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Bachelor of Science in Chemical and Biochemical Engineering

## **Modified Cation Exchange Membrane for Phosphate Recovery - a Comparative Study**

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of the requirements for the degree of

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Thank you all.

*"Love the problems, not the solutions. We want to see diverse  
views in problem solving"*

*- Peter Sarlin*

*"The most consistent part of science are the inconsistencies"*

*- Duco Bosma 2018*



## ABSTRACT

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This work aims to develop a new, sustainable technology for phosphate recovery from wastewater, and therefore contribute to solve the problem of water eutrophication and of phosphate rock depletion.

Commercial cation exchange membranes (CEM) were modified with an anionic layer, which contains positively charged guanidinium groups, in order to be used in an electro-dialysis setup for the adsorption and the desorption of phosphate. The performance of this system was compared to the adsorption capacity of modified  $\text{Fe}_3\text{O}_4$  nanoparticles.

Polyhexamethylene guanidine (PHMG), which was used in the coating of the membranes and nanoparticles (NP), was proved to be able to adsorb phosphate in a polystyrene sulfonate (PSS)/PHMG coacervate system.

The commercial CEM were coated using four different strategies: the entanglement of PHMG on the membrane surface by acrylamide, deposition of PHMG after a surface activation with  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$ , a chemically bound coating and a coating with modified  $\text{Fe}_3\text{O}_4$  NP. The last approach produced a membrane capable of adsorbing and desorbing phosphate. After five adsorption-desorption cycles, its adsorption capacity was estimated to be  $0.23 \text{ mg.P/cm}^2$ . For comparison, the modified NP could adsorb less than  $1.3 \text{ mg.P/g}$ . This is a very promising result as the membrane can still be improved, especially when it comes to the NP loading in the coating, which can further increase its adsorption capacity.

Therefore, this project may have resulted in the first step toward solving a major sustainability problem, as it showed a system capable of easily recovering phosphate.

**Keywords:** Phosphate recovery, ion exchange, electrodialysis, Iron oxide nanoparticles, membrane coating.

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## RESUMO

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Neste trabalho desenvolveu-se uma nova metodologia sustentável para a recuperação de fosfatos a partir de águas residuais, como forma para a resolução do problema da eutroficação da água e do esgotamento de reservas de fosforite.

O método aqui desenvolvido para a recuperação de fosfatos, combinou as técnicas de eletrodiálise (ED) e de adsorção. Para tal, membranas comerciais de troca catiónica (CEM) foram revestidas com uma camada aniónica, que contém grupos de guanidina carregados positivamente, permitindo assim a sua utilização em *setups* de eletrodiálise para a adsorção e a dessorção de fosfato. O desempenho deste sistema foi comparado com a capacidade de adsorção de nanopartículas de  $\text{Fe}_3\text{O}_4$  modificadas.

Utilizando um coacervado de poliestireno sulfonato (PSS) / PHMG, provou-se a capacidade de adsorção de fosfato do polihexametileno guanidina (PHMG), polímero utilizado no revestimento das membranas e das nanopartículas (NP).

Para o revestimento das CEM utilizaram-se as seguintes abordagens: entrelaçamento de PHMG na superfície da membrana por acrilamida, a deposição de PHMG após uma ativação da superfície com  $\text{H}_2\text{O}_2$  e  $\text{H}_2\text{SO}_4$ , um revestimento com ligação química à membrana e um revestimento de NP de  $\text{Fe}_3\text{O}_4$  modificadas. A última abordagem originou uma membrana capaz de adsorver e dessorver fosfato. Após cinco ciclos de adsorção-dessorção, a sua capacidade de adsorção foi estimada em  $0.23 \text{ mg.P/cm}^2$ . Para efeitos de comparação, as NP modificadas têm a capacidade de adsorver menos de  $1.3 \text{ mg.P/g}$ . Este sistema é bastante promissor, dado que a capacidade de adsorção da membrana pode, ainda, ser melhorada aumentando a quantidade de NP no revestimento.

O projeto desenvolvido mostrou um sistema capaz de recuperar fosfato facilmente. Logo, poderá ser o primeiro passo para a resolução de um grande problema de sustentabilidade da atualidade.

**Palavras-chave:** Recuperação de fosfato, permuta iónica, electrodiálise, nanopartículas de óxido de ferro, revestimento de membranas.

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## ACRONYMS

|            |                                                                          |
|------------|--------------------------------------------------------------------------|
| AEM        | anion exchange membrane.                                                 |
| BEC        | backscattered electron composition.                                      |
| CBC@CEM    | CEM with chemically bound coating.                                       |
| CEM        | cation exchange membrane.                                                |
| CPR        | chemical phosphorous removal.                                            |
| DLS        | dynamic light scattering.                                                |
| EBPR       | enhanced biological phosphorous removal.                                 |
| ED         | electrodialysis.                                                         |
| EDS        | energy-dispersive X-ray spectroscopy.                                    |
| ER         | electrical resistance.                                                   |
| FTIR       | Fourier transform infrared spectroscopy.                                 |
| IC         | ion chromatography.                                                      |
| IEM        | ion-exchange membrane.                                                   |
| MNP-WP@CEM | CEM coated with PEI, PSS and modified Fe <sub>3</sub> O <sub>4</sub> NP. |
| MNP@CEM    | CEM coated with modified Fe <sub>3</sub> O <sub>4</sub> NP.              |
| NP         | nanoparticles.                                                           |
| P          | phosphorus.                                                              |
| PAH-Gu     | polyallylamine hydrochloride functionalized with guanidinium groups.     |
| PAM        | polyacrylamide.                                                          |
| PEI        | polyethyleneimine.                                                       |

## ACRONYMS

---

|          |                                                |
|----------|------------------------------------------------|
| PHMG     | polyhexamethylene guanidine.                   |
| PHMG@CEM | PHMG Entangled on CEM surface with Acrylamide. |
| PR       | phosphate rock.                                |
| PSS      | polystyrene sulfonate.                         |
| PZC      | point of zero charge.                          |
| SEM      | scanning electron microscopy.                  |
| TGA      | thermogravimetric analysis.                    |

## INTRODUCTION

## 1.1 The Phosphate Sustainability Challenge: Depleting Resources and Increasing Demand

Phosphorus (P) plays a pivotal and irreplaceable role in all biological systems, as a vital nutrient. In modern society, this element is widely used in various industries for a plethora of products, ranging from computer chips and car batteries to pesticides and fertilizers. P is never found as a free element but bound in different minerals, most commonly phosphates. These geological reserves are known as phosphate rock (PR) and they are the main source of phosphates, as more than 80% of all phosphate is obtained from these [1, 2].

Approximately 180-190 million tons of PR are mined globally each year (data from 2012). Although many industries are dependent on it, the high consumption of phosphate is mainly driven by the production of fertilizers, which account for about 90% of its usage [2, 3]. Phosphates are taken up by plant roots, usually in the form of dihydrogenphosphate,  $\text{H}_2\text{PO}_4^-$ , derived from phosphoric acid,  $\text{H}_3\text{PO}_4$ . Some are also taken up in the form of hydrogen phosphate ( $\text{HPO}_4^{2-}$ ) [4]. P, along with potassium and nitrogen, is one of the primary macronutrients that inorganic fertilizers are based on. Thus, in the last four decades the demand for phosphate has nearly doubled and its production has increased in response to the growing world population and higher food demand [5, 6].

This increase in demand has two main consequences. Firstly, PR is getting depleted. The largest PR deposits in the world are found in northern Africa (mainly Morocco), China, the Middle East and the United States [2]. The depletion of the natural phosphate deposits are estimated to happen in less than 100 years [7], or within 100-400 years according to other sources [1, 2]. Despite the big variations in the estimates, there is no doubt that PR is a finite resource that is rapidly depleting [2]. This is especially alarming

for countries with no PR deposits, as the future price and availability of phosphate is highly insecure. As a consequence, the European Union has placed phosphate rock in the top 20 on the list of critical raw materials [8].

This problem will only increase in the future and it is therefore of key importance that the usage of phosphates is optimized, which is currently not the case. The amount of PR being mined far exceeds the actual need, illustrating a huge inefficiency in the global P balance [9]. Great amounts of the excess phosphate ends up in water bodies, which leads to the second great issue. Either as agricultural runoff or from wastewater, and due to the nutritious property of P, this has led to an increase of eutrophication processes – the rapid growth of aquatic algae and plankton in lakes and rivers [10, 11]. Eutrophication is an immediate environmental concern, as it leads to oxygen shortage in the water and ultimately threatens the aquatic biodiversity [12]. Additionally the leakage of P to waterbodies poses an increased risk to human health and phosphate is one of the most critical contaminants in wastewater [9, 12]. In 2009, the European union reduced the amount of allowed phosphate in disposed wastewater to 0.07 mg/L for rivers and to 100 mg/L for lakes [13].

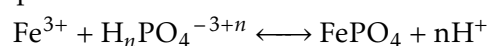
Closing the phosphorus balance is, therefore, a two-sided challenge of great importance and consequently a lot of research is focused on finding solutions to the problem. Withers *et al.* [9] found that in order to meet the challenge, it is needed to 1) set acceptable P sustainability targets, 2) consume less P and with greater efficiency and 3) minimize P losses and increase recycling.

The focus of this thesis lies in the latter category. Since generally the use of P is linear (as it has very few recycling routes [14]), a sustainable way of removing it from wastewater, and recovering it for future use is needed. The technology researched and evaluated in this project is described in section 1.3.

## 1.2 Current Methods for Phosphate Removal from Wastewater

Currently there are two main conventional methods for phosphate removal from wastewater - enhanced biological phosphorous removal (EBPR) and chemical phosphorous removal (CPR).

CPR, which is less costly and more widely used, employs aluminum (Al) or iron (Fe) salts, the latter being the preferred ones because of their low costs [15, 16]. The added salt precipitates the phosphate in the wastewater resulting in solid residuals. These residuals can be removed by settling under the force of gravity or by filtration. Although these precipitates are rich in phosphate, with the currently existing methods its recovery after it is chemically bonded to a salt is economically unfeasible [17]. The basic reaction behind the process is as follows:



Currently, iron phosphate ( $\text{FePO}_4$ ) produced through the CPR cannot be used to replace mined phosphate. Furthermore, iron phosphate has relatively low bio-availability under

normal pH conditions for plants [2, 18]. The sludge created by this process contains large amounts of heavy metals, and needs to be treated and disposed. Disposal is usually done by landfill discarding, but as this has been prohibited in most of first world countries, the sludge usually ends up in incinerators or in the sediments of canals and rivers. Finally, the disposed P-containing compound winds up in the natural water bodies, causing eutrophication [2].

EBPR, where microorganisms are used due to their ability to intracellularly store large amounts of phosphate in the form of polyphosphate, is commonly used as a preliminary water treatment. Among its advantages, are the high removal efficiency and low operation cost. However, it has three big disadvantages: as it is common for a biological process, a concentrated sludge is formed; the process' efficiency is strongly dependent on the process parameters (e.g. flow rate and composition changes due to heavy rainfalls); and there are long periods of time with no P uptake as the process relies on alternating between aerobic and anaerobic conditions (in which the microbes do not process P) [18, 19]. Although less sludge is produced than in the chemical process, its disposal still has a big environmental footprint, as it also contains heavy-metals [20].

Although both processes work for removal, neither of these methods allows an easy recovery of phosphate. Currently, most techniques that aim at recovering phosphate do it by dewatering reject streams. These techniques recover phosphate from the wastewater by feeding the phosphate rich wastewater into a precipitation/crystallization tank. The crystallization process can recover phosphate from the liquid phase either as calcium phosphates, which are similar to phosphate rocks, or as struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ), which is a slow release fertilizer. However, these methods do not prevent scaling problems in the sludge line before the precipitation/crystallization tank.

Also, some alternative methods have been developed such as ion exchange, reverse osmosis, nanofiltration, adsorption and **electrodialysis (ED)**. Reverse osmosis and nanofiltration are currently processes that are associated with elevated costs. Adsorption is regarded as a good option, because it is effective even at low concentrations of P, requires a simple design, can be less costly (depending on the sorbent) and flexible in operation. However, it exhibits low selectivity against competing ions and requires pre-treatment and sorbent regeneration [21]. ED is a technique that combines electrochemistry and membrane technology to separate macromolecules and non-ionic compounds from ions, creating two solutions: one concentrate of ions and another, that is nearly pure water. The first solution can be reintroduced to the industrial process and the water can be reused [18]. On the other hand, high capital cost is associated with this process and it does not always meet the requirements for phosphate selectivity [21].

It has been proved by Platrinieri *et al.* [22] that modified commercially available  $\text{Fe}_3\text{O}_4$  **nanoparticles (NP)** are a great system for phosphate recovery. It has also been proved that they work in a broad range of pH and can be reused. This system was not yet put into practice but it is very promising as its only disadvantage is that the desorption is not as straight forward as the one this project aims to achieve.

### 1.3 Aim of the Work

This project has two main objectives. One is to utilize the **ED** setup, which is present in most wastewater treatment plants, and a commercial **cation exchange membrane (CEM)** with anionic coating in order to easily adsorb and recover phosphate. The second is to compare the performance of these membranes with  $\text{Fe}_3\text{O}_4$  nanoparticles that were coated with the same polymer. The reason behind each of these objectives will be explained in this section.

The idea behind the coated **CEM** is to combine **ED** and adsorption of phosphate. A **CEM** is negatively charged, as is phosphate at the pH of operation, so it will not pass through. The coating is made of a positively charged, phosphate selective polymer (described in section 2.2), to which it will adsorb. This membrane will be in an **ED** setup which will apply a current in one direction in order to promote the adsorption of phosphate, and then in the opposite direction to promote desorption (figure 1.1). This system is an entirely new methodology which has not been tested before, and it is speculated that it will allow an easy recovery of phosphate that does not utilize any chemical products, which is its big advantage in comparison to the existing methods.

However, it has one possible disadvantage: it may not be as efficient, especially when compared to **NP**, since they offer a large surface area. Because both systems have pros and cons, it was found necessary to do a comparative study between the two systems, which is the second objective of this project.

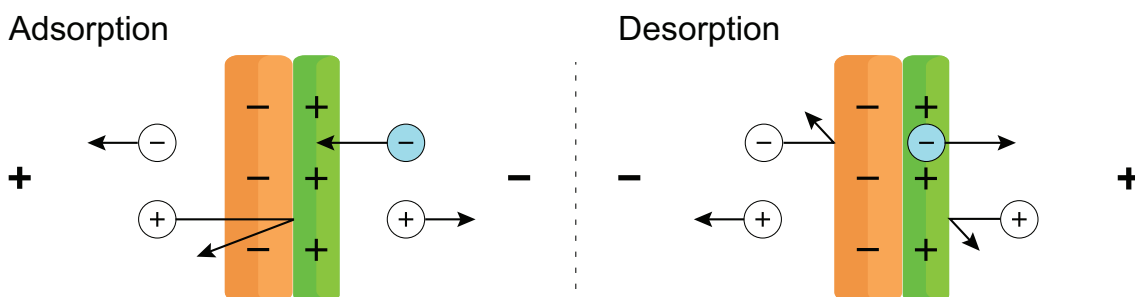


Figure 1.1: Schematic illustration of adsorption and desorption in the ED setup. The CEM membrane is shown in orange, the anionic coating in green and the phosphate ions in blue.



## THEORETICAL BACKGROUND

### 2.1 Phosphate

One of the challenges that is faced when trying to recover phosphate is that it has different forms depending on the pH. Figure 2.1 illustrates phosphate's speciation i.e. what ions are present in solution at different pH. Details about how the % of each species according to pH can be obtained can be found in Appendix A.1.

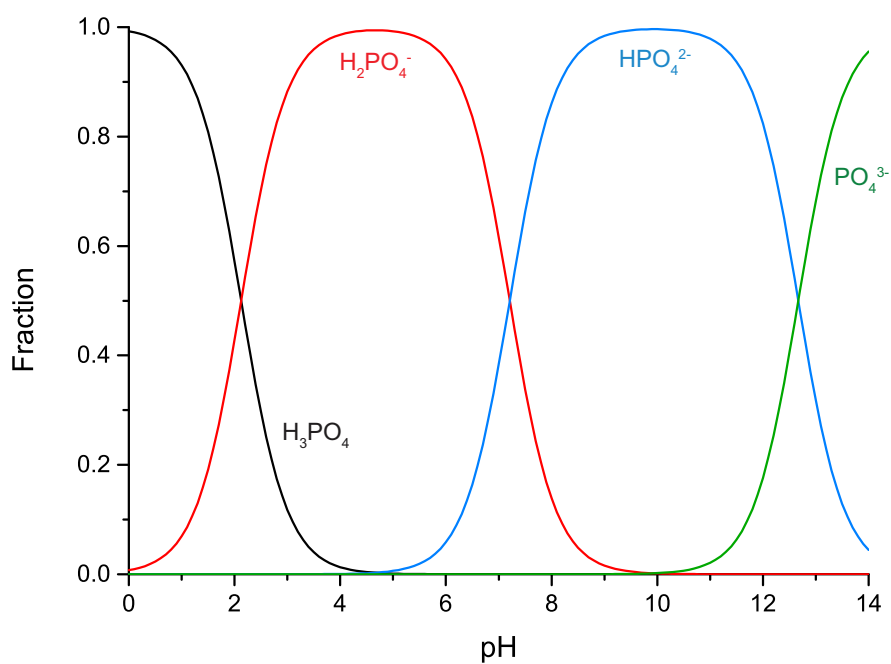


Figure 2.1: Phosphate Speciation

The wastewater this project aims to treat is provided by Friesland Campina (a dairy industrial company) and has a pH of approximately 5. At this pH value, phosphate is mostly (99,3%) present in the form of dihydrogen phosphate ( $\text{H}_2\text{PO}_4^-$ ). Thus, the phosphate solutions prepared in this work to replicate wastewater were prepared with  $\text{NaH}_2\text{PO}_4$  salt.

## 2.2 Polyhexamethylene Guanidine

As it is shown in literature, guanidinium groups have a strong affinity toward phosphate [23–25]. Figure 2.2 illustrates the electrostatic and hydrogen bond interactions responsible for this. Keeping this in mind, a commercial polymer with a guanidinium group was chosen for this work. This polymer is **polyhexamethylene guanidine (PHMG)**. Its structure is shown in Figure 2.3.

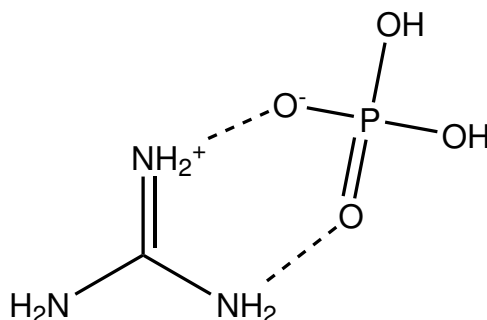


Figure 2.2: Complex formation between guanidinium groups phosphate.

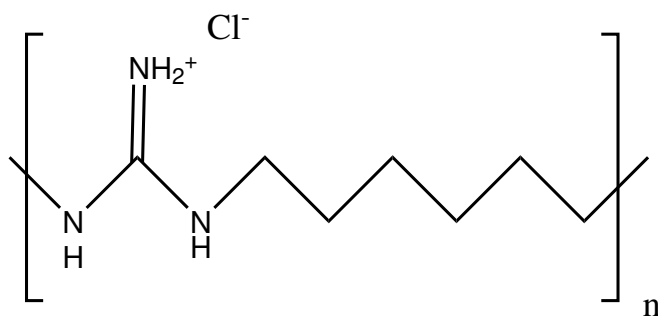


Figure 2.3: PHMG Structure.

## 2.3 Coacervates

Coacervation is described as the liquid-liquid phase separation that occurs when solutions of two oppositely charged polyelectrolytes are mixed, resulting in the formation of a dense macroion-rich phase, the precursors of which are soluble complexes [26–28].

Due to the ease in separation, an experiment was designed in this work, in which coacervates were used to determine whether or not PHMG had the potential of adsorbing phosphate. This was achieved by creating a coacervate between polystyrene sulfonate (PSS) and PHMG, richer in the latter, in order to ensure that there are guanidinium groups available to adsorb phosphate.

Another alternative to determine the PHMG's capacity of phosphate adsorption was to simply put the polymer in solution with phosphate and analyze the concentration of phosphate in solution using a colorimetric method. This was not opted for, because in practice it is troublesome to accomplish, due to the fact that the solutions created have a stable colour for only a short period of time [29].

## 2.4 Coated $\text{Fe}_3\text{O}_4$ Nanoparticles

Nanoparticles are typically particles with a diameter within 1 and 100 nm. NP are of great scientific interest because of their immense surface area. Also, the ratio between the surface area and volume is significant in a manner which can affect their properties in comparison to the bulk material from which they originate [30].

When it comes to adsorption, the large surface area is a great advantage. It allows a very efficient process, since large amounts of adsorbate can be adsorbed in a reduced volume.

Beside the surface area, iron oxide nanoparticles ( $\text{Fe}_3\text{O}_4$  NP), also known as magnetite, have three other important properties. They are ferrimagnetic, i.e. they are attracted to a magnet and can be magnetized to become a permanent magnet themselves. This property allows an easy separation by using external magnetic fields, and has been extensively employed in water treatment [31]. Additionally, they are chemically inert and biocompatible [32]. These are the properties which allow the surface modifications which were previously studied in this investigation group [22] and the one performed in this project.

The point of zero charge (PZC) of  $\text{Fe}_3\text{O}_4$  is reported to vary between 6.5 and 7.4 [33, 34], but is usually  $\approx 7$  [35]. When the pH is below the PZC (as is the case in the wastewater treated in this project), the surface of the iron oxide nanoparticles is positively charged. This promotes the adsorption of phosphate ions, which are negatively charged. Clearly, at  $\text{pH} > \text{PZC}$ , the  $\text{Fe}_3\text{O}_4$  NP become less effective.

Surface modification is easily performed and it's often employed in order to increase the NP sorbent capabilities. The reason behind these modifications is not only to improve the adsorption capacity of the NP at extended pH ranges, but also to avoid aggregation which occurs around the PZC [22].

## 2.5 Ion Exchange Membranes and Electrodialysis

The use of membranes to separate substances has become essential in chemical industry. Of the various separation membranes, the ion-exchange membrane (IEM) is one of

the most advanced and is widely used in various industrial fields: electrodialysis, diffusion dialysis, separator and solid polymer electrolyte in electrolysis, separator and solid polymer electrolyte of various batteries, sensing materials, medical use, a part of analytical chemistry, and more [36]. The IEM is a semi-permeable membrane which allows the transport of certain ions present in solution, and blocks other ions or neutral molecules. It is generally composed of a polymeric base with fixed charged groups. Depending on the sign of these charged groups, the membrane can be a CEM or a anion exchange membrane (AEM). CEMs contain negatively charged groups and AEMs contain positively charged groups.

ED is used to transport ions from one solution through IEM to another solution under the influence of an electric potential difference. It is generally used to create two solutions: one concentrate of ions and another, that is nearly pure water.

### 2.5.1 Fundamentals and Governing Equations

The theory and mathematics behind this process are vast and complex, but this section will only focus on what is directly correlated with this project.

For the full understanding of this section, three concepts should be clarified. Firstly, counter-ions are the ions which pass through the membrane, and they are cations in the case of the CEM. Secondly, co-ions are the ions which are rejected by the membrane, which are anions in this case. Lastly, the fixed ions are the charged groups which are part of the membrane.

Initially, Donnan [37] showed the model displayed in figure 2.4. This figure displays a porous membrane which is impermeable to the anion  $R^-$  and how the ions adjust in order to achieve equilibrium and maintain electroneutrality. Figure 2.4a shows the initial stage, where charge is unbalanced. NaCl will diffuse from (1) to (2) in order to reach the equilibrium. Figure 2.4b shows the final stage, where an equilibrium is present, however there is still osmotic pressure and an electric potential, since there are more ions in (1) [38]. In other words, the ions have adjusted in order to make their electrochemical potentials the same in both sides, which establishes an osmotic pressure and electric potential differences between the two sides. This type of equilibrium is called a Donnan Equilibrium [39].

However, this theory has been extended to various different situations. Consider the situation of an IEM in contact with an anionic solution (Figure 2.5). This is a two-phase ionic system, in which one charged component is chemically or physically restricted to one phase, but ions of any other species can freely move between the two phases. The presence of fixed charges results in a higher concentration of ions in the membrane, and the exclusion of co-ions by electrostatic repulsion. Therefore, as it can be observed in 2.5, the concentration of counter-ions in the membrane will be much higher than the concentration of co-ions. This phenomenon is called the Donnan exclusion [40].

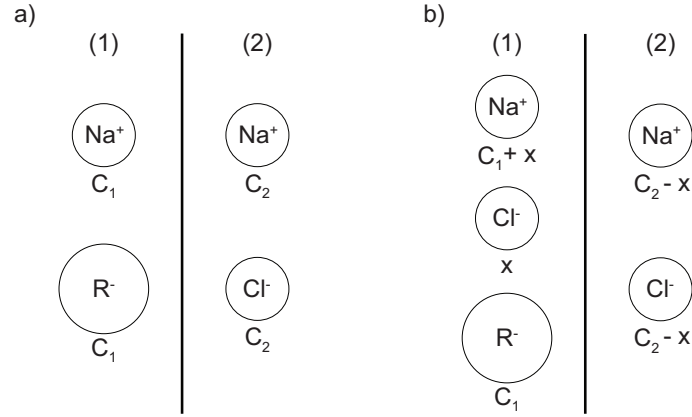


Figure 2.4: Donnan Equilibria. Two sides of a porous membrane, (1) and (2), and respective ions and their concentrations are displayed. a) shows the initial conditions, and b) shows stage of equilibrium.

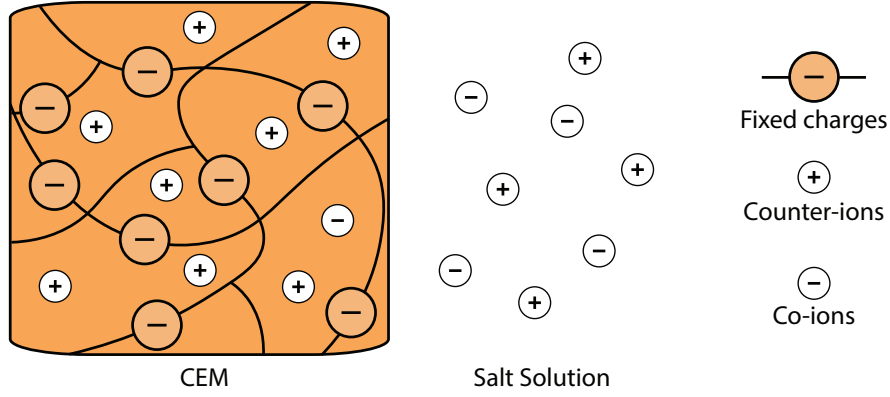


Figure 2.5: The exclusion of co-ions from the solution (right) by the CEM (left).

As it was mentioned above, the ions distribute between the membrane and the solution in order to balance their electrochemical potential,  $\eta_i$ . This can be calculated following equation 2.1, where  $\mu_i$  is the chemical potential,  $z_i$  is the electrochemical valence,  $F$  is the Faraday constant and  $\phi$  is the electrical potential.

$$\eta_i = \mu_i + z_i F \phi \quad (2.1)$$

If the pressure difference between solution and membrane is neglected, the chemical potential is given by equation 2.2, where  $\mu_i^0$  is the chemical potential in the reference state and  $a_i$  the activity of component  $i$ .

$$\mu_i = \mu_i^0 + RT \ln(a_i) \quad (2.2)$$

When the equilibrium state is reached, the electrochemical potential in the solution is equal to the electrochemical potential in the membrane. Solution is marked with "s" and the membrane is indicated with "m".

$$\mu_i^{0,s} + RT \ln(a_i^s) + z_i F \phi^s = \mu_i^{0,m} + RT \ln(a_i^m) + z_i F \phi^m \quad (2.3)$$

If the reference state for the chemical potential in the solution and in the membrane is equal, the Donnan potential ( $\phi_{\text{Don}}$ ) can be derived from equation 2.3.  $\phi_{\text{Don}}$  is the difference between the electrical potentials of the membrane and the solution.

$$\phi_{\text{Don}} = \phi^m - \phi^s = \frac{ER}{z_i F} \ln \frac{a_i^s}{a_i^m} \quad (2.4)$$

Equation 2.4 allows the calculation of concentration in each side, for instance, when a dilute solution is assumed and component activities can be replaced by concentrations. Detailed explanation of this process can be found in [41].

In order to calculate the charge that was being transported by the current applied, the flow of electric charge equation was employed (Equation 2.5), where  $Q$  is the charge in coulombs (C),  $I$  is the current in amperes (A) and  $t$  is the time in seconds (s).

$$I = \frac{Q}{t} \quad (2.5)$$

Afterwards, by using Faraday's law of electrolysis, (Equation 2.6), the concentration of phosphate could be calculated. In Equation 2.6,  $n$  is the molar quantity of an ion,  $z$  is the valence of the ion and  $F$  is Faraday's constant in  $\text{C.mol}^{-1}$ .

$$n = \frac{Q}{z \times F} \quad (2.6)$$

### 2.5.2 Performance and Parameters Evaluation

One of the most important parameters to evaluate in a membrane is its **electrical resistance (ER)**, because it directly relates to the energy consumption in an **ED** process. As it is stated by Ohm's law (Equation 2.7), the higher the **ER** of a membrane, the higher the potential that needs to be applied to maintain a current [42].

$$I = \frac{V}{R} \quad (2.7)$$

The practical resistance of a membrane is obtained by multiplying the **ER** by the surface area ( $S$ ), and is expressed in  $\Omega.\text{cm}^2$ . This is the parameter that is analyzed in this work.

Another important parameter is the limiting current density ( $i_{\text{lim}}$ ). It is generally determined by measuring the current-voltage relation ( $i$  vs.  $V$  curve) of the electrodialyzer. A representation of a typical  $i$  vs.  $V$  curve can be found in Figure 2.6. It can be observed that in the lower voltage region, as shown in red, it has a linear behaviour. This is called the ohmic region, because it follows ohm's law. After this point, when  $i_{\text{lim}}$  is reached, a phenomenon known as concentration polarization occurs. This is characterized by an abrupt increase in resistance [36]. This phenomenon occurs because when an electric

current is passed through an IEM, salt concentration on the desalting surface of the membrane is decreased, and reduced to zero at the  $i_{lim}$ . In this circumstance, there are no more salt ions available to carry the electric current. Thus, the voltage drop across the boundary layer increases drastically resulting in a higher energy consumption [43]. The last part of the current voltage curve is called the overlimiting region and it's the region where water-splitting occurs [44].

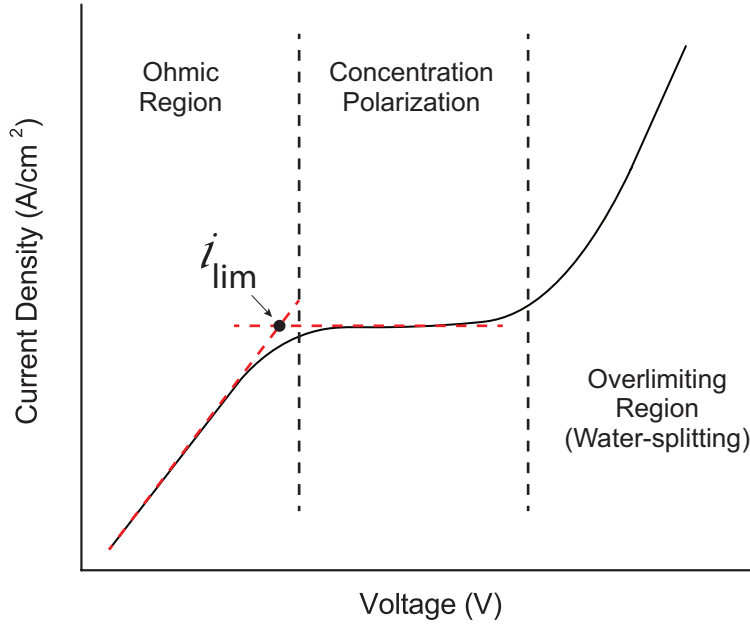


Figure 2.6: Typical  $i$  vs  $V$  curve of IEM

It is desirable to operate at about 80% of the maximum point of the ohmic region, because water splitting leads to the formation of  $\text{OH}^-$  and  $\text{H}^+$  ions, which drastically affect the pH, and because of their size, can easily pass through the membrane and negatively affect the selectivity of the process [36].

It is described by Strathmann *et al.* [45], how different parameters of a bipolar membrane affect the limiting current density, as these are used to create water-splitting. In their investigation, two bipolar membranes are compared and it is concluded that the thinner one has a higher limiting current density. This is because the thinner the membrane is, the higher the diffusion coefficient, and thus, the limiting current will also be higher.

As it was mentioned in section 1.3 the negatively charged commercial CEM is modified with a positively charged polymer. Therefore, water-splitting might also occur in the membranes discussed in this project. Only in this case, the anionic and the cationic layers do not have the same thickness. The anionic layer is just a few to a few hundred nanometers thick, while the CEM is around 130-160  $\mu\text{m}$ . Therefore, since the anionic layer is very thin, the limiting current densities are speculated to be quite high.

Another parameter that must not be ignored in order to ensure the possibility of application of a membrane, is its mechanical strength. If a membrane is too brittle for

instance, it becomes unfeasible to apply it in an actual scale plant. This may lead to the formation of cracks on the membrane and thus, the creation of preferential pathways for the solution to go through, and loss of selectivity.

Other important parameters are the transport number, the solute permeability coefficient, the electroosmotic coefficient, the water permeation coefficient and the swelling ratio, but these will not be studied in this work [42].

## 2.6 Ion Chromatography

**Ion chromatography (IC)** is used in this work as an analytical technique, although it is vastly used for as a separation technique. It can be applied on almost any kind of charged molecule. Since the aim was to determine concentrations of negatively charged ions, an anion-exchange chromatography was employed.

The principle behind this technique is tied with the attraction between oppositely charged ions. The ion-exchanger is typically composed by a porous matrix where a charged ligand or polymer is immobilized [46]. The ions are carried by an eluent through this matrix, allowing them to be separated depending on how strongly they are attracted to the matrix, which is characteristic to each ion. Therefore, it is said that each ion has a different retention time [47]. Then, a detector measures the electrolytic conductivity of the eluate and thus, determines the concentration of the ion [48].



## MATERIALS AND METHODS

This chapter will review the experiments performed in this work.

### 3.1 Materials and Chemicals

PHMG ( $\geq 99.0\%$  purity) was supplied by Sinotech (China) and used without any further purification. All membranes used in this project were cut from a 50cm x 2m roll of type 2 CEM produced by Fujifilm Manufactory Europe. Sodium phosphate solutions were prepared with sodium phosphate monobasic monohydrate ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ),  $\geq 99.5\%$ , purchased from Sigma-Aldrich. Milli-Q water was purified using a Milli-Q IQ-7000 equipment. IC required the use of sodium bicarbonate ( $\text{NaHCO}_3$ ,  $\geq 99.5\%$ , Sigma-Aldrich), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ,  $\geq 99.0\%$ , Sigma-Aldrich), a phosphoric acid solution ( $\text{H}_3\text{PO}_4$ , 85 wt%, Sigma-Aldrich), chloride standard for IC ( $1000 \pm 4$  mg/L, Sigma-Aldrich), and phosphate phosphorus standard for IC ( $1000 \pm 4$  mg/L, Sigma-Aldrich). Iron oxide nanoparticles were also purchased from Sigma-Aldrich in the form of Iron(II,III) oxide nanopowder with a 50-100 nm diameter, as determined by SEM. Sodium chloride ( $\text{NaCl}$ ,  $\geq 99.0\%$ , Sigma-Aldrich), hydrochloric acid solution ( $\text{HCl}$ , 1M, Merck Millipore), sodium hydroxide solution ( $\text{NaOH}$ , 1M, Merck Millipore), sulphuric acid ( $\text{H}_2\text{SO}_4$  95-97%, Merck Millipore), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 35 %w/w aqueous solution, AlfaAesar), poly(sodium 4-styrenesulfonate) (PSS, M.W.  $\approx 70\,000$ , Sigma-Aldrich) and branched polyethyleneimine (PEI, M.W.  $\approx 25000$ , Sigma-Aldrich), N,N-Methylenebis(acrylamide) ( $(\text{H}_2\text{C}=\text{CHCONH})_2\text{CH}_2$ ,  $\geq 99\%$ , Sigma-Aldrich), 2-hydroxy-2-methyl-1-phenyl-1-propane (Darocure1173, Ciba Specialty Chemicals) were also utilized.

### 3.2 Coacervates Preparation, Characterization, and Batch Adsorption Experiment

To study the optimal ratio between PSS and PHMG, five 50mL solutions were created. Table 3.1 shows the molar quantities and the ratio between the two polyelectrolytes.

Table 3.1: PHMG/PSS solutions.

| Solution Number | n(PHMG), (mol)        | n(PSS), (mol)         | Ratio (PHMG/PSS) |
|-----------------|-----------------------|-----------------------|------------------|
| 1               | $2.83 \times 10^{-4}$ | $2.83 \times 10^{-4}$ | 1/1              |
| 2               | $2.83 \times 10^{-4}$ | $1.41 \times 10^{-4}$ | 2/1              |
| 3               | $2.83 \times 10^{-4}$ | $2.85 \times 10^{-5}$ | 10/1             |
| 4               | $2.83 \times 10^{-4}$ | $1.34 \times 10^{-5}$ | 21/1             |
| 5               | $2.83 \times 10^{-4}$ | $5.65 \times 10^{-4}$ | 1/2              |

It is important to note that the PSS solution was added dropwise (over the period of two minutes) to the PHMG solution, and not the other way around. This was to ensure that PHMG's positively charged groups were on the outside of the coacervates particles.

Each of these solutions was analyzed using dynamic light scattering (DLS) Malvern Zeta-sizer equipment, in order to obtain the size and  $\zeta$ -potential of the formed particles.

After the solution with the optimal ratio had been chosen, it was centrifuged at 5000 rpm for 5 minutes in a Hermle Z 326 K centrifuge. The supernatant was then removed, and the coacervate solid phase was re-dispersed in 50mL of ultra-pure Milli-Q water. This procedure was repeated 3 times, in order to remove the counter-ions that might be present in solution so that they don't interfere with the phosphate adsorption. In the last cycle, instead of re-dispersing the solid phase in Milli-Q water, it was re-dispersed in a 2,8 mM solution of  $\text{NaH}_2\text{PO}_4$  for the batch adsorption experiment, and was left stirring for 24 hours. The concentration of the phosphate solution was chosen so that the ratio PHMG/PSS/phosphate was maintained 2:1:1.

Four more solutions with the same ratio but with different concentrations were also prepared, and the same procedure was followed. These solutions had a concentration of PSS and phosphate varying between 1.5 and 50mM, and double that amount of PHMG.

### 3.3 $\text{Fe}_3\text{O}_4$ Nanoparticles Coating, Characterization and Batch Adsorption Experiment

The  $\text{Fe}_3\text{O}_4$  NPs were coated with PHMG following the subsequent procedure. Firstly, an aqueous solution of PHMG (2.5 g/L) was prepared using a sonicating bath for 20 minutes to ideally mix the solution. Similarly, a  $\text{Fe}_3\text{O}_4$  NP suspension (0.5 g/L) was prepared in MilliQ water and sonicated under the same conditions. Afterwards, the pH of both solutions was adjusted to 9.5 by the addition of (1M) HCl or NaOH, in order to

ensure that the  $\text{Fe}_3\text{O}_4$  NPs have a negative surface charge, while the polyelectrolytes are positively charged.

The  $\text{Fe}_3\text{O}_4$  NP suspension was added drop-wise to the PHMG solution and stirred for 24 hours at room temperature to ensure the complete adsorption to the  $\text{Fe}_3\text{O}_4$  NP surface. Afterwards, the NPs were collected with a magnet and the supernatant solution containing the excess polymer was removed. Then the NPs were re-dispersed in Milli-Q water. This procedure was repeated 3 times.

The resulting coated  $\text{Fe}_3\text{O}_4$  NPs (PHMG@ $\text{Fe}_3\text{O}_4$ ) were analyzed using thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) and  $\zeta$ -potential. For comparison, the same analysis were performed on bare  $\text{Fe}_3\text{O}_4$  NPs.

The NP were dried in a Binder oven at 50 °C for 24 hours. The TGA analysis was performed in a GA2/SF1100 STAR<sup>e</sup> system from Mettler Toledo. Between 7 and 10 mg of dry NP were exposed to a temperature increase from room temperature to 800 °C, with a 5 °per minute step. The analysis was performed in a nitrogen environment, because since iron oxide has both species of iron present, iron (II) and iron (III), it would oxidize in an air environment. However, this allowed it to only be a qualitative analysis, because the organic part will not combust and therefore only degradation will be visible in weight loss, not the complete absence in the polymer. For the FTIR measurement, the NPs were removed from the solution and dried in the same manner as described for TGA. With this powder, a KBr pellet was made using a manual press. This pellet was made with 100 mg of KBr and very little amounts of NP (less than 1 mg). With the press, 10 tons of force were applied for 1 minute.

The  $\zeta$ -potential analysis was performed in a Malvern Zeta-Sizer. The dry NP powder was dispersed in Milli-Q water and sonicated for 10 minutes to ensure that the possible formed aggregates were dispersed.

The aim of the batch adsorption experiment was to vary between four different concentrations of phosphate and maintain the adsorbent (NPs) concentration, in a similar fashion to what is described by Yoon *et al.* [49]. The tested concentrations of phosphate were 2, 5, 10 and 20 mg/L, and the NP were maintained at 0.5 g/L. To ensure that the concentrations were correct, the NPs were dried (as described for TGA analysis) and weighed before preparing the solutions. Once prepared, they were left stirring on a Vortex for 24h. Since this experiment was performed close to limit of detection of the IC equipment, the measurements were executed 3 times, and a standard deviation was calculated. The errors bars shown in figure 4.6 just represent the reproducibility of the experiments, not the replicability (three different samples were taken from the same experiment).

### 3.4 Membrane Modifications

In order to simplify the transition from laboratory scale to application of the project, all the membranes are commercial CEMs. As mentioned in section 3.1, they are type 2 CEM from Fujifilm.

## 3.4.1 PHMG Entangled with Acrylamide

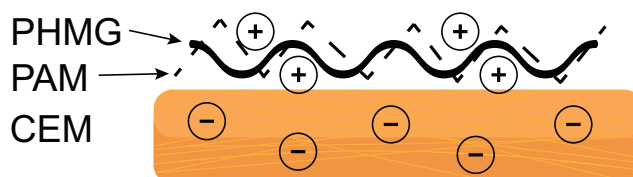


Figure 3.1: Schematic illustration of CEM coated with PHMG entangled by acrylamide.

The coating of **CEM** was prepared using the following materials: **PHMG**, the acrylamide monomer (delivered by Fujifilm), N,N-methylene-bis-(acrylamide) (99%, Sigma) as cross-linker, 2-hydroxy-2-methyl-1-phenyl-1-propane (Darocure1173, Ciba Specialty Chemicals) as the free-radical photo-initiator, TEGO® Glide (Evonik) as an inhibitor. In detail, 0.053 mol of acrylate monomer and 0.017 mol of cross-linker were added to 2 mL of distilled water and 1.7 mL of iso-propanol and mixed until a clear solution was obtained. Next, 1 wt % of TEGO®Glide and 0.05 wt % of Darocure1173 were added to the mixture. Finally, the mixture was divided in three containers each of it having 5, 10 and 20 wt. % of PHMG, for a total of three separate solutions. The mixture was cast on top of a CEM (Fuji) by coating with a 12  $\mu\text{m}$  wire-wound coating bar. The membrane was exposed to UV-irradiation (240 W/cm) through a bench-top conveyor system (Heraeus Noblelight Fusion UV inc. USA), in order to promote the polymerization of the acrylamide monomer (into **polyacrylamide (PAM)**). A mercury H-bulb (240-280 nm) working at 100% intensity was used, and the conveyor speed was 30  $\text{m}\cdot\text{min}^{-1}$  with a double pass. Figure 3.2 displays a schematic illustration of this process. From this point on, this membrane will be referred as **PHMG@CEM**.

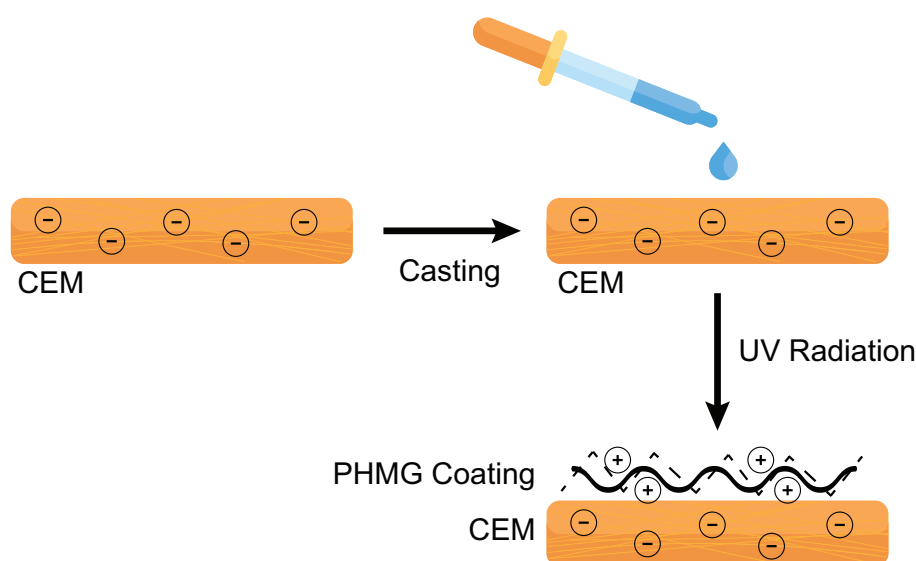


Figure 3.2: Schematic illustration of the membrane preparation process.

### 3.4.2 PHMG Deposition After Surface Activation

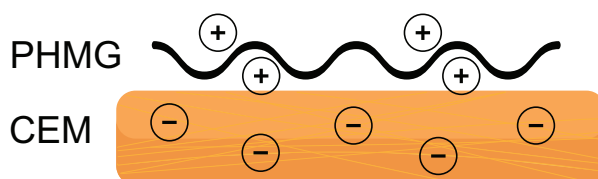


Figure 3.3: Schematic illustration of CEM with deposited PHMG after surface activation.

With the purpose of obtaining a more stable coating, an activation of the membrane's surface before the modification was performed. This was done following a method that has been described in literature by White *et al.* [50]. The method consists in immersing the membrane in hydrogen peroxide 3% w/t ( $\text{H}_2\text{O}_2$ ) for 30 minutes, afterwards in distilled water, as a washing step, for another 30 minutes, in a 1 M solution of sulphuric acid ( $\text{H}_2\text{SO}_4$ ) for one hour, and finally, once again in distilled water for 30 minutes. After the  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$  immersions, the membrane was thoroughly rinsed with distilled water in order to remove any traces of unwanted chemicals.

This oxidation process would increase the amount of negatively charged sulphonated groups at the surface of the CEM, which would interact with the positively charged PHMG, and therefore increase the strength of the electrostatic interactions. The method also has the advantage of being relatively fast and easy to execute.

After the activation, a solution of 35% w/t PHMG was casted on one of the sides of the membrane. This concentration was chosen by keeping in mind the solubility of PHMG in water, and with the aim of maximizing adsorption capacity and the coating stability.

### 3.4.3 Chemically Bound Coating

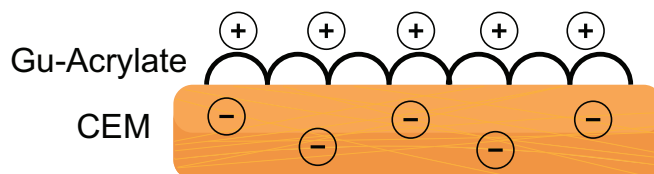


Figure 3.4: Schematic illustration of the CEM with chemically bound coating.

With the aim of further improving the coating stability, a membrane with chemically bound coating was developed. Because PHMG does not have any active groups that could bind to the membrane, a different approach was employed. A guanidinium acrylate monomer was synthesized in our laboratory according to the following procedure [51]. In detail, 0.07 mol of guanidinium acrylate monomer were added to a mixture containing N,N-methylene-bis-(acrylamide) as cross-linker, 2-hydroxy-2-methyl-1-phenyl-1-propane as the free-radical photo-initiator, TEGO® Glide as an inhibitor in the same ratio as described in section 3.4.1 The mixture was cast on top of a CEM (Fuji) by coating with

a 12  $\mu\text{m}$  wire-wound coating bar. The membrane was exposed to UV-irradiation (240 W/cm) through a bench-top conveyor system (Heraeus Noblelight Fusion UV inc. USA). A mercury H-bulb (240-280 nm) working at 100% intensity was used, and the conveyor speed was 30  $\text{m}\cdot\text{min}^{-1}$  with a single pass. The resulting membrane will be referred as **CBC@CEM**.

### 3.4.4 Functionalized $\text{Fe}_3\text{O}_4$ Nanoparticles Coating

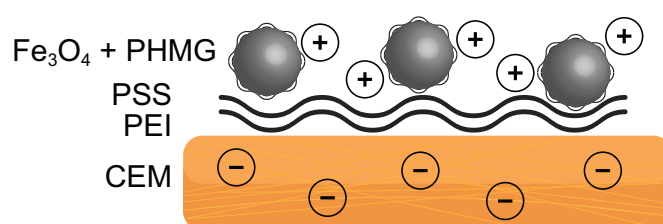


Figure 3.5: Schematic illustration of CEM coated with PHMG functionalized  $\text{Fe}_3\text{O}_4$  NP.

For this coating two approaches were put into practice. In both of them the **CEM** was initially activated by argon plasma treatment, for two minutes, in a Harrick Plasma PDC-002-CE plasma cleaning equipment, at high RF level. This step had the aim of generating free radicals which could potentially react with the **CEM** surface and increase its charge [52]. Afterwards, the membrane was inserted in an ultra-filtration setup, without no pressure reduction, simply to provide a support for the coating process.

In the first approach, 3 mL of a 0.5 g/L solution of **PHMG** coated **NP** were directly cast on the activated membrane and left to deposit for 24h.

In the second approach, firstly 2 mL (enough to cover the membrane) of a branched **polyethyleneimine (PEI)** solution with a concentration of 1 g/L was cast on the membrane. It was kept there for 5 minutes and afterwards it was removed and the membrane was rinsed with distilled water twice. Next, 2 mL of a **PSS** 1 g/L solution with the same concentration was cast for the same period of time and a washing step was performed. Finally, 3 mL of a 0.5 g/L solution of **PHMG** coated **NP** were added and left for 24h.

The idea behind this second approach was that because **PEI** is branched it would increase the surface charge. Also, because primary, secondary and tertiary amines are present in its structure, it would be protonated in a wide pH range. **PSS** had to be added on top to make sure the surface had a negative charge which would interact with the positively charged **PHMG**.

The membrane created by the first approach shall be called **MNP@CEM**, and the one by the second approach (with polyelectrolytes) **MNP-WP@CEM**.

## 3.5 Membrane Characterization

### 3.5.1 Scanning Electron Microscopy and Energy-dispersive X-ray Spectroscopy

In order to determine whether the coating is present or not, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) techniques were utilized.

A tiny piece of the membrane was cut and immobilized on a carbon tape for the SEM analysis. It was then loaded into a JSM-6010 electron microscope (JEOL). Micrographics were taken at different amplifications at a 5kV voltage. The same equipment was utilized for the EDS analysis. For this analysis, first an image of backscattered electron composition (BEC) is taken at a voltage of 20kV. Afterwards, the elemental analysis is performed over 10 scans.

### 3.5.2 Coating Stability Tests

As PHMG is soluble in water, it was necessary to verify if the coating is stable when the membrane is immersed in water. This was done by doing an SEM-EDS analysis before and after a membrane has been in contact with water. It was immersed in ultra-pure Milli-Q water for one hour and then rinsed thoroughly with a wash bottle. Afterwards, before being analyzed with SEM-EDS for the second time, it was dried overnight in a Binder vacuum oven, at 50°C.

### 3.5.3 Adsorption Capacity Estimations

In order to study the adsorption capacity of a membrane, a very simple test was employed. It was immersed in Milli-Q water for 24 hours to allow the release of chloride, the coating's counter-ion. If each counter-ion is bound to one active group on the coating, this will provide a fairly accurate estimation of the membrane's adsorption capacity. The only source of error may be the unreleased chlorine, but again, this test just aims to obtain a rough estimation.

### 3.5.4 Electrodialysis Setup for Electrical Resistance Measurements

ER measurements were performed in an ED setup. This setup has six compartments and a four electrode configuration. A schematic view of the setup can be seen in Figure 3.6. The electrodes in compartments 1 and 6 are connected to an Metrohm Autolab PGSTAT 128N potentiostat and are used to apply an electrical current across the whole setup. They must be in contact with a 0.5 M solution of sodium sulphate ( $\text{Na}_2\text{SO}_4$ ). The other two electrodes were installed close to the membrane under investigation (in blue) and are used to measure the potential drop across it. The membrane under investigation was placed in the middle of the setup, between compartments 3 and 4 (in blue in Figure 3.6), and left to equilibrate for 24h before the measurement.

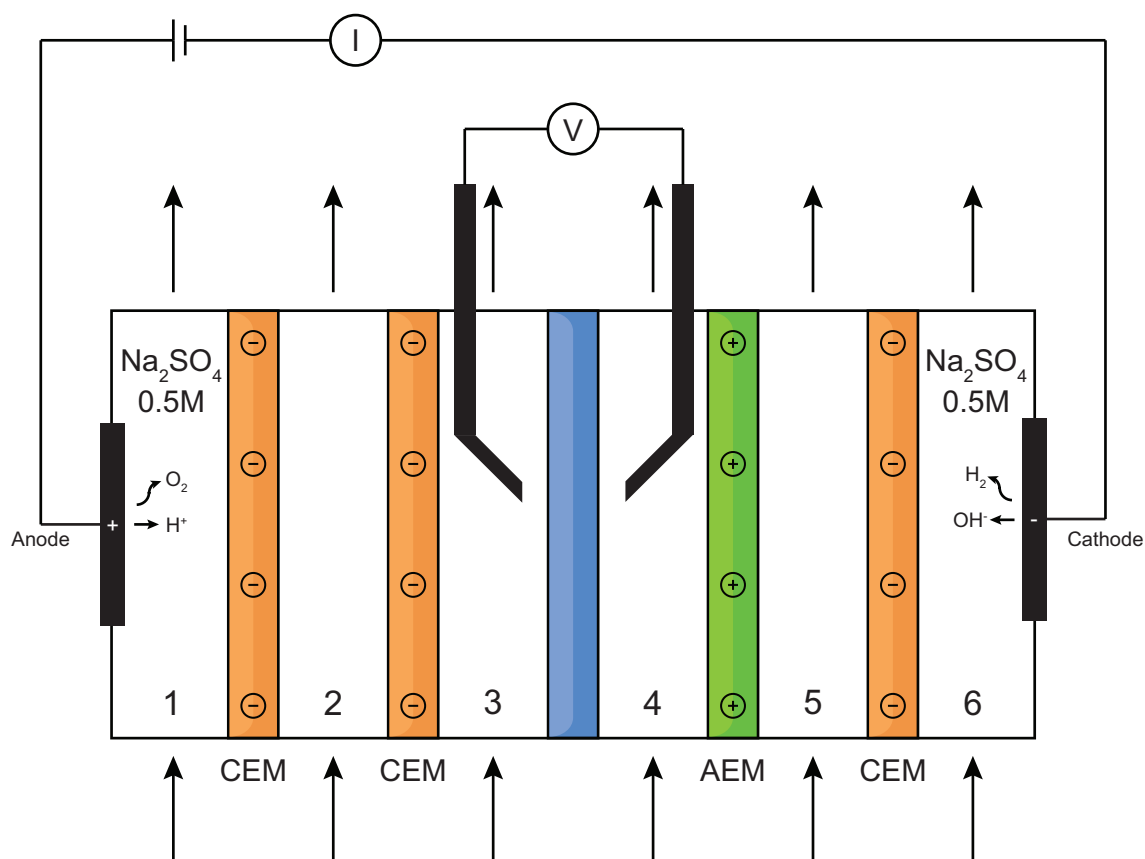


Figure 3.6: Schematic representation of the ED Setup

In this case, [ER](#) was measured in phosphate so a solution of 0.5M sodium phosphate ( $\text{NaH}_2\text{PO}_4$ ) (pH=5) was introduced in compartments 2-5. During the measurements, the solutions in all compartments were kept flowing with a MasterFlex L/S pump operating at 327 rpm. The temperature of the solutions was maintained constant at 25 °C using a thermostatic bath.

A picture of the whole setup can be seen in [Figure 3.7](#).

On the figure, it can be seen, from left to right:

1. a thermostatic bath with all the solutions;
2. two pumps which keep the flowrate of the solutions;
3. the [ED](#) setup;
4. and finally the potentiostat.

This is a potentiometric measurement because a current is applied and varied from 0 to around 0.3 A, and the potential is measured. The maximum current applied depends from membrane to membrane because a membrane with higher resistance will reach the limitations of the potentiostat, which is around 14 V, at a lower current.



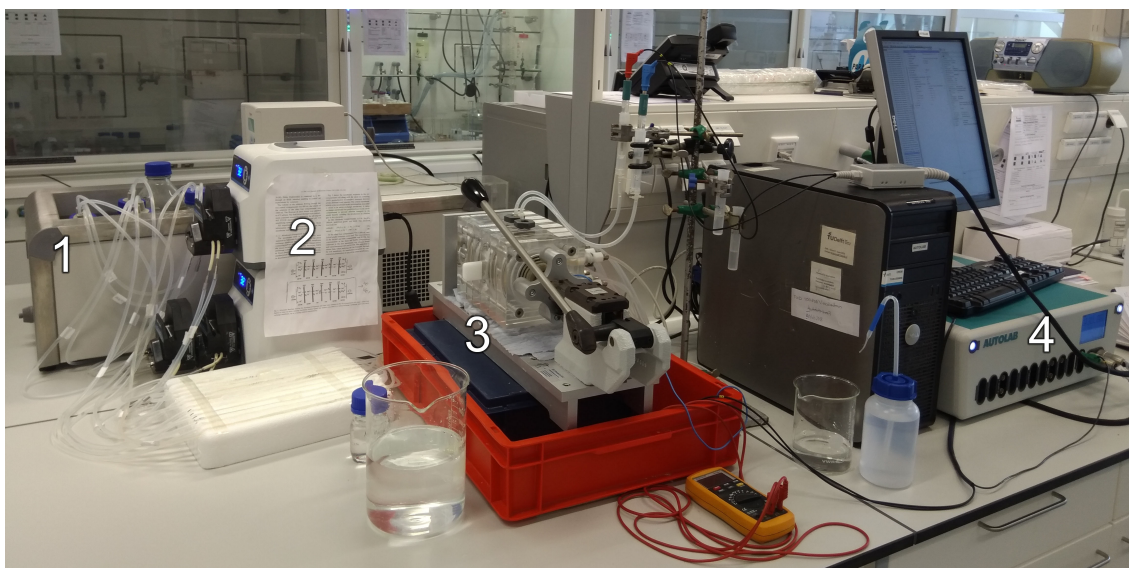


Figure 3.7: Picture of the whole laboratory setup for electrodialysis.

### 3.6 Electrodialysis Setup for Adsorption-Desorption Experiments

In this case, compartments 2 and 3 of the ED setup (Figure 3.6) were filled with 0.2M NaCl solution and compartments 4 and 5 with a 0.2M  $\text{NaH}_2\text{PO}_4$  solution (pH=5). These concentrations were chosen because of the detection limit of the IC, which was used to determine the phosphate concentration in the samples. Higher concentration would generate an overlap between the phosphate and chloride peak.

The membrane under investigation was placed in Milli-Q water for one hour and then placed in the setup. For adsorption, the membrane was placed in the setup with the coating side facing towards the cathode, and a current of 100mV was applied for 90 seconds. These values were chosen using the equations described in section 2.5.1, and assuming a 100% efficiency, this would mean that 0.09 mol of phosphate would be treated per adsorption cycle. Afterwards, the setup was emptied and the membrane was dipped in distilled water, in order to remove the remaining phosphate solution from the membrane's and the sample holder surface, and placed back in the setup but facing the opposite direction. Then the setup was filled again and the same current (100 mV) was applied for 5 minutes to promote desorption. A longer time for desorption was chosen to ensure that all phosphate is released. Five cycles of adsorption-desorption were performed.

A 10 mL sample was taken from the exiting fluid of the receiving compartment (compartment 3, figure 3.6) before the experiment was started, and after each adsorption or desorption step. This way, by analyzing these samples in the IC, the concentration of phosphate desorbed into compartment 3 could be known.

The remaining conditions, like the temperature and flow of the solutions were maintained the same as for the [ER](#) measurements.

The experiment was performed with a bare [CEM](#) in order to obtain a baseline for the coated membranes. This was done because the membrane has to be physically turned the other way around, because of the different solutions in the feeding and receiving compartments. Therefore, some traces of phosphate will inevitably be transported into the receiving compartment instead of being only desorbed from the membranes.

### 3.7 Ion Chromatography

All samples from adsorption/desorption experiments and batch adsorption experiments were filtered using a 0.45  $\mu\text{m}$  Supor® PES filter and analyzed in a 881 Compact IC Pro, 150 mm A Supp 5 column, Metrohm equipment. A mixture of sodium carbonate and sodium bicarbonate (339 mg/L and 84 mg/L, respectively) was used as eluent, and a 0.3M solution of  $\text{H}_3\text{PO}_4$  was used as regenerator. Only the samples produced in the coacervates experiment described in section [3.2](#) were filtered with a 0.2  $\mu\text{m}$  PVDF filter due to the possibility of small polymer based particles remaining in solution.

## RESULTS AND DISCUSSION

In this chapter, the results of the experimental work described in chapter 3 will be shown and discussed. The discussion is done alongside the results due to the vastness of approached topics.

As it was done in chapter 3, a schematic illustration of each studied membrane will be shown in the respective section.

Aside from the very short sections, the main conclusion of each section will be shown at the beginning of it, to facilitate reading and navigation through this chapter.

### 4.1 PHMG's Adsorption Capacity

**In this section it will be concluded that PHMG does, in fact, adsorb phosphate.**

As mentioned in section 2.3, coacervates were used to test PHMG's phosphate adsorption capacity. In order to do this, firstly an optimal ratio between PHMG and PSS had to be chosen. Table 3.1 shows the solutions which were analyzed in order to discover their  $\zeta$ -potential and approximate size. The results of this analysis can be found in table 4.1.

Table 4.1: Zeta Sizer results from Coacervates analysis. \*-low quality fit of data.

| Ratio (PHMG:PSS) | $\zeta$ -potential (mV) | Size (nm) |
|------------------|-------------------------|-----------|
| 1:1              | $11.5 \pm 2.95$         | 4041*     |
| 2:1              | $37.4 \pm 4.99$         | 5267*     |
| 10:1             | $46 \pm 6.37$           | 58.79     |
| 21:1             | $27.8 \pm 5.54$         | 40.17     |
| 1:2              | $-49.2 \pm 8.49$        | 3739*     |

Because PSS was added to PHMG and not the other way around, it is expected that a solution with 1:1 ratio will have a slightly positive zeta potential, since PHMG is positively

charged. This result also confirms that as expected, when the ratio is inverted the charge on the surface is negative. The fact that the solution with a ratio of 21:1 has a smaller surface charge than the one with a 10:1 ratio, is speculated to be due to saturation of the PSS. Once all PSS is bound to PHMG, the remaining PHMG will just remain in solution interfering with the measurement.

The size was used as a qualitative analysis because the coacervates have a gel appearance and they are not exactly particles, so it carries a significant error.

The solution with a 2:1 ratio was chosen for the experiment because it is positively charged on the surface and the coacervates formed were big enough to be centrifuged. While this solution had a visibly turbid appearance, the 10:1 solution looked completely transparent. Figure 4.1 shows the solutions with ratios 10:1 and 2:1, and also how the chosen solution looks after centrifugation.

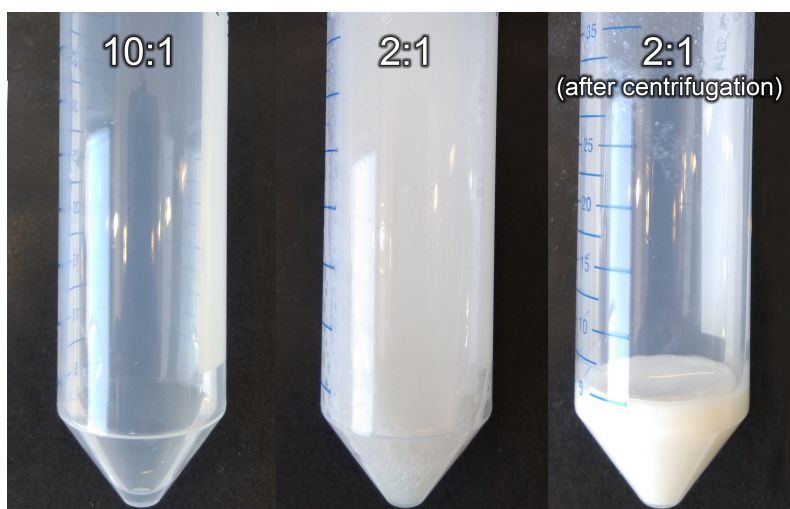


Figure 4.1: Coacervate solutions with a PHMG:PSS ratio of 10:1 (left), 2:1 (middle) and 2:1 after centrifugation (right).

In the batch adsorption experiment, a ratio between PHMG:PSS:PO<sub>4</sub> of 2:1:1 was maintained. This means that for the different phosphate concentrations, PSS had the same concentration, and the concentration of PHMG was the double.

Figure 4.2 shows the result of the batch adsorption experiment. The average adsorption capacity is 11.17% and a trend can clearly be observed, where the adsorption capacity of the coacervate increases with the concentration. It was expected that all the solutions would adsorb approximately the same amount, since the ratio is the same. However, the increase of adsorption with concentration can be explained by the swelling of these "particles" with the ionic strength, and by the increase of surface charge density. A schematic illustration of what is speculated to be occurring at a lower and a higher concentrations is shown in Figure 4.3. It illustrates how the swollen coacervates have a higher availability of PHMG active groups. From Equation 4.1 [53] (where  $\delta$  is the diffuse layer thickness,  $R$  is the gas constant,  $T$  is the temperature,  $F$  is the Faraday constant,  $I$  is the ionic strength, and  $\epsilon_0$  refer to the permeability of the electric medium) it can be concluded that

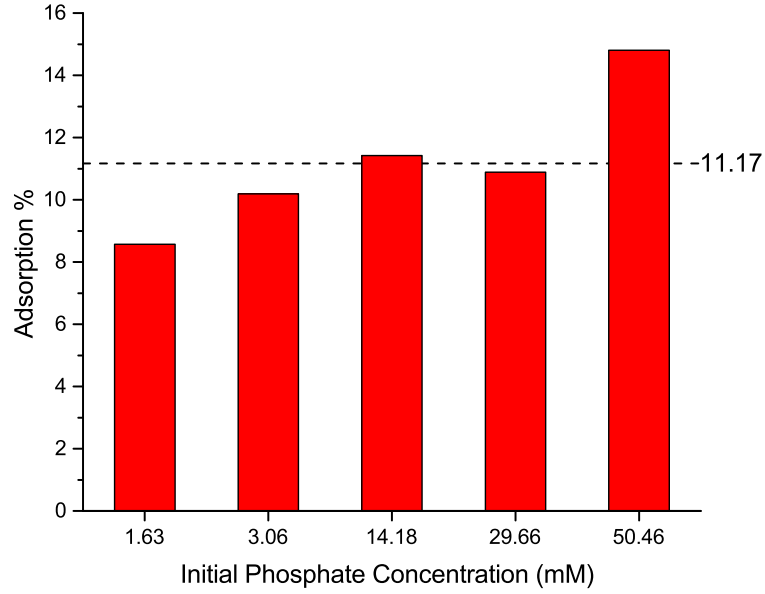


Figure 4.2: Adsorption % by the PSS - PHMG coacervates in function of  $[\text{PO}_4]_0$ .

the diffuse layer thickness is reduced by the increase of ionic strength. From equation 4.2 [53] (where  $\delta$  is the surface charge density,  $\eta$  is the viscosity of solution, and  $u$  is the electrophoretic mobility), it can be concluded that the surface charge density increases with the decrease of diffuse layer thickness. Therefore, the increase in ionic strength will cause an increase in surface charge density, which in its turn, increases the adsorption capacity of a coacervate.

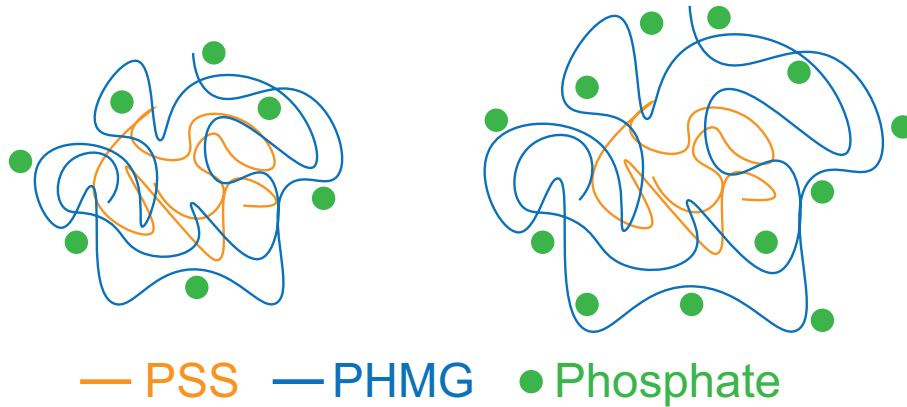


Figure 4.3: Schematic illustration of the coacervates' swelling.

$$d = \sqrt{\frac{\epsilon \cdot \epsilon_0 R T}{d F^2 I}} \quad (4.1)$$

$$\delta = \frac{u \cdot \eta}{d} \quad (4.2)$$

The ease in the manufacture, separation and the performance of these coacervates, is evidence that these should be further investigated on. Perhaps after optimization could serve as a new recovery system, *e.g.* in a column chromatography.

From this section can be concluded that PHMG does, in fact, adsorb phosphate.

## 4.2 Modified $\text{Fe}_3\text{O}_4$ Nanoparticles

### 4.2.1 Characterization

The characterization of the modified particles proves that the coating was successful.

Figure 4.4 displays the TGA of modified and unmodified NP. The presence of the PHMG coating was proven by differences in weight loss between the two measurements. While the bare NP are stable throughout the measurement, the modified NP show a weight loss related to the polymer degradation. Yet, the weight loss is only 3% and this can be explained by the low amount of PHMG compared to inorganic NP. The  $\text{Fe}_3\text{O}_4$  NPs have a diameter of 50-100 nm and the layer of coating is in the few nanometer range.

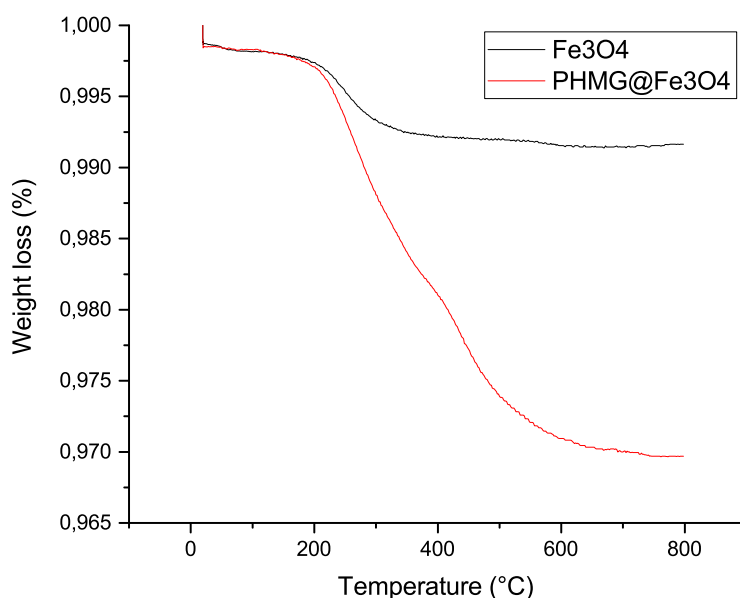


Figure 4.4: TGA analysis of bare  $\text{Fe}_3\text{O}_4$  and of  $\text{PHMG@Fe}_3\text{O}_4$

The FTIR analysis (figure 4.5) showed only two relevant regions - between 4000 and 2700  $\text{cm}^{-1}$  and 1000 and 500  $\text{cm}^{-1}$ , in correspondence with the peaks of interest. The broad peak at 3437  $\text{cm}^{-1}$  is associated with the O-H bond stretching. This is because of the water that is physically adsorbed on the sample, and can be entrapped by the polymeric chains. Two peaks that indicate the presence of the polymer can be seen at 2925 and 2857  $\text{cm}^{-1}$  and they are associated with the asymmetric and symmetric stretching of C-H

bonds, respectively [54, 55]. The intensity of these peaks could also signify that there is a low amount of PHMG on the NP. They are also present in the FTIR analysis of PHMG which can be found in Appendix A.2. The peak at  $596\text{ cm}^{-1}$  confirms the presence of iron oxide as it is associated with the Fe-O bond [56].

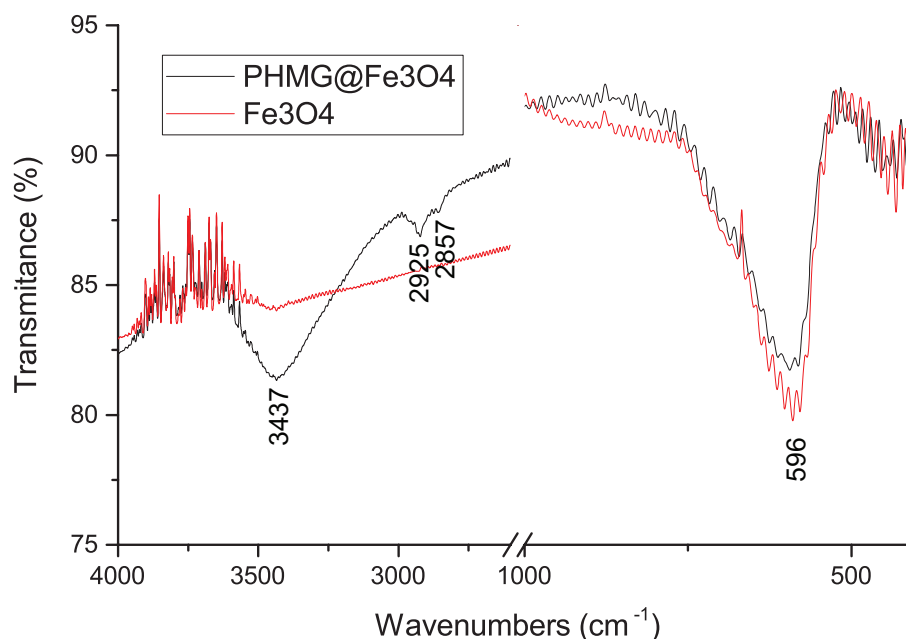


Figure 4.5: FTIR Analysis of bare  $\text{Fe}_3\text{O}_4$  and of  $\text{PHMG@Fe}_3\text{O}_4$

As it can be observed in Table 4.2, the  $\zeta$ -potential after the modification is significantly higher, in comparison with the one of bare NP. As expected at  $\text{pH}=6.3$ , the  $\text{Fe}_3\text{O}_4$  NP are mostly uncharged, as the PZC is between 6.5-7.4, thus the zeta-potential value is close to zero and NP are unstable. The PHMG at the NP surface improves the pH stability of the NP, shifting the  $\text{pK}_a$  to higher values, therefore the total  $\zeta$ -potential is positive and stability of NP is improved. To summarize, characterizations on the coated NP point to the same result: **PHMG is present at the surface, probably at low concentration, and the coating procedure was successful.**

Table 4.2:  $\zeta$ -potential of  $\text{PHMG@Fe}_3\text{O}_4$  and bare  $\text{Fe}_3\text{O}_4$  NP. ( $\text{pH}$  of measurement  $\approx 6.3$ )

| Sample                       | $\zeta$ -potential (mV) |
|------------------------------|-------------------------|
| $\text{Fe}_3\text{O}_4$      | $6.27 \pm 5.71$         |
|                              | $3.42 \pm 5.10$         |
| $\text{PHMG@Fe}_3\text{O}_4$ | $48.6 \pm 3.64$         |
|                              | $50.5 \pm 3.63$         |
|                              | $51.9 \pm 4.23$         |



### 4.2.2 Batch Adsorption Experiment

From the adsorption experiments it was concluded that the modified particles can adsorb less than 0.042 mol P/g NP.

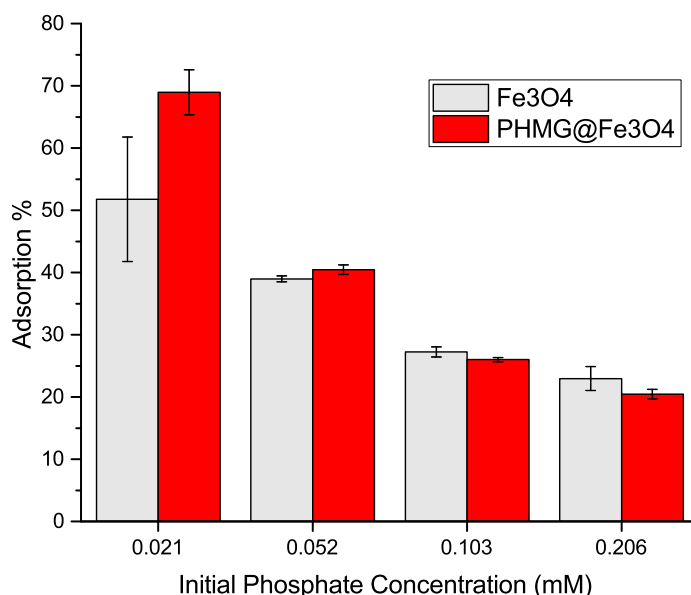


Figure 4.6: Batch adsorption experiment with PHMG@Fe<sub>3</sub>O<sub>4</sub> and bare Fe<sub>3</sub>O<sub>4</sub> NPs.

Figure 4.6 displays the batch adsorption experiments of coated NP in triplicate. It shows a trend of reduction of the % of the initial amount of phosphate which is adsorbed, as this concentration increases.

After analyzing this figure, it was concluded that the NP have reached their point of saturation, even at the lowest concentration tested. This would mean that to properly compare the types of NP tested, even lower concentrations should be analyzed. However, this experiment was already performed at the limit of detection of IC, so this was not possible in this work. Alternatively, a higher concentration of NP can be used.

Aside from the error of the measurement, the experiment itself also carries an error. It involves the weighing of only 5mg of NPs, which is a low value even for scales with 0.1 mg of sensibility. The other option would be to create one batch of NPs solution and then separate it in four solutions, but this was not opted for, since because of the particles' size they deposit rather swiftly (Brownian motion is not enough to keep them dispersed in solution). This would result in four solutions with different concentrations.

Although there is a significant error, at the lowest analyzed concentration there is evidence that after modification the NP have an increased adsorption capacity. Previous expertise acquired in this investigation group also supports this [22].

Besides, the objective of this project, which as mentioned in section 1.3, is to compare the two systems in the closest conditions possible. Therefore, for comparison reasons, the



NPs should be coated with the same polymer as the membranes (PHMG).

In terms of adsorption capacity, it can be concluded from the figure 4.6, that **the modified particles can adsorb less than 0.042 mmol P/g NP, or 1.3 mgP/gNP**. This value is slightly lower, but still in line to what is found in literature [22, 32, ]. The fact that it is lower can be explained by the fact that the NP used in this project were larger, and therefore have a lower surface area, than what is generally used.

### 4.3 CEM Coated with PHMG Entangled by Acrylamide

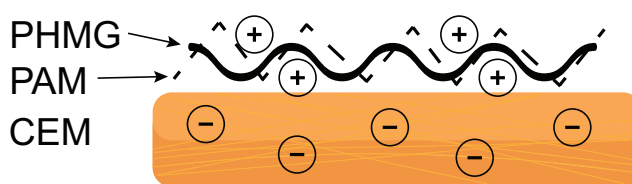


Figure 4.7: Schematic illustration of PHMG@CEM.

#### 4.3.1 Adsorption Capacity

**In this section it is concluded that solutions with more than 1mM of concentration could potentially be treated in each adsorption cycle.**

In order to obtain a rough estimation of the amount of phosphate this membrane could adsorb, the surface area of the membrane was divided by the calculated area covered by PHMG's repetitive unit. Details about this calculation can be found in Appendix A.3. From the theoretical calculation it was assumed that  $3.3 \times 10^{-9}$  mol of phosphate could be adsorbed, which corresponds to a volume of wastewater (with 0.01M of phosphate) of 0.33  $\mu$ L. This is of course an underestimation of the adsorption capacity of the membrane because there is more than just one layer of repetitive units of PHMG on the membrane. The polymer has its own 3D structure and does not behave like a monolayer.

In comparison, using the same calculation approach, a concentration of 5.56 g/L of  $\text{Fe}_3\text{O}_4$  NP was estimated to be able to treat such a solution.

The adsorption capacity was also tested by simply submerging a membrane in  $\text{NaH}_2\text{PO}_4$  solutions. Two concentrations of phosphate were used - 0.01 and 0.1 mM, because this was thought to be the amount the membrane could adsorb. No phosphate adsorption was observed, however the release of chloride was detected. As it can be seen on Figure 4.8, this release approximates to around 1 mM. It is speculated that this release occurs due to repulsions between the chloride ions and the fixed charges of the CEM.

It is known that chloride ion is the counter-ion of the active sites of the PHMG polymer, therefore we can correlate the amount of chloride found (1mM) with the adsorption capacity of the membrane. This means that the adsorption capacity of the membrane was underestimated and it shows great potential for water-treatment. Although, this value

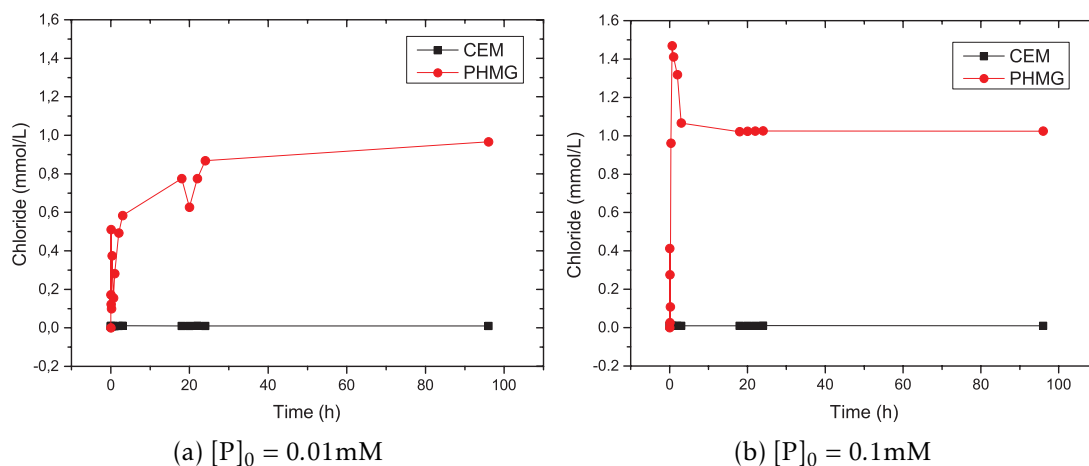


Figure 4.8: Chloride release over time.

could also be underestimated because it is highly likely that not all chloride ions have been released.

In conclusion, **solutions with more than 1mM of concentration could potentially be treated in each adsorption cycle**, which meets the requirements for this membrane.

### 4.3.2 Coating Stability Test

**The coating on this membrane proved to be unstable.**

On figure 4.9 it can be observed that the frontside (right) has a clear pattern which the backside (left) does not have. This is due to the presence of the coating. From this image it was also concluded that the coating was uneven.

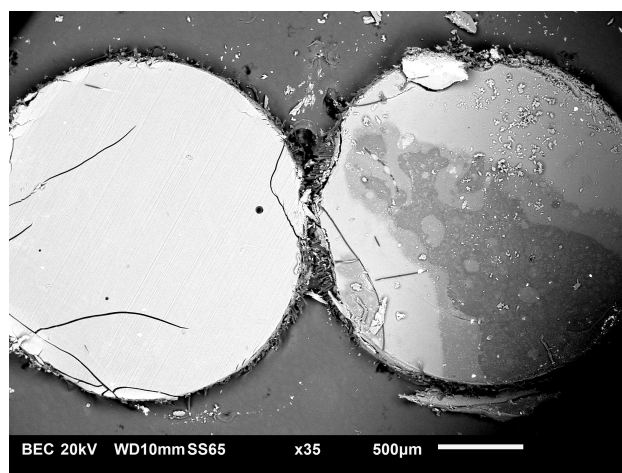


Figure 4.9: SEM image of PHMG@CEM, at the backside (left), which is uncoated, and on the coated frontside (right)

The image shown in figure 4.10 was taken at an area that is on the edges of the coating. It can be clearly seen that there are two sides. On the top part of the images, which corresponds to the coating, chlorine (figure 4.10 B) can be observed, which is the

counter-ion of PHMG, and carbon (figure 4.10 F), which is also present in the polymer. On the bottom, which is the uncoated side of the membrane, sodium (figure 4.10 C), sulphur (figure 4.10 E), oxygen (figure 4.10 D) and carbon (figure 4.10 F) can be observed. Carbon is present in the polystyrene polymer from which the membrane is composed, and sulphur and oxygen can be observed because they're in its active groups ( $\text{SO}_3^-$ ). Sodium is the counter-ion of the active sites. Therefore, the conclusion that the coating is present before contact with water can be taken.

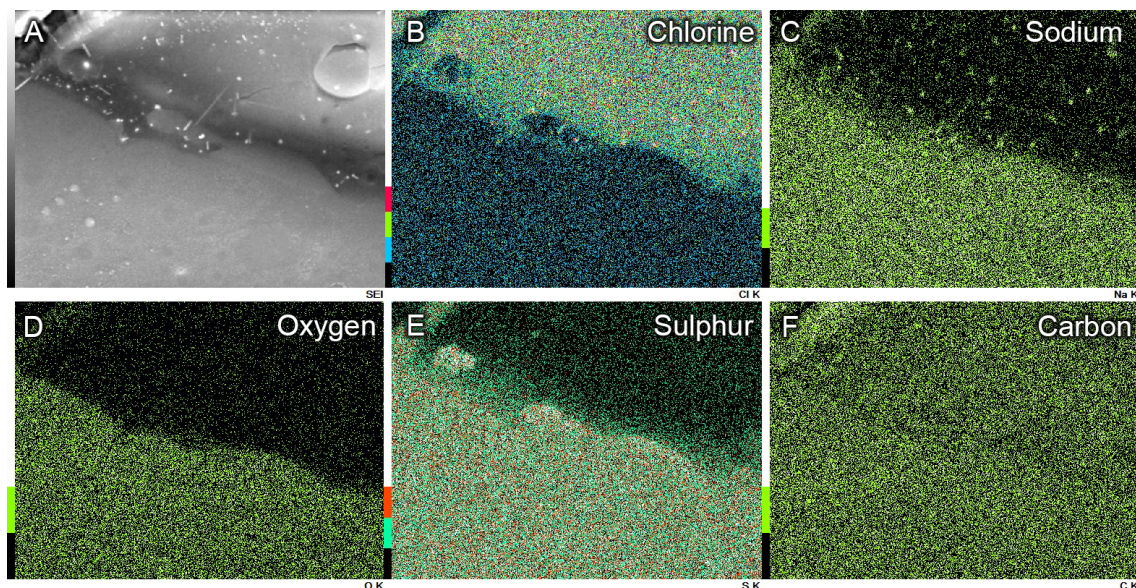


Figure 4.10: SEM-EDS images of unused CEM coated with PHMG entangled by acrylamide.

The SEM images shown in figure 4.11 were taken exactly at the same place of the membrane, before and after contact with water. On left side of the figure two distinct regions are present, just like in figure 4.10, while on the right side, the top region is no longer present. The cracks that can be observed in this image were formed during the drying process. This leads to the conclusion that the coating is not stable. EDS data was in agreement with this. It is shown in Figure 4.12 that no chlorine is present after the test, and the area that previously had coating now looks the same as the uncoated area. It was expected that the chlorine would be released, as it was observed in section 4.3.1. Although unexpected because of the entanglement of PHMG, this result can be explained by the fact that this polymer is highly soluble in water. Its solubility in water is 280 g/L [1].

Thus, it was concluded that **the coating is not stable** and a way to improve this stability is needed.

#### 4.3.3 Electrical Resistance

When the ER was measured, an unusual behaviour was observed.



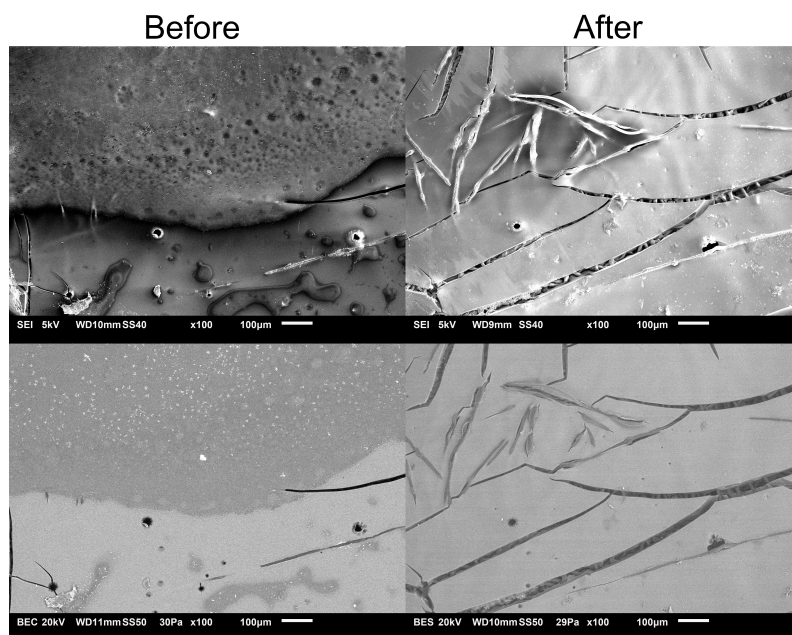
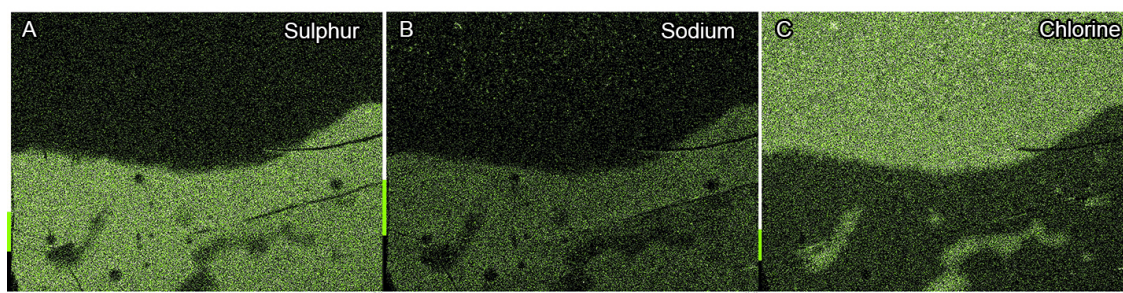


Figure 4.11: SEM images of the coating before and after the water stability test.

Before:



After:

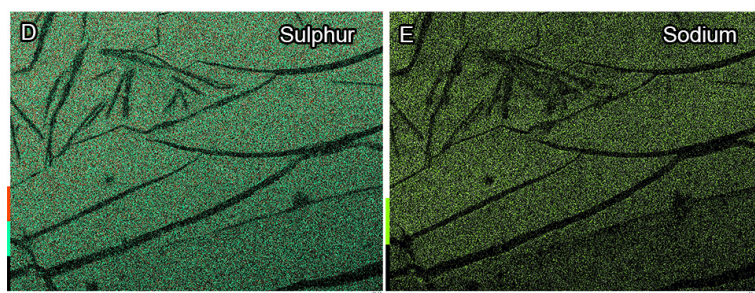


Figure 4.12: EDS analysis after coating stability test.

Without removing the membrane from the setup, 15 runs of the measurement were performed with 30 seconds of interval between each other. As it can be observed in Figure 4.13, there are two slopes in the ohmic region. This effect gets lost over the runs and if the time between runs is reduced the membrane displays a behaviour close to the one of a bare CEM. If the membrane is left in Milli-Q water overnight, and the measurement is repeated, this same effect can be observed again. More detailed information about these

experiments, like the values of each slope shown in figure 4.13 can be found in appendix A.4.

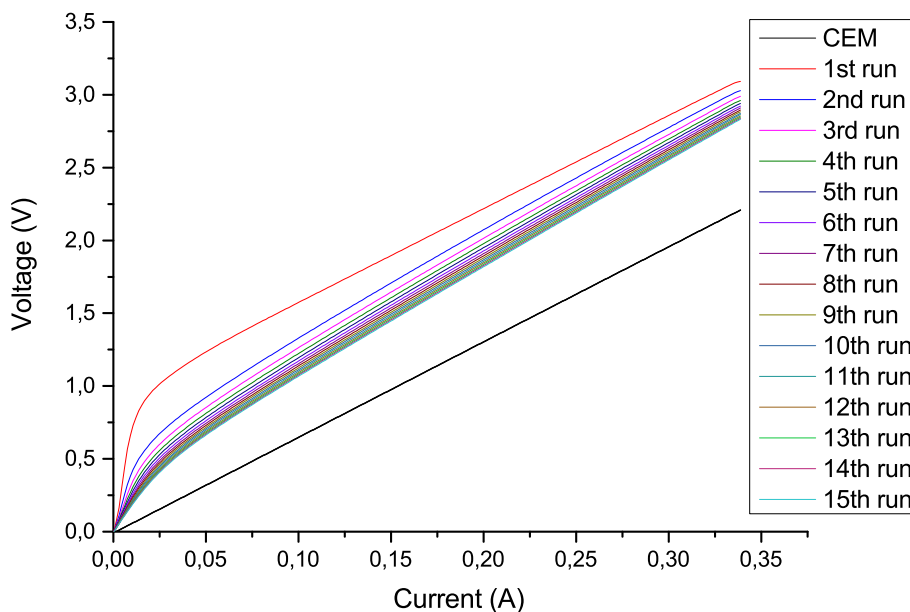


Figure 4.13: ER of CEM with entangled PHMG by acrylamide coating over the course of consecutive 15 runs.

As it was concluded in the previous section, the coating is not stable. And since the coating is the only difference between a bare CEM and the analyzed membrane, it was suspected that a nanoporous structure could have been formed on top of the membrane (which because of its thickness, could not be detected on the SEM). This may have possible applications, but it is outside of the scope of this investigation.

#### 4.4 PHMG Deposited on CEM After Surface Activation

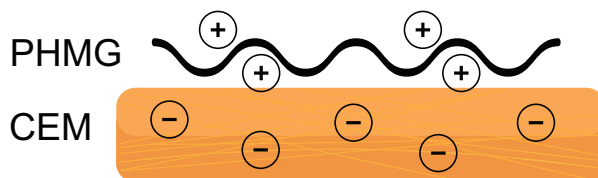


Figure 4.14: Schematic illustration of CEM with deposited PHMG after chemical surface activation.

**This method did not originate a stable coating.**

After coating this membrane was washed thoroughly with demi-water in order to remove any not bound polyelectrolyte. The result was visible to the naked eye, that

only small parts of the membrane were still covered, but it looked as if it was mostly washed away. This can be observed on Figure 4.15a. SEM and EDS data confirmed these observations (Figures 4.15b and 4.16). On figure 4.15b it can be observed that the membrane appears perfectly clean, as a bare CEM would. Figure 4.16 shows that only the elements present in a bare CEM were detected in the EDS analysis. If the coating was present nitrogen and chlorine would have been detected.

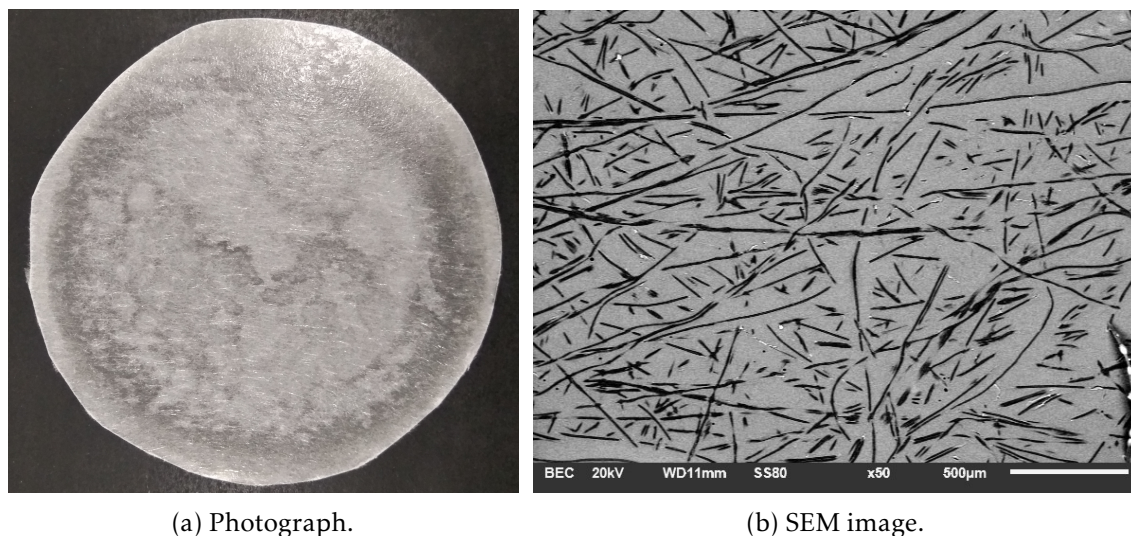


Figure 4.15: PHMG Deposited on membrane after surface activation.

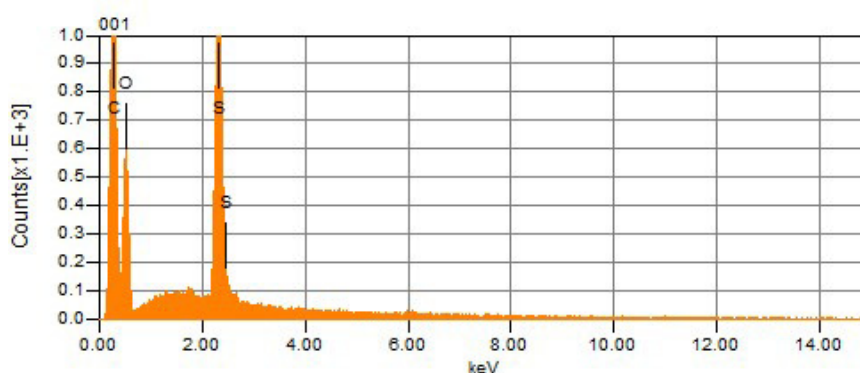


Figure 4.16: EDS analysis of the membrane with deposited PHMG, after contact with water.

Despite the increase in surface charge on the CEM, the electrostatic bond between its sulphate groups and PHMG is not enough to keep it from dissolving. Therefore, it was concluded that a system with an even more stable coating was needed, and for this, a chemically bound coating was chosen. This will be discussed in the next section.



## 4.5 CEM with Chemically Bound Coating

### 4.5.1 Coating Stability Test

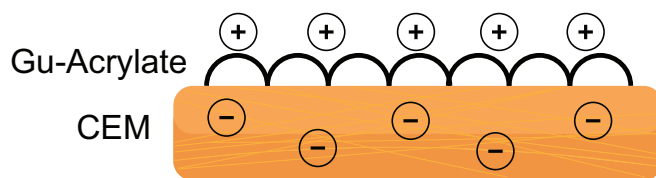


Figure 4.17: Schematic illustration of the CBC@CEM.

**In this section it is proved that the coating is stable.**

As mentioned in section 3.4.3, a different compound was used in order to create this membrane. However, this compound has the same counter-ion,  $\text{Cl}^-$ .

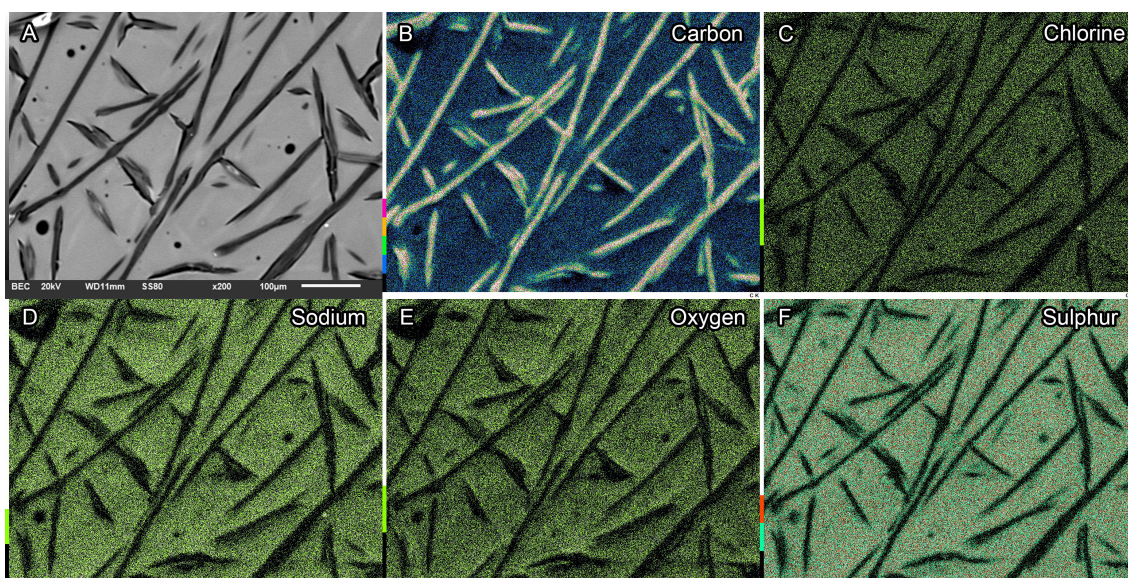


Figure 4.18: EDS analysis of a CEM with chemically bound coating.

Figure 4.18 shows the result of the EDS mapping of the CEM with chemically bound coating (CBC@CEM). The elongated features that can be observed in this figure, are the polypropylene fibers which are in the constitution of the membrane to enhance its mechanical properties. Nitrogen, which would be a good indicative of the presence of the polymer since it is present 3 times in the PHMG repeating unit, could not be observed due to the overlaying of the signal with carbon (figure 4.18 B), which is present throughout the whole membrane - the fibers for stability, the sulfonated polystyrene from which it is made, and the coating. Sulphur, oxygen and sodium (figure 4.18 D, E and F) can be observed because the first two constitute the membrane, and the latter is its counter-ion.

Chloride (figure 4.18 C) is the counter-ion of the coating and therefore this analysis proves the presence of the coating before the washing step. However, chlorine might be washed during this step and because of the homogeneity of the membrane and the

difficulty of detecting nitrogen and the thinness of the coating, its presence after this step might be difficult to confirm.

Figure 4.19 displays the result of the EDS analysis after the membrane had been in an aqueous environment. As predicted, chlorine could not be detected after the washing step. On the other hand, nitrogen could be detected, but not quantified.

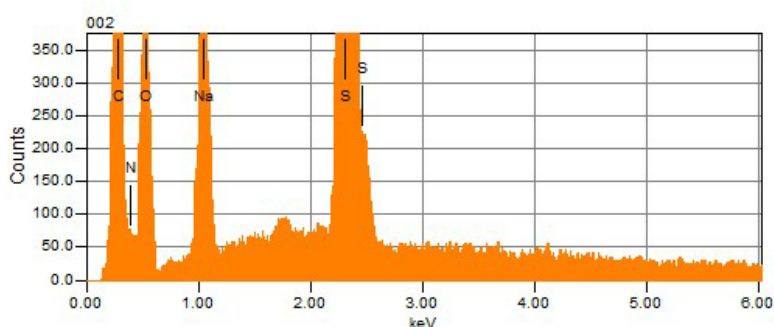


Figure 4.19: Element analysis of the CEM with chemically bound coating after the washing step.

In order to have a reassurance that the coating is not dissolved by water, a side piece of the membrane was analyzed. This side piece is shown in Figure 4.20 and was chosen for this analysis in hope to provide a clearer result because it has less components. It is formed just by the coating and the membrane's active polymer - it does not have the polypropylene fibers.

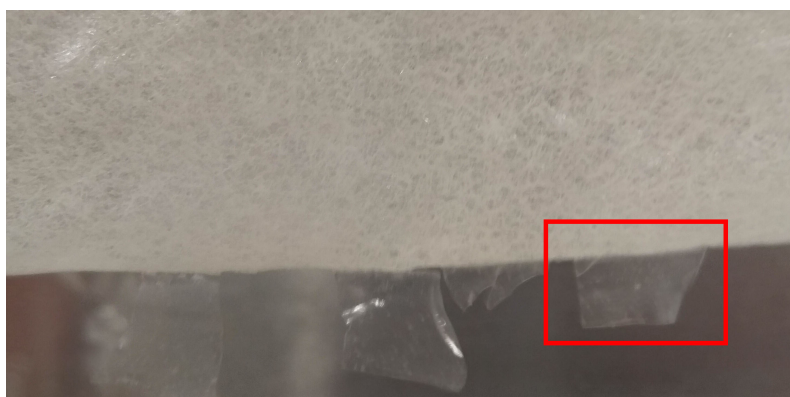


Figure 4.20: Side pieces of the CEM with the chemically bound coating.

Its SEM-EDS analysis (Table 4.3) before any contact with water showed two areas: a darker and a lighter one. The darker area was rich in chlorine and nitrogen, while the lighter area was very poor in these elements. The SEM image is shown in Table 4.3 and the table shows the elemental composition of points 2 and 3 displayed on the figure.

It can be concluded that the darker area corresponds to a coated area, because of the presence of nitrogen and chlorine which are associated with the acrylate with a guanidinium group. Carbon is present both in the coating and the CEM, and sulphur, oxygen



and sodium are present in the membrane's body.

After the washing step, a similar area with lighter and darker spots was found. When EDS analysis was performed (figure 4.21), no chlorine (figure 4.21 C) could be observed, as expected. However, nitrogen (figure 4.21 D) could be detected. Also, sodium and oxygen (figure 4.21 E and F) are less visible. Therefore, it was concluded that **the coating remains stable after contact with water** and further characterization and an adsorption-desorption experiment were in order.

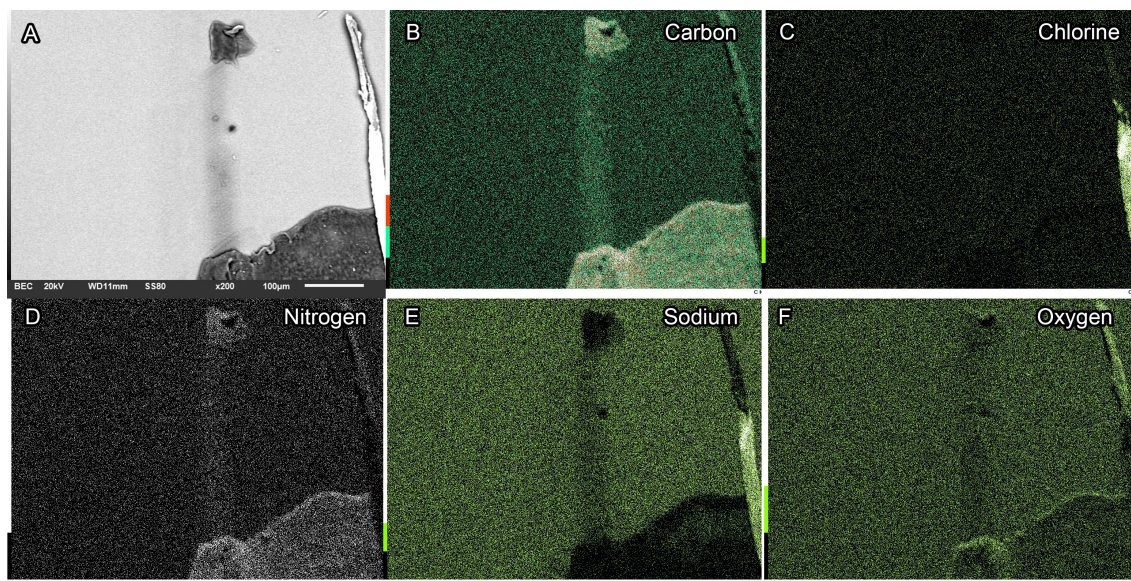


Figure 4.21: EDS analysis of side piece of CBC@CEM after contact with water.

Table 4.3: Percentage of each element present on the two areas seen in the side piece of the membrane.

| Chemical Formula | Spot 002 |        | Spot 003 |        |
|------------------|----------|--------|----------|--------|
|                  | Mass %   | Atom % | Mass %   | Atom % |
| C                | 50.24    | 60.43  | 51.71    | 63.28  |
| N                | 19.65    | 20.26  | n.d.     | n.d.   |
| O                | 12.29    | 11.10  | 28.28    | 25.98  |
| Na               | 2.67     | 1.68   | 8.90     | 5.69   |
| S                | 8.42     | 3.80   | 9.98     | 4.58   |
| Cl               | 6.72     | 2.74   | 1.13     | 0.47   |

#### 4.5.2 Adsorption Capacity

After the CBC@CEM had been for 24 hours in 200 mL of Milli-Q water, the chlorine concentration in the solution was 1.02 mM. This only further proved that this membrane was very promising. If it could **treat over 1 mM of phosphate per adsorption cycle**, this

membrane would meet all the requirements expected from it, and its performance would be comparable to the one of the modified NP.

### 4.5.3 Electrical Resistance

Table 4.4: Electrical resistance of CEM with chemically bound coating.

| Sample           | ER ( $\Omega$ ) | Error |
|------------------|-----------------|-------|
| CEM              | 6.35            | 0.11  |
| CBC@CEM          | 2.14            | 0.05  |
| CBC@CEM_Inverted | 2.19            | 0.05  |

Table 4.4 shows the ER of a bare CEM, of the CBC@CEM, and the same membrane but inverted. Without prior knowledge, one would think that adding a layer onto a membrane would increase its resistance. As it is schematically illustrated on figure 4.22, it would be expected that the bare CEM would offer less resistance to the transport of the current since more ions can cross the membrane. However, as it can be observed on table 4.4, the modification has a significant impact on the ER since it lowers it approximately 3 times. The lower resistance can have different explanations. The first one, which does not seem probable, is that the positively charged coating helps anions pass through the membrane. This seems unlikely as the CEM is the same in both cases and it does not allow phosphate anions to pass through. Another explanation would be that when ions meet at the interface between the coating and the CEM, they bind and pass through the membrane together. This also doesn't seem to be the case, since when they bind they are no longer transported by the current and the fact that the inverted membrane does not show an increase in resistance also disproves this theory. The third one is that the interface between the anionic coating and the CEM is responsible for pH changes. The pH changes would result in the formation of  $H^+$  or  $OH^-$  ions which can easily pass through the membrane as they are smaller and carry the current which is being applied, therefore reducing the resistance. Although this is likely the case, it is just a speculation as the pH at the surface of the membrane was not measured because the setup did not allow a trouble-free way of doing this.

### 4.5.4 Adsorption-Desorption Experiment

**No significant adsorption by the CBC@CEM could be observed.**

Figure 4.23 shows the concentration of phosphate in compartment 3 of the ED setup (Figure 3.6), which initially has no phosphate, after each desorption cycle.

As it can be observed in Figure 4.23, a bare CEM displays more phosphate release than a coated one. This is most probably due to the transported phosphate during the inversion of the membrane which was not removed in the washing step. Meaning, that the coating of the membrane had no significant effect in terms of adsorption.

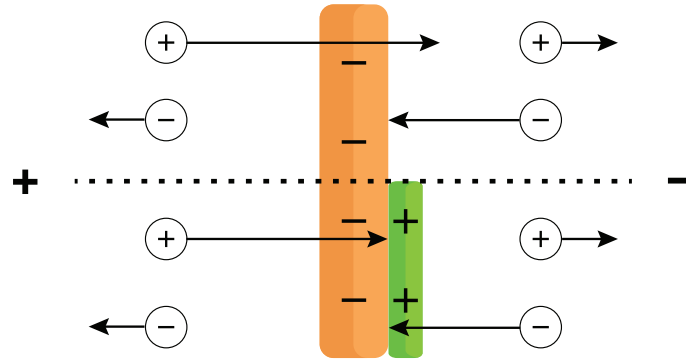


Figure 4.22: Ions transport through CEM (above) and modified CEM (below).

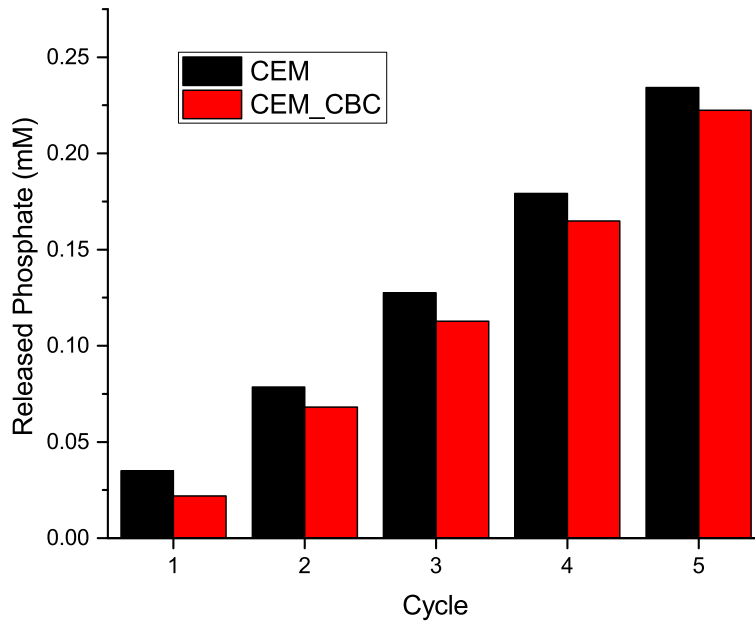


Figure 4.23: Desorption of phosphate by CBC@CEM

This result goes against the expectations, due to the conclusions taken in sections 4.5.1 and 4.5.2. Nevertheless, it can be explained. These membranes have one big disadvantage which was feared to prove significant. This is the fact that the negative charges from the CEM itself can interfere with the adsorption onto the coating. Because the top layer is quite thin, and the fact that the negative charges might be in higher concentration than the positive ones, they will repel the negatively charged phosphate ions. **Therefore, adsorption is not possible.**

This issue can be solved by the formation of a thicker anionic layer, which will guarantee that there will be enough positively charged groups to compensate the CEM's negatively charged groups in proximity and still have enough free active groups to adsorb phosphate.

Section 3.3 describes a system where the coating is composed of modified  $\text{Fe}_3\text{O}_4$  NP. This is the system that was believed to solve this issue, because NP offer a large surface area and thus, a higher concentration of positive charges. The NP could also form multiple layers on top of the membrane. The results of this system will be reviewed in the next section.

## 4.6 CEM Coated with modified $\text{Fe}_3\text{O}_4$ Nanoparticles

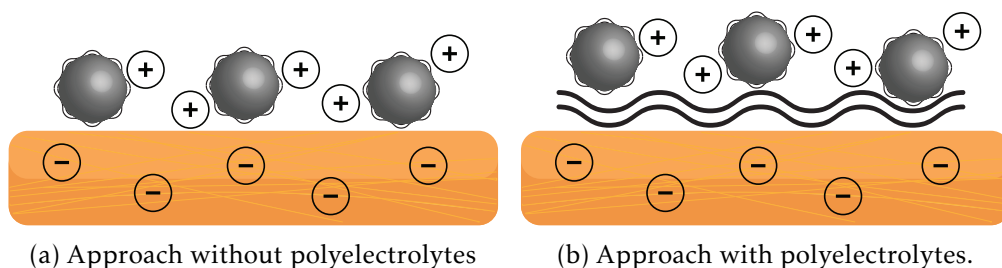


Figure 4.24: Schematic illustration of CEM coated with PHMG functionalized  $\text{Fe}_3\text{O}_4$  NP.

Keeping in mind the conclusions from the previous section and section 4.2.2, it was decided that the coating should be done with modified NP and not bare NP, since they have a higher surface charge, as shown with the  $\zeta$ -potential result in section 4.2.1. A membrane coated with bare NP should also be tested but due to time constraints, this experiment was not performed in this work.

As mentioned in section 3.4.4, two approaches for this coating were performed. This section will present and discuss the results of both, keeping the same order of appearance - first the approach without polyelectrolytes (CEM coated with modified  $\text{Fe}_3\text{O}_4$  NP (MNP@CEM)) and then the approach with polyelectrolytes before the coating (CEM coated with PEI, PSS and modified  $\text{Fe}_3\text{O}_4$  NP (MNP-WP@CEM)).

The adsorption capacity of this membrane could not be estimated in the same way it was done before, as the counter-ions of the coating had already been washed off during the coating process.

### 4.6.1 Characterization and Coating Stability Test

**In this section it is proved that the coating is stable.**

The coating of both membranes could be seen by the naked eye. It can be seen in Figure 4.25. These observations were confirmed by SEM-EDS (Figures 4.26 and 4.27).

Figure 4.26 shows spotted light areas, which can be associated with the layer of modified NP. It can be observed that the coating does not fully cover the membrane which indicates that there is space for optimization in the coating process. The loading of NP can be further increased to enhance the adsorption capacity of the membrane. However, it allows the conclusion that the coating was successful. On the third picture, a high concentration of iron can be observed, and on the 2<sup>nd</sup> and 5<sup>th</sup> pictures, absence of intensity in



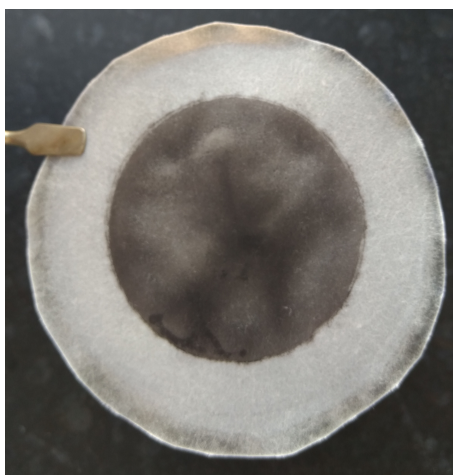


Figure 4.25: Photograph of MNP@CEM.

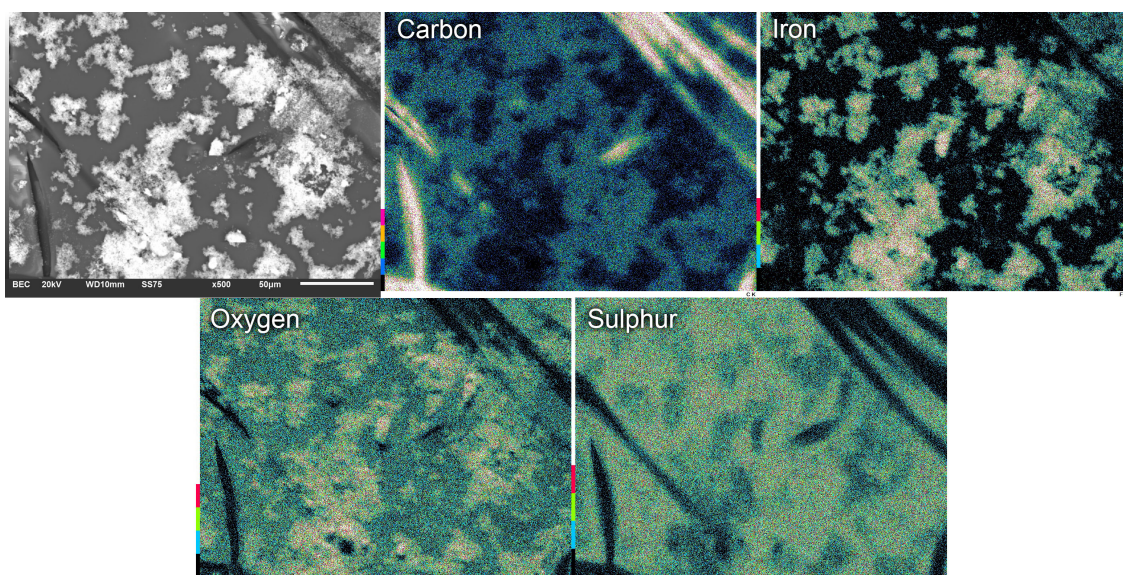


Figure 4.26: EDS mapping of MNP@CEM.

carbon and sulphur in the coated areas can be seen. Oxygen is more present on the coated areas as the NP are composed of iron oxide, but it can also be found in the composition of the membrane, as it has sulfonated groups. Nitrogen was also detected but it was assumed to be part of a contamination, either on the membrane or the apparatus itself.

A similar figure with similar conclusions about the membrane prepared by the second approach can be found in appendix A.5.

Figure 4.27 shows the SEM images before and after contact with water. Although the image was not taken at exactly the same spot, the conclusion that the NP count on the membrane has not diminished by the test can be drawn.

Results for both approaches were the same. The result for the approach not shown in the section can be found in appendix A.5.

**This allows the conclusion that both coatings remain stable.**

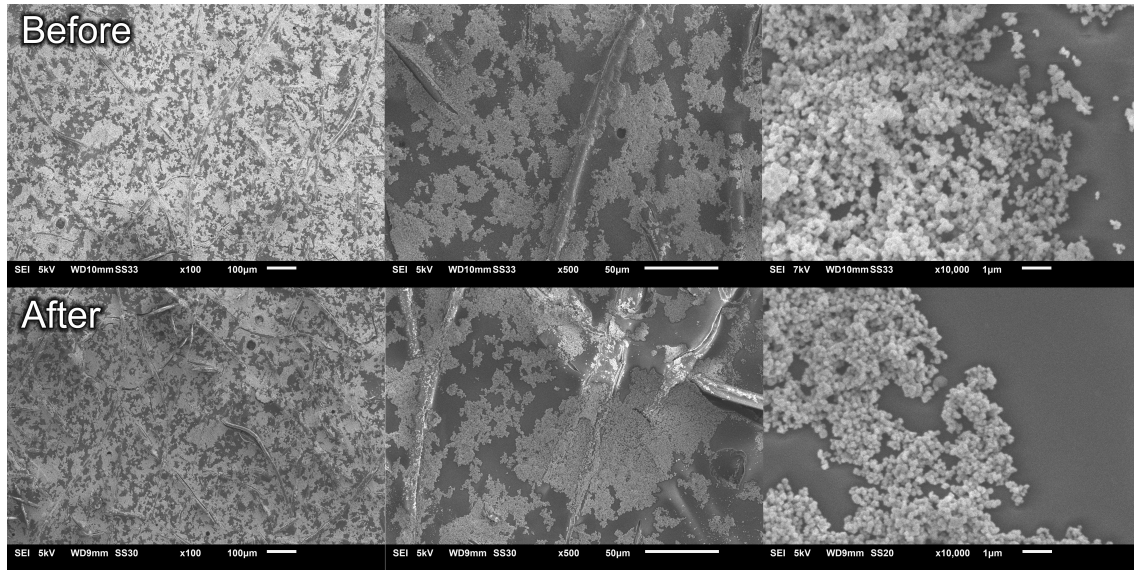


Figure 4.27: SEM images before and after MNP-WP@CEM has been in contact with water.

The size of the NP was also estimated using SEM. The result can be seen in Figure 4.28, and a rough average of the NP sizes would be 140 nm.

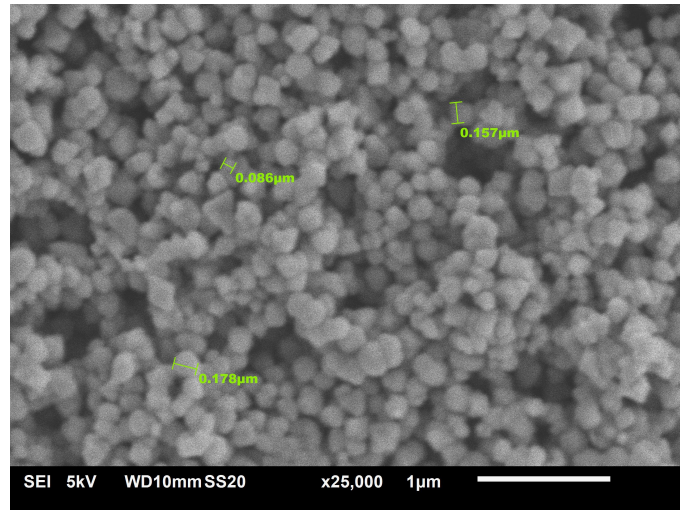


Figure 4.28: SEM image with sizes of NP deposited on CEM.

#### 4.6.2 Electrical Resistance

Table 4.5: Electrical resistance of CEM with modified NP coating.

| Sample     | ER ( $\Omega$ ) | Error |
|------------|-----------------|-------|
| CEM        | 6.56            | 0.08  |
| MNP@CEM    | 6.29            | 0.09  |
| MNP-WP@CEM | 5.97            | 0.09  |

As it is shown on table 4.5, the ER is affected by the coating. It is reduced when just modified NP are deposited on CEM and further reduced when two polyelectrolyte layers are added between the CEM and the NP. This reduction is much less significant than the one described in section 4.4, but it could have a similar explanation.

### 4.6.3 Adsorption - Desorption Experiment

**The MNP-WP@CEM can successfully adsorb and desorb phosphate.**

The adsorption-desorption experiments is where the membranes created with the two different approaches display different performances.

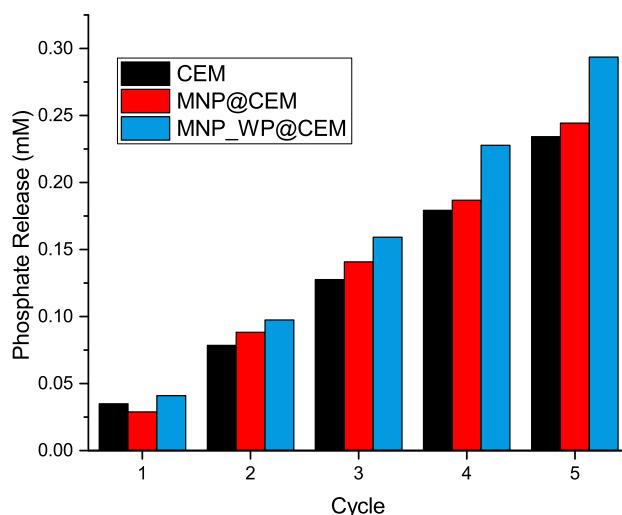


Figure 4.29: Desorption results of CEM, MNP@CEM, and MNP-WP@CEM.

Figure 4.29 displays the phosphate concentration in the receiving compartment (compartment 3 of the ED setup shown in figure 3.6) after each cycle. An increase in the phosphate concentration after each cycle can be observed. It can also be observed that both membranes show adsorption and desorption capacities but the one displayed by MNP@CEM is not very significant. MNP-WP@CEM however, proves to be very promising. This difference in performance is theorized to be due to the fact that the branched polyethyleneimine has created a rougher surface and therefore distancing the CEM from the phosphate ions. Although there is a layer of PSS on top of PEI, this results in less repulsion by the sulfonated groups of the CEM as the negative charges of PSS are probably compensated by the positive charges of PEI and  $\text{Fe}_3\text{O}_4$ .



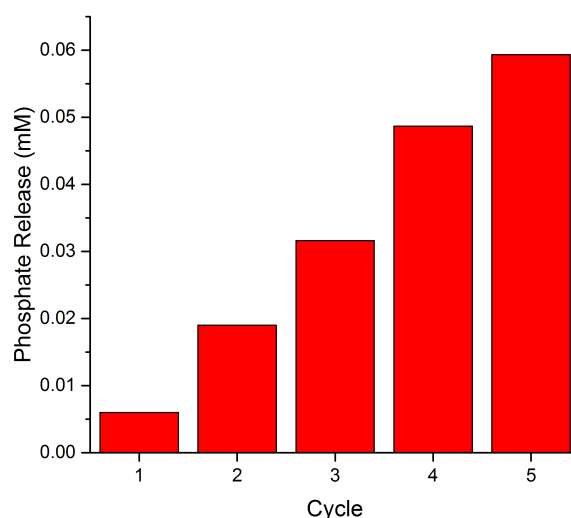


Figure 4.30: Difference between phosphate release by MNP-WP@CEM and bare CEM during adsorption-desorption experiments.

Figure 4.30 shows the difference between the phosphate released into the compartment 3 of the ED setup (Figure 3.6) by the MNP-WP@CEM and the bare CEM (which as mentioned in section 3.6, was used as a baseline). Although this result carries some error, it can undoubtedly prove that **the MNP-WP@CEM can successfully adsorb and desorb phosphate**. However, its efficiency still has room for improvement. As mentioned in section 4.6.1, the loading of NP can be improved, which would increase the amount of positively charged groups on the surface, and therefore improve the efficiency.

In terms of adsorption capacity, over 5 adsorption - desorption cycles this membrane has treated  $\approx 0.06$  mmol of phosphate in an  $8.14 \text{ cm}^2$  area. Therefore its capacity can be estimated at  $0.007 \text{ mmol.P/cm}^2$ , or  $0.23 \text{ mg.P/cm}^2$ . This value is comparable to what was estimated for the NP in section 4.2.2, which was  $1.3 \text{ mg.P/g}$ . Although these values are in different units, and comparison is not straightforward because the two systems are vastly different, the membrane appears to be very promising since it still has plenty of room for improvement and allows a much easier desorption. Another way of comparing them would be to estimate the surface area of the NP and of the membrane. This is easily done, however it induces a very significant error. While the NP in solution have the majority of their surface area available for adsorption, this may not be true for the NP immobilized on the surface of the membrane. Part of them have the role of keeping the coating stable on the surface of the membrane and they are much more aggregated than they would be in solution. Therefore, this was not opted for.

To sum up the comparison between the two systems,

1. The modified CEM methodology allows a much easier desorption, as it only requires the inversion of the electrical current in the ED setup.



2. Both show very good adsorption capacity, but comparison is not straightforward, hence it should be studied more in depth after optimization of the systems.
3. They are both cost effective. All the materials in both systems are commercial materials. The adsorption using NP has the disadvantage of needing more chemicals for desorption, while the adsorption using ED requires a higher energy consumption. Therefore, an economical study should also be performed after the optimization of the systems.
4. Because of the fact that the MNP-WP@CEM process does not utilize chemicals for desorption, it is a greener process.



## CONCLUSIONS

In this project, commercial cation exchange membranes (CEM) were modified with an anionic layer, which contains positively charged guanidinium groups, in order to be used in an electrodialysis setup for the adsorption and the desorption of phosphate. The performance of this system was compared to the adsorption capacity of modified  $\text{Fe}_3\text{O}_4$  nanoparticles (NP).

In order to accomplish this, firstly the adsorption capabilities of polyhexamethylene guanidine (PHMG) were studied using coacervates. These coacervates were formed using polystyrene sulfonate (PSS) and PHMG. In a ratio of PHMG:PSS: $\text{PO}_4$  of 2:1:1, these coacervates adsorbed approximately 12% of the phosphate in solution. This value increases with ionic strength and vice-versa. This proved that PHMG can adsorb phosphate.

Further research should be done on the increase of adsorption capacity by the modification of the  $\text{Fe}_3\text{O}_4$  nanoparticles, but in this work, they were successfully coated and they do appear to have an increase in performance. Their adsorption capacity was estimated to be around 1.3 mg.P/g.

The first two approaches to coat a CEM, namely the entanglement of PHMG on the membrane surface by acrylamide, and deposition of PHMG after a surface activation with  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$ , did not originate a stable coating. Because of the high solubility of PHMG in water, the electrostatic bond between PHMG and the sulphonate groups of the CEM was not enough to maintain the coating stable, when in aqueous environment.

The third approach was a chemically bound coating. This was done with polyallylamine hydrochloride functionalized with guanidinium groups since PHMG does not have any active groups. This generated a stable coating and the membrane's adsorption capacity was estimated to be relatively high. However, no adsorption was observed in the adsorption-desorption experiment. This was speculated to be due to the repulsion between the CEM and the negatively charged phosphate ions. Perhaps this issue can be

solved by the addition of a neutral, porous layer between the CEM and the coating in order to avoid this interaction.

The final approach was to coat the CEM with modified  $\text{Fe}_3\text{O}_4$  NP, after a plasma treatment. This was done using two methods: one was a direct deposition of NP after the surface activation and the other involved the creation of two layers of polyelectrolytes in order to increase the surface area and charges. Both methods originated a stable coating, but SEM images showed that the membranes were not fully covered, which means that there is space for improvement when it comes to the NP loading on the coating. Only the second method proved to be efficient when it comes to adsorption. After five adsorption-desorption cycles, this membrane treated  $0.23 \text{ mg.P/cm}^2$ . Despite not being in the same units, this value is comparable to the adsorption capacity of the nanoparticles,  $1.3 \text{ mg.P/g}$ . Even though this system has room for improvement, the membrane's performance is very promising, since it allows a very easy phosphate recovery. Moreover, its efficiency may improve after the scale-up since it will have a higher area of contact with the wastewater.

Further studies will need to be done on the membrane's surface modification, performance against competing ions and economical advantages against existing systems. Nevertheless, this project originated a very important result as it may be the first step to solving a major current sustainability problem. This system may allow an easy and economically feasible method for phosphate recovery, which is currently nonexistent.

## CHAPTER 6

### FUTURE WORK

With this project it was proved that the cation exchange membrane with modified  $\text{Fe}_3\text{O}_4$  coating has the capacity of easily adsorbing and desorbing phosphate. However, in order to ensure it is suitable for application, more steps should be taken. Namely, 1) to improve and optimize the coating process in order to increase the loading of NP on the membrane and thus the adsorption capacity; 2) to test the membrane's performance in the presence of competing ions, with the aim of proving its phosphate selectivity; 3) to study the coating's stability over a longer period of time of usage. If the membrane proves to be promising after these steps are taken, a scale-up of the process might be in order.

The modification and the choice of nanoparticle size should also be investigated. The performance of a membrane coated with bare nanoparticles and a membrane coated with modified nanoparticles should be compared. This will confirm whether the modification has a significant impact on adsorption performance. Also, in order to broaden the application possibilities of the membrane, different pH should be studied. As it is known, different forms of phosphate are present at different pH, therefore the performance of the membrane is strongly tied with the pH conditions.

This project has also illuminated the path for some side-projects, the most important being the study of the coacervates system. The optimal ratio between PSS and PHMG can be further investigated and an easy method of recovering the phosphate might also be found. For instance, a chromatography column with such a loading could prove to be a great system, or even the immobilization of these coacervate particles between two porous membranes.



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## APPENDIXES

### A.1 Phosphate Speciation

In order to calculate how much of each phosphate species is present at the required pH, the  $K_a$  values of each two species was required. []

Equilibrium equations at 25°C:

$$K_{a_{H_3PO_4}} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \approx 7.59 \times 10^{-3} \quad (A.1)$$

$$K_{a_{H_2PO_4^-}} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \approx 7.17 \times 10^{-8} \quad (A.2)$$

$$K_{a_{HPO_4^{2-}}} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} \approx 4.79 \times 10^{-13} \quad (A.3)$$

Phosphate balance:

$$[PO_4^{3-}] = \frac{K_{a_{HPO_4^{2-}}}K_{a_{H_2PO_4^-}}K_{a_{H_3PO_4}}[PO_4]_{tot}}{K_{a_{HPO_4^{2-}}}K_{a_{H_2PO_4^-}}K_{a_{H_3PO_4}} + [H^+]K_{a_{H_2PO_4^-}}K_{a_{H_3PO_4}} + [H^+]^2K_{a_{H_3PO_4}} + [H^+]^3} \quad (A.4)$$

$$[HPO_4^{2-}] = \frac{[H^+]K_{a_{H_2PO_4^-}}K_{a_{H_3PO_4}}[PO_4]_{tot}}{K_{a_{HPO_4^{2-}}}K_{a_{H_2PO_4^-}}K_{a_{H_3PO_4}} + [H^+]K_{a_{H_2PO_4^-}}K_{a_{H_3PO_4}} + [H^+]^2K_{a_{H_3PO_4}} + [H^+]^3} \quad (A.5)$$

$$[H_2PO_4^-] = \frac{[H^+]^2K_{a_{H_3PO_4}}[PO_4]_{tot}}{K_{a_{HPO_4^{2-}}}K_{a_{H_2PO_4^-}}K_{a_{H_3PO_4}} + [H^+]K_{a_{H_2PO_4^-}}K_{a_{H_3PO_4}} + [H^+]^2K_{a_{H_3PO_4}} + [H^+]^3} \quad (A.6)$$



$$[\text{H}_3\text{PO}_4] = \frac{[\text{H}^+]^3 [\text{PO}_4]_{\text{tot}}}{K_{\text{aHPO}_4^{2-}} K_{\text{aH}_2\text{PO}_4} K_{\text{aH}_3\text{PO}_4} + [\text{H}^+] K_{\text{aH}_2\text{PO}_4} K_{\text{aH}_3\text{PO}_4} + [\text{H}^+]^2 K_{\text{aH}_3\text{PO}_4} + [\text{H}^+]^3} \quad (\text{A.7})$$

By dividing both sides of the equations by  $[\text{PO}_4]_{\text{tot}}$ , a ratio of the presence of each species is obtained. Afterwards, by plotting each of these ratios with the pH, a graph like shown in Figure 2.1 can be obtained.

## A.2 PHMG Characterization

PHMG was delivered as white crystals. It was analyzed with FTIR to confirm its authenticity, and for future comparison reasons.

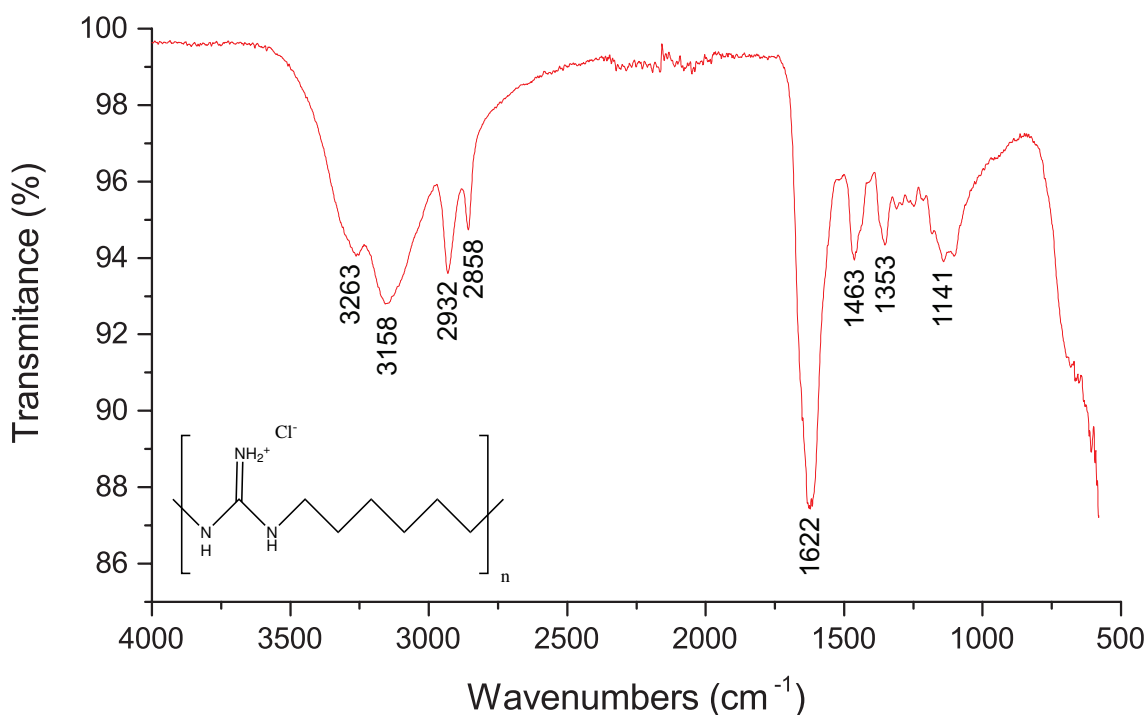


Figure A.1: FTIR analysis of PHMG

A broad band can be observed between 3500 cm<sup>-1</sup> and 2700 cm<sup>-1</sup>, with a peak at 3158 cm<sup>-1</sup> that is related to the stretching of water's O-H bond. At 3263 cm<sup>-1</sup>, although partially covered by the O-H band, a peak is present and it corresponds to the stretching of N-H bonds. Two peaks can be also observed for the asymmetric and symmetric stretching of C-H bonds, at 2932 cm<sup>-1</sup> and 2858 cm<sup>-1</sup>, respectively. The peak at 1622 cm<sup>-1</sup> corresponds to the stretching of C=N bond from the Gu group. At 1463 cm<sup>-1</sup> the bending movement of C-H bonds can be observed. The peaks at 1353 cm<sup>-1</sup> and 1141 cm<sup>-1</sup> correspond to the stretching of the C-N bonds, of the Gu group and the bonds between the Gu group and hexane moiety, respectively.

## A.3 Estimation of Adsorption Capacities

### A.3.1 PHMG Surface

First, the surface area of PHMG was calculated. For this, the bond length between each atom of its structure (Figure 2.3) and the angle between them was taken into account.

[]

Table A.1: Bond lengths of PHMG.

| Bond         | C-C   | C-N (sp3) | C-N (sp2) | C=N  | C-N (vertical) | N-H (bottom) | N-H (top) |
|--------------|-------|-----------|-----------|------|----------------|--------------|-----------|
| Length (Å)   | 1.533 | 1.47      | 1.47      | 1.16 | 1.47           | 0.99         | 0.99      |
| Angle (°)    | 111.9 | 109       | 120       | -    | 120            | -            | 120       |
| Number       | 5     | 2         | 2         | 1    | 1              | 1            | 1         |
| Distance (Å) | 1.270 | 1.197     | 1.273     | 1.16 | 0.735          | 0.990        | 0.495     |
| Total (Å)    | 6.351 | 2.393     | 2.546     | 1.16 | 0.735          | 0.990        | 0.495     |

By adding the result of the first 3 columns, the length of a PHMG monomer can be obtained, and by adding the result of the last 4, the height is obtained. Multiplying the height by the length an estimate of the area is obtained. This value is  $\approx 0.38 \text{ nm}^2$ .

### A.3.2 Fe<sub>3</sub>O<sub>4</sub> Nanoparticles

If we consider that the NP are spherical and that they have a diameter (d) of 75 nm (it varies between 50 and 100) we can easily obtain the surface area. Equation A.8a shows how to calculate the surface area of a sphere.

The obtained surface area was  $1.77 \times 10^4 \text{ nm}^2$ . By dividing this area by the surface area of a PHMG (assuming complete, monolayered coverage) it is possible calculate the number of monomers of PHMG on a single NP and thus, the amount of NP required to adsorb 1 mol of phosphate. Afterwards, by calculating the volume of a single NP (Equation A.8b), and knowing the density,  $5.17 \text{ g/cm}^3$ , we can obtain the the mass required to adsorb one mol of phosphate.

$$S = \pi \times d^2 \quad (\text{A.8a})$$

$$V = \frac{4}{3} \pi \left(\frac{d}{2}\right)^2 \quad (\text{A.8b})$$

In conclusion, to treat the wastewater of FrieslandCampina which contains  $\approx 0.01 \text{ M}$  of phosphate, a concentration of  $5.56 \text{ g/L}$  of Fe<sub>3</sub>O<sub>4</sub> NPs would be required.

### A.3.3 CEM coated with PHMG Entangled by Acrylate

The membrane used in this project has a diameter of 7 cm. Also, it was created with a solution that contained 20% PHMG. Therefore, it was assumed that the membrane

had a surface coverage of 20%, meaning that there is an available area of  $7.7\text{cm}^2$ . Taking the superficial area of each PHMG molecule into account, it was concluded that this membrane can adsorb  $3.3 \times 10^{-9}$  mol of phosphate. This means that it can treat 0.33 of wastewater. This result is discussed in section 4.3.1.

## A.4 Electrical Resistance of PHMG@CEM

Table A.2 shows the values of ER of each slope represented on figure 4.13, in section 4.3.3. It also shows the results for the same experiment performed on the same membrane in two different days (PHMG@CEM\_3), and on another membrane (PHMG@CEM\_2) which was cut from the same original piece. It can be observed that the second slope is the one that behaves in a more similar fashion to a CEM and that the two slopes become less visible over the course of the measurements. Because the experiments performed on the same membrane have different results, it can also be concluded that this effect is strongly correlated with sample history.

Table A.2: ER values of the two slopes over 15th consecutive runs.

| Experiment         | Electrical Resistance ( $\Omega \cdot \text{cm}^2$ ) |         |         |         |         |          |          |          |        |  |  |  |  |  |  |
|--------------------|------------------------------------------------------|---------|---------|---------|---------|----------|----------|----------|--------|--|--|--|--|--|--|
|                    | 1st run                                              | 3rd run | 5th run | 7th run | 9th run | 11th run | 13th run | 15th run |        |  |  |  |  |  |  |
| CEM                | 7.35                                                 |         |         |         |         |          |          |          |        |  |  |  |  |  |  |
| 20/03 – PHMG@CEM_3 | 1st slope                                            | 377.98  | 234.82  | 179.25  | 149.54  | 126.63   | 114.63   | 105.47   | 98.25  |  |  |  |  |  |  |
|                    | 2nd slope                                            | 5.21    | 11.54   | 12.39   | 12.84   | 13.14    | 13.34    | 13.55    | 13.65  |  |  |  |  |  |  |
| 21/03 – PHMG@CEM_2 | 1st slope                                            | 131.44  | 69.33   | 55.99   | 49.09   | 44.77    | 41.72    | 39.47    | 37.65  |  |  |  |  |  |  |
|                    | 2nd slope                                            | 3.98    | 9.81    | 10.64   | 11.10   | 11.40    | 11.61    | 11.75    | 11.86  |  |  |  |  |  |  |
| 21/03 – PHMG@CEM_3 | 1st slope                                            | 530.19  | 224.76  | 173.05  | 147.07  | 131.02   | 119.39   | 110.74   | 103.80 |  |  |  |  |  |  |
|                    | 2nd slope                                            | 6.11    | 12.26   | 12.96   | 13.30   | 13.52    | 13.66    | 13.74    | 13.82  |  |  |  |  |  |  |

Figure A.2 shows how the values tend to reach a plateau, over the consecutive runs.

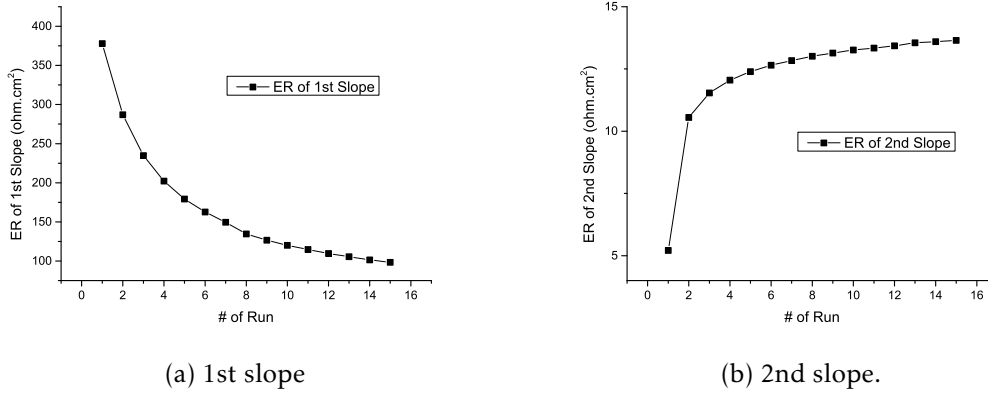


Figure A.2: ER membrane PHMG@CEM\_3, first experiment

## A.5 Characterization of CEM with Modified $\text{Fe}_3\text{O}_4$ Coating

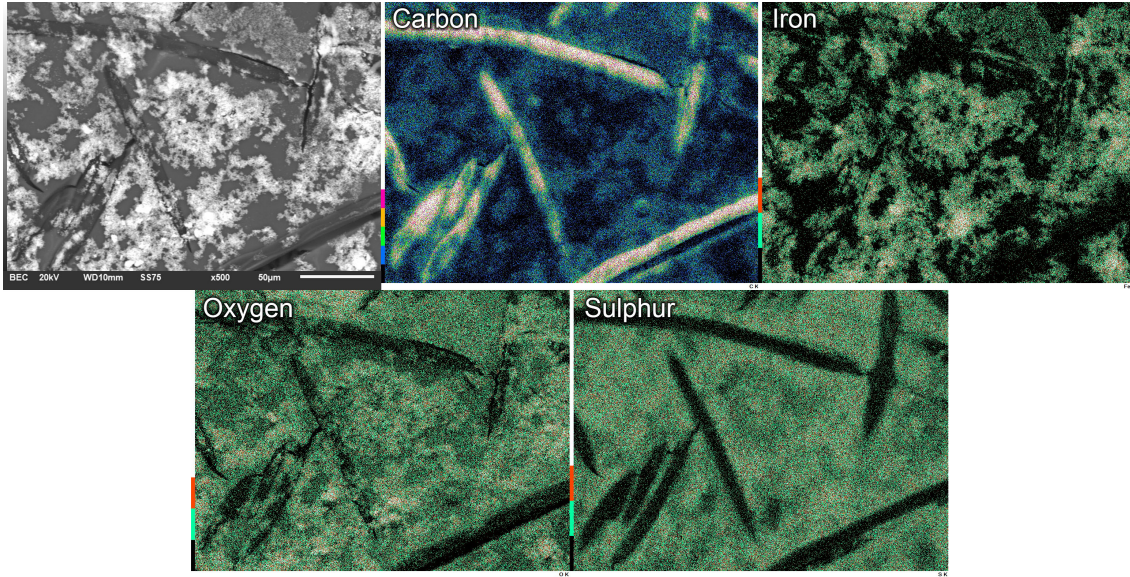


Figure A.3: EDS mapping of MNP@CEM.

On figure A.3 it can be observed that this coating also does not fully cover the membrane. This indicates that there is space for optimization in the coating process. The loading of NP can be further increased to enhance the adsorption capacity of the membrane. However, it allows the conclusion that the coating was successful. On the third picture, a high concentration of iron can be observed, and on the 2<sup>nd</sup> and 5<sup>th</sup> pictures, absence of intensity in carbon and sulphur in the coated areas can be seen. Oxygen is more present on the coated areas as the NP are composed of iron oxide, but it can also be found in the composition of the membrane, as it has sulfonated groups. Nitrogen was



also detected but it was assumed to be part of a contamination, either on the membrane or the apparatus itself.

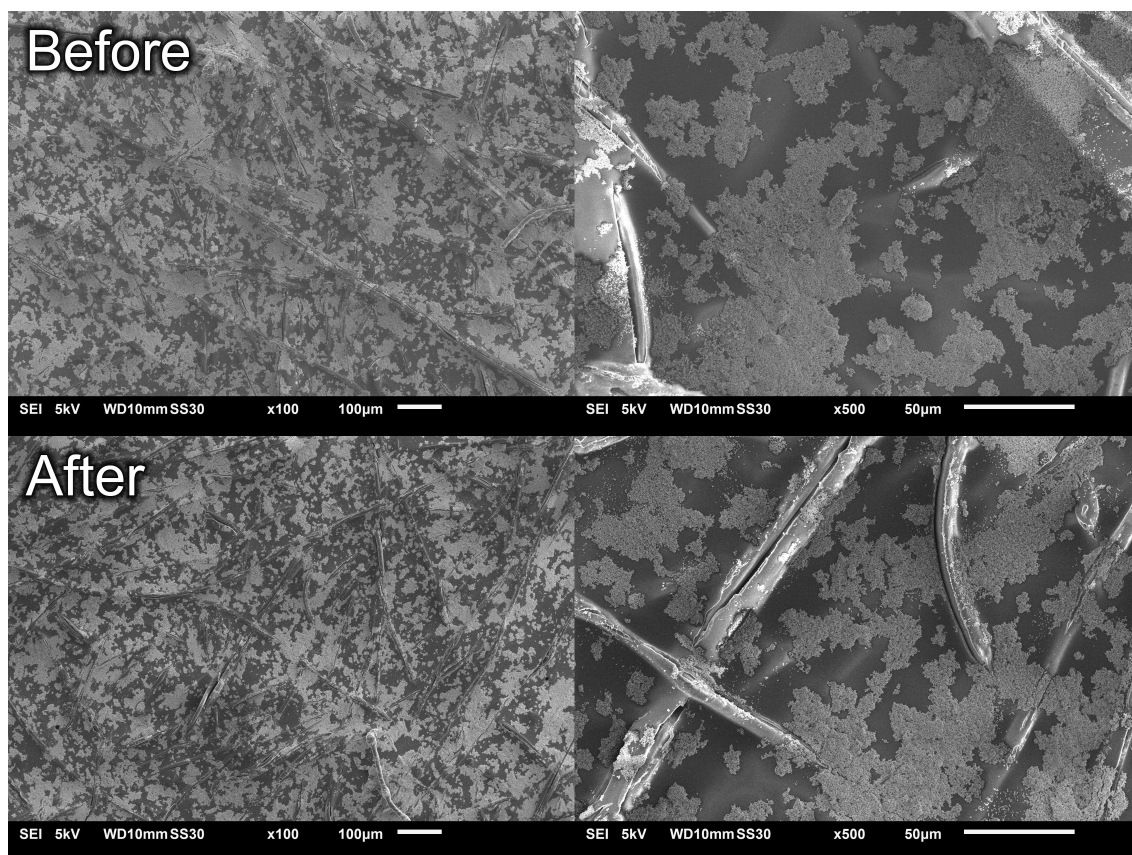


Figure A.4: SEM image of NP@CEM before and after water contact.

Figure A.4 shows the SEM images before and after contact with water. Although the image was not taken at exactly the same spot, the conclusion that the NP count on the membrane has not diminished by the test can be drawn.