction. *Chemistry of Solid Fuel*, **2009,** N4, pp. 62-81. (in Rus)

Chapter 4

Book chapter (in Rus)
Lygina O.S., Lyubchik S.B., Tret'yakov V.F., Galushko O.L., Galushko L.Ya., Dmitruk A.F. Thermogravimetric analysis of co-pyrolysis of coal with carbon-containing waste *Book of Donetsk Technical University,* "Chemistry and Chemical Technology", **2007**, 8pp.

Chapter 5

S. B. Lyubchik, I. I. Perepichka, O. L. Galushko, A. I. Lyubchik, E. S. Lygina, I. M. Fonseca. Optimization of the Conditions for the Cr (III) Adsorption on Activated Carbon, *Adsorption* **2005**, 11 (5-6), pp. 581-593.

Chapter 6

S. B. Lyubchik, A. I. Lyubchik, E. S. Lygina, S. I. Lyubchik, T. L. Makarova, J. Vital, A. M. B. do Rego, I. M. Fonseca. Simultaneous removal of 3d transition metals from multi-component solutions by activated carbons from co-mingled wastes *Separation and Purification Technology,* **2008**, Vol. 60/3, pp 264-271.

The research has promoted an extensive international co-operation within work objectives implementation and collaboration with other institution/industries within the results dissemination. Overview of these activities is followed:

Dissemination of results to EU Programs

1. Organization of the NATO Advanced Research Workshop "Recent Advances in Adsorption Processes for Environmental Protection and Security" http://www.dq.fct.unl.pt/anw2006/

Collaboration with National State Authorities of Ukraine

2. Joint Stock Company "Electrode", Donetsk, Ukraine

   Dissemination of work results towards pilot-scale activated carbons production. Prototype activated carbons production from co-mingled waste

Collaboration with National and International Institutions

3. INETI – Instituto Nacional de Engenharia, Tecnologia e Inovação, Portugal

   Demonstration of the work Eco-design concept in its triple dimension (waste reuse, recycling and energy recovery) via project result implementation towards Portuguese waste sources (the improvement of the resulted char properties, gas product composition and energetic content)

4. FCT/UNL-CENSE, Dept. Ciências e Engenharia do Ambiente, Portugal

   Demonstration of the work Eco-efficiency concept via result implementation towards EU electrodialitic soil remediation technique (solution to the problem of electrolytes contamination by heavy metals)

5. UPM – University Pierre et Marie Curie, Paris, France

   Analyses of surface groups of novel activated carbon from wastes

6. IST – Instituto Superior Técnico, Centro de Química -Física Molecular, Complexo Interdisciplinar Lisboa, Portugal

   XPS study of spent adsorbents surface

7. Bruker AXS Company, Germany

   Solid state NMR C^{13} study of main structural units of the activated carbon from co-mingled wastes

8. UU – Nobel Prize Winner Prof. Kai Siegban, Uupsala University, Sweden

   Evaluation of the structure of the activated carbons from co-mingled waste

Abstract

The main objective of this research was the recovery of natural carbon-containing wastes into environmentally friendly secondary products, and their re-use as selective adsorbents for heavy metals removal from wastewater streams. The natural carbon containing wastes were: *Sunflower husks*, *D-grade coal*, *AKKhZ sludge* and *Spent petroleum product waste*.

To achieve this purpose, the research was focused on three different types of studies:

1. Study the thermolysis process of the single carbon-containing wastes components and their blends aimed at: (i) determination of the reference onset of the thermal stages, assigning the reference structural fragments of the parent *Sunflower husks*, *D-grade coal*, *AKKhZ sludge* and *Spent petroleum product waste*; and (ii) evaluation of the synergetic effects observed during their co-thermolysis.
2. Development of a recovery concept to the waste recycling *via* co-activation of the co-mingled carbon-containing waste materials, in order to obtain a porous activated carbon.
3. Optimization of the experimental conditions for the adsorption of heavy metals from contaminated waste waters.

In order to gain some insight into the reactions which may occur between the components of the co-mingled wastes during the activation process, in the first part of the work the pyrolysis behavior of the single components and their blends were investigated by thermogravimetric analysis. On this stage, the data obtained suggested a new approach to the problem of assessing the selectivity of the co-processing concept. Based on the direct monitoring of the reference structural fragments during co-thermolysis, the synergetic effects were evaluated for the co-mingled systems.

The data obtained were used in the second part of the work, for the development of the *co-activation* concept to the co-mingled solid and liquid recovery into secondary solid porous products. The development of the design parameters for the activated carbons syntheses was done considering the re-polymerization, re-association and the polycondensation reactions between the reference structural fragments of the

components in the ternary composite systems «*Spent Petroleum Product Waste – Biomass – D-grade D*» and «*AKKhZ sludge – Biomass – D-grade coal*». The factors influencing the char formation and the properties of the resulting activated carbons were evaluated at laboratory scale.

The *co-activation* approach developed to the solid and liquid co-mingled waste recycling, was implemented at pilot scale. Novel powder and granular activated carbons have been obtained with surface area of 400-1050 m^2/g, total pore volume of 0.32-0.47 m^3/g and yield of 21-27%.

A comprehensive adsorption study using the novel activated carbons, was performed in the third part of the work. The influence of various textural and surface characteristics of carbon materials (porosity, surface area, oxygen functional groups) and the conditions of the adsorption process (initial solution acidity, contact time, components ratio) were investigated in batch mode for single- and multi-component model solutions containing Fe (II), Co (II), Cu (II), Cr (III), Ni (II), Mn (II).

Under optimized conditions, a total chromium uptake of 1.09 mmol/g was achieved using as adsorbent the novel activated carbon from co-mingled wastes. The uptake is slightly higher than the one obtained for the commercial GAC Norit 1240 Plus (A–10128) activated carbon oxidised by HNO_3.

Moreover, in the course of this work, it became clear, that the usage of the activated carbon from co-mingled waste for the 3d transitional metals adsorption offered an attractive approach to simultaneous metal removal from multi-component solutions. The total metal removal combined the process of metal hydroxide precipitation (up to 50–55 % by total removal) with the metal cation adsorption on negatively charged carbon surface (up to 15–20 % by total removal) in a single operation unit. Finally, the mechanism of the 3d transition metals adsorption on the activated carbon from co-mingled waste was considered.

Within this context, the natural organic waste recovery into porous solid environmentally friendly products offered a technological alternative to their disposal.

Resumo

O objectivo deste trabalho de investigação foi a recuperação de resíduos naturais de carbono, transformando-os em produtos secundários amigos do ambiente com valor acrescentado. Estes produtos foram usados como adsorventes na remoção de metais pesados de águas contaminadas.

Para se conseguir este objectivo, o estudo foi dividido em 3 secções principais:

1. Estudo do processo de co-termólise de resíduos sólidos e líquidos ricos em carbono:
2. Estudo da recuperação e reciclagem de resíduos mistos para obter, como produtos secundários, sólidos porosos amigos do ambiente;
3. Estudos de adsorção de metais de transição em carvões activados obtidos do tratamento dos resíduos mistos.

O ponto de partida para este trabalho de investigação foi a identificação das várias etapas térmicas que ocorrem durante a termólise dos materiais de origem. Estes materiais são cascas de sementes de girassol, resíduos de carvão (hulha), lamas do processamento de carvão (AKKZ) e resíduos de produtos petrolíferos. Avaliaram-se os fenómenos sinergéticos que ocorrem durante a co-termólise da mistura destes resíduos (co-termólise de resíduos mistos) quer na presença ou ausência de catalisador. Usou-se como catalisador uma mistura eutéctica de carbonato de potássio e sódio.

Para melhor compreender e avaliar as reacções que podem ocorrer entre os componentes dos resíduos mistos durante o processo de activação, foram efectuados estudos de análise termogravimeétrica (TG/DTG) da pirólise dos componentes simples e das misturas.

Com os resultados obtidos usou-se uma nova abordagem para determinar a selectividade do co-processamento. Esta nova perspectiva considera não só a avaliação cumulativa dos produtos gasosos primário e secundários gerados durante a co-termólise, mas também avalia as interacções químicas (fenómenos sinergéticos) entre os fragmentos estruturais da fase sólida durante a co-termólise destes complexos componentes ricos em carbono.

Os resultados obtidos, tendo em conta o efeito os sinergéticos observados e a influência do catalisador, permitiram desenvolver um processo de co-activação destas misturas tendo como objectivo a produção dum carvão activado .

Para a optimização dos parâmetros experimentais da preparação dos carvões activados, consideraram-se as possíveis reacções de re-polimerização, re- associação e de policondensação entre os fragmentos estruturais de referência dos componentes dos sistemas compósitos ternários "*Resíduos de Petróleo – Biomassa- D-grade D Carvão*" e "*Lamas AKKhZ – Biomassa – D-grade Carvão*". A optimização das condições de co-activação foi realizada á escala laboratorial.

Após esta optimização, a co-activação dos resíduos mistos foi implementada à escala piloto. Os protótipos de carvão activado produzidos foram obtidos usando diferentes misturas de resíduos, biomassa, resíduos petrolíferos e carvão de baixa qualidade. O material obtido por co-activação apresenta boas propriedades: Área superficial de 400-1050 m^2/g, volume total de poros 0.32- 0.47 m^3/g e um rendimento de 21-27%.

Para optimizar as condições de adsorção para a remoção de metais pesados utilizando os novos carvões activados, estudou-se a influência das várias características texturais e da superfície dos materiais (porosidade, área superficial, grupos funcionais) e a influência das condições do processo de adsorção (acidez da solução, tempo de contacto, razão entre os componentes).Os ensaios foram realizados em condições batch usando soluções contendo multi ou mono componentes. As soluções aquosas continham Fe (II), Co (II), Cu (II), Cr (III), Ni (II), Mn (II).

Os resultados mostram que em condições optimizadas, a capacidade de remoção de crómio usando os novos carvões activados sintetizados a partir dos resíduos mistos, é de 1.09 mmol/g, que é um valor ligeiramente superior a 1.01 mmol/g obtido para o carvão comercial GAC NORIT 1240 Plus (A-10128) oxidado com HNO_3.

A utilização do carvão activado sintetizado a partir dos resíduos mistos na remoção de metais de transição 3d de soluções com multi-componentes apresenta-se como uma técnica muito atractiva. A remoção do metal é realizada numa única etapa, combinando o processo de precipitação do hidróxido do metal (50 a 55%) com a adsorção do catião do metal na superfície do carvão carregada negativamente (15-20%). Embora os precipitados de hidróxido de metal raramente sejam processados para a recuperação do metal, a adsorção e/ou a troca iónica com a superfície do carvão pode permitir a recuperação dos metais.

Neste contexto, a recuperação de resíduos orgânicos e a sua transformação em sólidos porosos, apresenta-se como uma boa alternativa tecnológica no processamento de resíduos.

List of Abbreviation and Notations

Abbreviations

Symbol	Description
3*R*s	"*Reduce, Reuse* and *Recycle*" concept to waste utilization
ACW-Ar2	Activated carbon from ternary co-mingled waste system, based on aromatic tar stock
AFR	Alternative Fuels and Raw materials
AKKhZ sludge	Coal processing waste of the Avdeevka Coke-Chemical Plant of Ukraine
BET	*Brunauer, Emmett* and *Teller* theory for physical adsorption of gas molecules on a solid surface
CCW	Carbon Containing Waste
C_n	Components of co-mingled system
$(CH_3COO)_2Co\times 4H_2O$	Cobalt (II) acetate, tetrahydrate
$(CH_3COO)_2Cu\times H_2O$	Copper (II) acetate, monohydrate
$(CH_3COO)_2Ni\times 4H_2O$	Nickel (II) acetate, tetrahydrate
$[Cr(H_2O)_5OH]^{2+}$	Hydroxopentaaquachromium (III)
$[Cr(H_2O)_6]^{3+}$	Heksaaquachromium (III)
$Cr_2(SO_4)_2(OH)_2$	Chromium sulfate
DA	Dubinin-Astakhov equation
daf	Dry ash free
D-grade coal	Long-flame coal
DR	Dubinin-Radushkevich equation
DSC	Differential Scanning Calorimeter
ICP	Inductively Coupled Plasma
FAT	Fixed Analyzer Transmission
$Fe(NO_3)_3\times 9H_2O$	Iron (III) nitrate nonahydrate
GAC Norit	Granular Activated C arbon produced by NORIT
K/Na eutectics	Binary mixture of sodium and potassium carbonates, having compositions of 29 % Na_2CO_3 and of 71 % K_2CO_3
MID	Multiple Ion Detection
Me	Metal
OMC_n	Pseudo-macro-components of coal organic matter
pH_{PZC}	pH at point of zero charge
SEM	Scanning Electron Microscopy
S_n	Synergetic Efects

SPPW	Spent Petroleum Product's Waste
TGA	Thermogravimetric Analysis
TPD	Temperature Programmed Desorption
TI	Toluene-insoluble
TPD	Temperature-Programmed Desorption
UHV	Ultra High Vacuum
Vis	Visible
VOCs	Volatile Organic Compounds
UV	Ultraviolet
XPS	X-ray Photoelectron Spectroscopy

Variables and Notations

A	Adsorption potential, i.e. change in differential free energy of adsorption, (kJ mol^{-1})
A^d	Ash content (on dry basis), (%)
C_{eql}	Equilibrium aqueous concentration, (mmol·l^{-1})
C_{init}	Initial aqueous concentration, (mmol·l^{-1})
d_p	Pore diameter, (nm)
E	Free energy of the adsorption, (kJ·mol^{-1})
(H_{ar})	Integration interval of hydrogen attached to aromatic carbon, (ppm)
($H_{\alpha\text{-}2}$)	Integration interval of hydrogen of methyl groups attached to aromatic rings, (ppm)
(H_{α})	Integration interval of hydrogen attached to α–carbon atoms, (ppm)
(H_{β})	Integration interval of hydrogen attached to β –carbon atoms, (ppm)
(H_{γ})	Integration interval of hydrogen attached to γ–carbon atoms, (ppm)
$\Delta H_{adsorption}$	Enthalpy of the adsorption, (kJ·mol^{-1})
m	Carbon dosage, (g·l^{-1})
K_L	*Langmuri* constant related to energy of adsorption, (l·$mmol^{-1}$)
K_F	*Freundlich* constant, a unit-capacity parameter (amount adsorbed at C_{eql} equal to unity, i.e. (mmol·g^{-1})(l·$mmol^{-1}$)$^{1/n}$
[Me_{eql}l	Equilibrium metal concentrations in the solution, (mmol·l^{-1})
[Me_{init}l	Equilibrium metal concentrations in the solution, (mmol·l^{-1})
Me_{Rem}	Metal removal, (%)
Me_{uptake}	Maximum adsorption capacity towards metal, (mmol·g^{-1})

n_m	Monolayer capacity, (mmol·g^{-1})
n/n_0,	Fractional filling of the micropore volume
$1/n$	*Freundlich* constant, a dimensionless parameter related to the site-energy
P	Constant related to free energy of the adsorption
p/p^0	Relative pressure
Rem	Sorption efficiency, (%)
S_{BET}	BET Surface area, (m^2·g^{-1})
T	Temperature, (^{0}C)
q_{eql}	Adsorption capacity, amount of adsorbate adsorbed per unit mass of adsorbent, (mmol·g^{-1})
q_{max}	Maximum adsorption capacity, (mmol·g^{-1})
V	Pore volume, (cm^3·g^{-1})
V^{daf}	Volatiles content (on dry, ash free basis), (%)
ΣV_p	Cumulative pore volume, (cm^3·g^{-1})
$\triangle V_p/\triangle d_p$	Pore size distribution, (cm^3/g nm^{-1})
W^a	Wetness (on ash free basis), (%)
WL	Weight loss, (%)
δWL	Change in a weight loss, (%)

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