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Master’s Thesis

Preconcentration of heavy metals by Donnan dialysis

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UNIVERSITY OF OULU **Abstract of thesis**

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Abstract

The aim of this study was to investigate the applicability of Donnan dialysis for the preconcentration of iron from synthetic wastewaters. Moreover, the competition between magnesium and calcium on the preconcentration of iron as well as the effect of adding a complexing agent (EDTA) on the enrichment factor of iron were also studied.

Heavy metals are of great concern because of their extreme toxicity, even at low traces. Even with the sensitivity and selectivity of existing analytical techniques, direct determination of heavy metals is not always possible due to the low concentration of the ions. For this reason there is a great necessity for the preconcentration of heavy metals prior to their determination.

Donnan dialysis experiments were performed in a laboratory scale with a dialysis cell, according to an experimental design created with the MODDE 8.0 software also used for modelling the process. Experiments were conducted with a full factorial design, which consisted in 11 experiments, three (3) of were central points.

Donnan dialysis was proved to be a feasible technique to preconcentrate iron from synthetic wastewater samples. However, the metal competition decreased the enrichment factors of the main metal to be preconcentrated and the presence of the complexing agent in the receiver side did not affect the preconcentration process.

Microscope images were taken to study the membrane structure. Membrane fouling caused by the absortion of iron explained the low enrichment factors and poor reproducibility of the process. Moreover, it was observed that the regeneration process was not good enough to regenerate properly the membrane.

Different studies were done with another membrane and with another metal such as copper; nonetheless similar results were achieved.

Key words: Donnan dialysis, preconcentration, iron, magnesium, calcium, EDTA.

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EXPERIMENTAL PART

Symbols

a	Activity [mol$^{/}$m^{3}]
C_0	Initial feed concentration of the analyte i [mol/dm^{3}]
C_i	Receiver concentration of the i analyte [mol/dm^{3}]
C_t	Feed concentration at time t [mol/dm^{3}]
F	Faraday constant [As/eq^{1}]
F_i	Feed solution of the experiment i [mg/dm^{3}]
J	Flux [mol/m^{2}s^{1}]
N_i	Experiment number i
Q^2	Variation of the response predicted by the model [%]
R	Gas constant [J/°K^{1}mol^{1}]
R^2	Variation of the response explained by the model [%]
R_i	Receiver solution of the experiment i [mg/dm^{3}]
T	Temperature [°K]
z	Valance [eq/mol^{1}]
η	Electrochemical potential [J/mol^{1}]
φ	Electrical potential [V]

Abbreviations and Nomenclature

AAS	Atomic absorption spectroscopy
ANOVA	Analysis of variance
BLM	Bulk liquid membranes
CMC	Critical micelle concentration
DD	Donnan dialysis
DF	Degrees of freedom
DNA	Deoxyribonucleic acid
EDTA	Ethylenedinitrilo-tertaacetic acid
EF	Enrichment factor
ELM	Emulsion liquid membrane
FIB	Focused ion beam
F_{value}	F-distribution value
ICP	Inductively coupled plasma
ICP-AES	Inductively coupled plasma atomic emissions spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
LPR	Liquid phase polymer based retention
MEUF	Micellar-enhanced ultrafiltration
MF	Microfiltration
MPT-AES	Microwave plasma torch-atomic emission spectrometry
MS	Mean square
NF	Nanofiltration
P	Probability
PEI	Polyethilenimine
RF	Recovery factor
RO	Reverse osmosis
SD	Standard deviation
SEM	Scanning electron microscope
SLM	Supported liquid membrane
SS	Sum of squares
UF	Ultrafiltration
WHO	Worth Health Organization

1 Introduction

Heavy metals are of great concern because of their extreme toxicity, even at low traces. Since heavy metals cannot be degraded or destroyed, they bioaccumulate over time meaning they can be ingested by humans through food, water and air. Due to their accumulation in sediments and organism, they can easily be transferred into the food chain.

Even with the sensitivity and selectivity of existing analytical techniques, direct determination of heavy metals is not always possible due to the low concentration of the ions. For this reason there is a great necessity for the preconcentration of heavy metals prior to their determination.

Membrane technologies such as Donnan dialysis (DD) have gained considerable interest as a means of sample preparation in analytical chemistry. DD is an energy saving process compared to the conventional process since it does not use electrical current. It is also a continuous process, allowing easier operations. Therefore, in this study, DD was chosen as the method to preconcentrate heavy metals prior to their determination.

In DD, the preconcentration of metals from mixtures of different ions with the same charge can be obtained, but without any preference within the metals. Hence, to achieve the separation towards a desired metal a complexing agent is needed.

The resulting data was analyzed with statistical experimental design. This helped to optimise the design of the experiments extracting maximum amount of relevant information with the fewest number of experimental runs. It also aided in delivering a valid and objective conclusion.

In this study, the preconcentration of iron by Donnan dialysis from synthetic wastewater samples was studied. The feed samples contained iron and different amounts of magnesium and calcium. EDTA was added as the complexing agent in the receiver side.

LITERATURE REVIEW

2 Heavy metals

2.1 Definition of a heavy metal

The term of “Heavy metal” has been widely used in scientific articles and legislation related to chemical hazards and the safe use of chemicals. Any official authority such as IUPAC (International Union of Pure and Applied Chemistry) has never defined the term “heavy metal”. However, different definitions have been published based on density, atomic weight, atomic number or other chemical properties, which sometimes can be contradictory (Duffus JH 2002). For instance, one definition based on the atomic weight classified magnesium as a heavy metal while another definition based also in the same property excludes alkaline earth metals and consequently excludes magnesium as a heavy metal (Hodson ME et al. 2004).

In addition, the term of “heavy metal” has been widely associated to a group of metals and semimetals (metalloids) which are contaminants, potential toxins or ecotoxins (Duffus JH 2002). In concentrations above the legal limits, heavy metals are harmful for the human organism due to their interference with the normal body biochemistry in the normal metabolic process; i.e. they act as a poison (Duruibe JO et al. 2007). Further, heavy metals bioaccumulate over the time and are dangerous for the body system which they enter through food, water and air. They also accumulate in sediments and organism from where they may be transfered into the food chain (Duruibe JO et al. 2007; Landaburu-Aguirre J et al. 2006).

Some legal regulations have published lists of “heavy metals” or priority hazardous substances which differ from each other. The European Commission published in Directive 2008/105/EC a reviewed list of priority substance, including the priority hazardous substances. The same commission establishes in Directive 2000/532/EC that any compound of antimony, arsenic, cadmium, chromium (VI), copper, lead, mercury, nickel, thallium and tin, classified as dangerous substances, are heavy metals.

2.2 Legislation regarding heavy metals

2.2.1 Priority substance

According to the Directive 2000/60/EC those substance which present a significant risk to or via the environment are classified as “Priority substance”. Among these substances, some are classified as “Priority hazardous substances” since they are toxic, persistent and liable to bio-accumulate or which give rise to an equivalent level of concern.

European Commission established in the Directive 2008/105/EC a reviewed list of priority substances, including the priority hazardous substances, with recommendations of the Directive 2000/60/EC. This list includes, as priority substances, cadmium, mercury, lead and nickel; the two first ones also classified as priority hazardous substances.

2.2.1.1 Lead (Pb)

Before the introduction of unleaded petrol, most of lead emissions to the environment were from petrol. Now lead can be found in mines, smelters, welding of lead painted metal and battery plants. Low and moderate exposures may occur in glass industry and areas near mines and smelters may have high levels of air lead pollution. Once in the air, lead can reach human food through the contaminated soil and water (Järup L 2003).

Lead causes a wide range of toxicity effects, one of the most serious is the teratogenic effect. Some examples of lead consequences are inhibition of the synthesis of haemoglobin; dysfunctions in the kidneys, joins and reproductive systems, cardiovascular system and acute and chronic damage to the central nervous system and peripheral nervous system. It a can also cause severe and permanent brain damage and a poor development of children’s brain resulting in a poor intelligent quotient (Duruibe JO et al. 2007).

According to the Directive 2008/105/EC the environmental quality standard for lead in terms of annual average, in surface waters including rivers, lakes and related artificial water or heavily modified water bodies, is 7.2 µg/dm^3 (2008/105/EC).

2.2.1.2 Cadmium (Cd)

Cadmium enters into the environment in a natural way through weathering of minerals, forest fires and volcanic emission but most is due to anthropogenic source such as mining and smelling operations or fuel combustion (Kaličanin BM 2009).

Cadmium is considered as one of the most harmful metal poison since it is toxic at extremely low levels. Long term exposures results in renal dysfunctions and high inhalations of dust and fumes can cause pulmonary problems such as obstructive lung disease and cadmium pneumonitis. Cadmium is also associated with bones defects (Duruibe JO 2007).

The symptoms of effects, depending of the seriousness of the expose, include nausea, vomiting, abdominal cramps, dyspnea and muscular weakness. A strong expose may cause pulmonary odema and death (Duruibe JO 2007).

The best known health problem due to cadmium has been the itai-itai disease where a long-term high level cadmium exposure caused severe damages to the Japanese population. For this reason the World Health Organization recommended a tolerable weekly intake of cadmium of 7 µg/kg body weight (Kaličanin BM 2009).

According to the Directive 2008/105/EC the environmental quality standard for cadmium system in surface waters or heavily modified water bodies depends of the hardness of the water. The most restrictive value is less than 0.08 µg/ dm^3 (2008/105/EC).

2.2.1.3 Mercury (Hg)

Mercury, as a raw material, exists in inorganic (metallic element) and organic (methyl) forms. The latter one is the most dangerous since it is very stable and absorbed by the body tissues. Metallic mercury is used in measuring apparatus as thermometers and in the chloralkali industry which uses mercury as the electrode to produce chloride. The inorganic mercury is converted to the stable form (methyl) and it enters in the human organism via food, fish and dental amalgam.

Metallic mercury may cause a lung damage with a severe exposure and a kidney damage but the damage is reversible after stopping the exposure. It also can give rise to spontaneous abortions, congenital malformations and gastrointestinal disorders. Its organic form may cause, among others, neurological disorders, total damage to the brain and central nervous system and are associated with congenital malformations (Duruibe JO et al. 2007).

According to the Directive 2008/105/EC the environmental quality standard for mercury in terms of annual average, in surface waters including rivers, lakes and related artificial water or heavily modified water bodies, is 0.05 µg/ dm^3 (2008/105/EC).

2.2.1.4 Nickel (Ni)

Modern industry uses nowadays metallic nickel and its compounds for a wide range of products such as in electroplating and electroforming industry and for productions of nickel-cadmium batteries and electronic equipment. They are also used in jewellery and medical prostheses. Tools, machinery, armaments, and appliances are produced with nickel alloys such as stainless steel. Production and recycling nickel-containing products as well as the production and processing of that element are the sources of environmental nickel contamination.

The exposure to nickel can cause adverse effects to the human health; the most common reaction is nickel allergies in the form of contact dermatitis. Due to nickel accumulation in the body, a chronic exposure can give to lung fibrosis and cardiovascular and kidney diseases which are the most serious problems related to nickel’s carcinogenic activity. For this reason, nickel compounds except metallic form, were classified as carcinogenic to humans (Denkhaus E et al. 2002).

According to the Directive 2008/105/EC the environmental quality standard for nickel in terms of annual average, in surface waters including rivers, lakes and related artificial water or heavily modified water bodies, is 20 µg/ dm^3 (2008/105/EC).

2.2.2 Essential trace metals with potential for toxicity

Despite the concern of some metals due to toxic properties there are some metals essential for survival and health of humans. A lower intake of such metals causes a risk of developing deficiency and with higher concentrations the metal turns to be toxic. Trace elements accepted as essential for humans' health include, among others, iron, zinc and copper (Nordberg GF et al. 2007, 6).

2.2.2.1 Iron (Fe)

Products of iron mining are present in many products ranging from structural elements in buildings to iron-based pigments and pharmaceuticals. Their ores are mined, processed to remove impurities, and smelted into the metallic iron. It is also possible to find iron in water, in soils, in air mainly on iron oxides, foodstuffs such as red meat or milk, and beverages such as beer.

Iron is an essential metal for the organism required for the growth and the survival of humans, due to its versatility as a biological catalyst. It is involved in many essential biological functions as well as oxygen transport, electron transfer and DNA synthesis. The most significant consequence of iron deficiency is anemia which causes defective hemoglobinization. This defect leads to the reduction of the production of red blood cells and haemoglobin; both of them are significant in the cellular functions of many organs.

On the other hand, an exposure to excess iron leads to numerous pathological consequences due to the iron limitation in the metabolism of humans. Inhalation of iron fumes can give rise to an increase in iron in the lungs with consequences such as siderosis or iron pneumoconiosis. Iron overload may also be developed due to an administration of excess iron parenterally like a blood transfusion or by a chronic ingestion which is not so common. The accumulation in organs including liver, pancreas and heart may cause cirrhosis, diabetes, heart dysfunctions and leads to death without treatment.

Just 10-20 mg/kg of elemental iron may produce symptoms such as nausea, vomiting, diarrhoea, and abdominal pain. Significant systemic toxicity requires, at least, 40 mg/kg and lethal doses is estimated to be 200-250 mg/kg of elemental iron (Nordberg GF et al. 2007, 578-595).

2.2.2.2 Zinc (Zn)

It is possible to find zinc in protective coating of other metals, in dye casting and the construction industry, as well as for alloys. Its inorganic compounds are used for automotive equipment, storage and dry batteries, and dental, medical and household applications. Beside in fungicides, organic zinc compounds are also used as topical antibiotics and lubricants (WHO, 2001).

The presence of zinc in water and air is due to both natural and anthropogenic sources. The main natural emission of zinc comes from erosion, just like igneous emissions and forest fires. The principal anthropologic sources of zinc are from mining, zinc production facilities, iron and steel production, corrosion galvanized structures, coal and fuel combustion, waste disposal, incineration, and the use of zinc-containing fertilizers and pesticides (WHO, 2001).

A zinc deficiency can lead, for example, to neurosensry changes, oligospermia, impaired neuropsychological functions, growth retardation, delayed wound healing, immune disorders and dermatitis. In the opposite side, an acute exposure can cause system dysfunctions that result in impairment of growth and reproduction and their clinical signs of toxicity are vomiting, diarrhoea, bloody urine, liver failure, kidney failure and anaemia (WHO 2001; Duruibe JO et al. 2007).

According to the World Health Organization (WHO), the estimated ranges of the daily dietary intakes of zinc are 5.6–10 mg/day for the infants and children until 11 years, 12.3–13.0 mg/day for children ages between 12 and 19 years, and 8.8–14.4 mg/day for adults. From drinking water, it is estimated to be < 0.2 mg/day (WHO 2001).

2.2.2.3 Copper (Cu)

Copper is present in many commercial products because of its versatility. Electrical wirings, pipes, valves, fittings, coins, cooking utensils and building materials are examples of copper use. It is possible to find its compounds in fungicides, insecticides and wood preservatives and in electropainting, azo-dye manufactures, petroleum refining, among others. Nutrients and colouring agents can contain copper compounds as food additives as well as in animal feeds which acts as a nutrient to support plant and animal growth.

A copper excess exposure can cause gastrointestinal bleeding, haematuria, intravascular haemolysis, metheamoglobinaemia, hepatocellular toxicity, acute renal failure and oliguria. It has also been reported that some compounds are carcinogenics. Despite copper toxicity at high concentrations the deficiency of this metal can cause symptoms such as headache, nausea, vomiting and diarrhoea.

Copper is found in the air, in the water and in the food but the latter one is the principal source of human expose. World Health Organization (WHO) recommends a copper intake for adults to range from 1 to 5 mg/day where just the range of 0.1–1 mg/day is contributed by drinking water (WHO 2004).

3 Preconcentration

Heavy metals are a natural part of the earth crust and will always be environmental contaminants since they cannot be degraded or destroyed (Duruibe JO et al. 2007). Due to their bioaccumulation, heavy metals are hazardous to human health and they are targeted by international environmental legislation (Landaburu-Aguirre J et al. 2006).

Legislation concerning heavy metals is more restrictive every day. Therefore, there is the necessity to develop new analytical techniques and methods capable of identifying and quantifying trace metals in water samples. Despite the good sensitivity of analytical tools, concentration levels required by regulation agencies might be near or above the detection limits. For this reason, analyses of trace elements require a preconcentration step prior to its determination. These methods can reduce the matrix effect improving detection limits and providing accurate results (Melquiades FL et al. 2007; Duran C et al. 2009).

Many preconcentration techniques have been used for the determination of metals including conventional techniques or membrane technology which is an attractive alternative.

3.1 Conventional heavy metal preconcentration techniques

There are different conventional heavy metal preconcentration techniques used nowadays, some of them are described in this chapter. They are liquid-liquid extraction, ion-exchange resins, cloud point extraction, coprecipitation and solid phase extraction.

3.1.1 Liquid-liquid extraction

Liquid-liquid extraction is based on the transfer of an analyte from the aqueous sample to a water-immiscible solvent. As it is shown in Figure 1, a small volume of organic phase is placed in a conventional cuvette and then a large volume of sample, the aqueous phase, passes through the small organic volume in order to achieve a gradual enrichment and a high preconcentration factor (Pena-Pereira F et al. 2009; Agudo M et al. 1993).

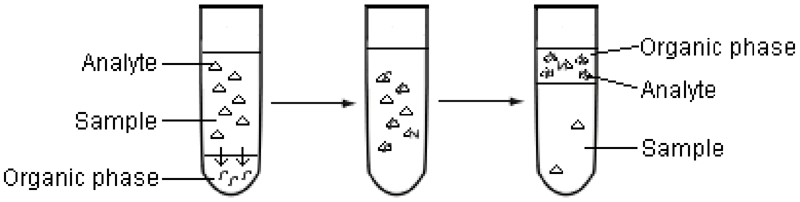

Figure 1. Schematic drawing illustrating the liquid-liquid extraction process.

Liquid-liquid extraction is an expensive method due to the large volume of solvent needed which are expensive and toxic to the environment and the public health. The latter fact increases the cost of this technique through the performance of environmental protection regulations. In addition, liquid-liquid extraction is a time-consuming technique due to shortcomings such as the emulsion formation or the use of large amounts of samples (Pena-Pereira F et al. 2009; Huddleston JG et al. 1998).

This method is being widely used for the development of separation processes. Ferreira et al. reported recovery factors in the range of 88 to 110 % and 98 to 115 % for cadmium and lead, respectively, using ethanol as a solvent (Ferreira SLC 2007).

3.1.2 Ion-exchange resins

Ion-exchange resin is another separation technology used in numerous industrial applications such as in water treatment, food industry, processing of pharmaceuticals, waste water treatment, purification of chemicals and in hydrometallurgy.

When a solution of an electrolyte comes into contact with an ion-exchange resin, ions of a given charge are fixed by the resin while an equivalent quantity of ions of the same charge are released by the resin into the solution. Resins are useful to remove all ions from solution, thus purifying the solvent, to capture and recover some of the ions by eluding the resin, or to remove specific ions and eventually replacing them with other ions in order to give the desired composition to the solution (Zaganiaris EJ 2009, 19-21).

Ion-exchange resins are broadly used for preconcentration of trace elements prior to their determination. Kong et al. studied the determination of cobalt and nickel by MPT-AES with previous preconcentration of these ions by a cation-exchange resin. That resin achieved recovery of 95–104 % for cobalt and nickel ions from tea samples. Due to the preconcentration step, the analytical method offered a low limit of detection, good sensitivity and precision (Kong X et al. 2007).

3.1.3 Cloud point extraction

Most non-ionic surfactants in aqueous solutions have the property to form micelles and become turbid when heated to a temperature called the cloud point temperature. Above the cloud point, the solution is separated into two phases, a surfactant-rich phase in a small volume and a poor phase with a surfactant concentration close to the critical micelle concentration (Figure 2). The analytes can be separated and concentrated in the small volume of the surfactant-rich phase due to solubilization of analytes into to the hydrophobic core of the micelles (Manzoori JL et al. 2002).

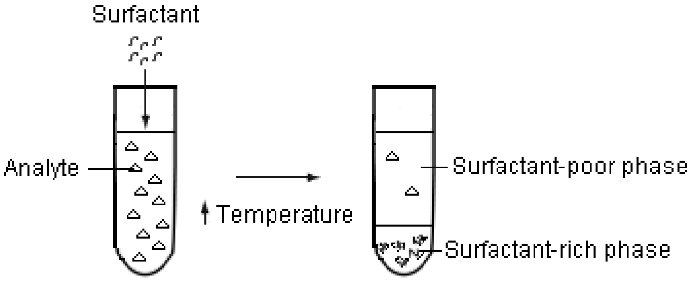

Figure 2. Schematic drawing illustrating the cloud point extraction process.

Cloud point extraction is a versatile and simple technique that reduces the consumption of large amounts of toxic solvents and thus the disposal costs and extraction time are reduced. In addition, it can lead to higher recovery efficiency and a large preconcentration factor because the presence of surfactant can minimize losses of analytes due to their adsorption onto the container. It has been reported that it is possible to reach a preconcentration factor of nickel and cadmium of around 100 % in stock standard solutions of Ni(II) and Cd(II) (Afkhami A et al. 2006; Manzoori JL et al. 2004).

This method has been successfully used for preconcentration of lead and cadmium, removal of organic pollutants, such as pesticides, polychlorides and phenols, and as an extraction technique prior to the determination of vitamins, drugs and proteins. It is also used for the treatment of contaminated environmental compartments, particularly water and soils (Maranhão TA et al. 2005).

3.1.4 Co-precipitation

Co-precipitation is a useful technique for the recovery of trace metals and to achieve sufficient separation factors for alkali and alkaline earth elements. It is employed when direct precipitation cannot separate the desired metal ions due to their low concentrations, and characterised by the formation of insoluble compounds (Bulut VN et al. 2008).

Metals, at trace levels, react with an organic or inorganic compound and thereby are retained onto the precipitate surface or precipitate structure via various mechanisms, forming a solid phase. The major precipitate reacts with other metals to form chalets and finally solid particles are separated by filtration or centrifugation from the aqueous media and re-dissolved in acid or in an organic solvent (Komjarova I 2 et al. 2006; Bulut VN et al. 2008).

In order to form a precipitate, large amounts of a carrier element together with organic co-precipitants are needed. This may cause contamination and background adsorption, hence creating interferences during analysis. Despite of the drawbacks, co-precipitation is used for its simplicity, high preconcentration factor, low consumption of organic solvents and short analysis time for the procedures (Bulut VN et al. 2008; Bulut VN et al. 2010).

Peker et al. studied a co-precipitation system for the separation-preconcentration of lead, copper, nickel, cobalt, cadmium, magnesium ions by dysprosium hydroxide from a table salt and natural water samples. The recoveries achieved in all the systems studied were higher than 90 % (Peker DSK et al. 2006).

4 Membrane technology

The membrane technology is characterised by the use of a membrane to accomplish a particular separation. A membrane is a permselective barrier existing between two homogeneous phases and has the ability to transport one component more readily than another because of difference in physical and/or chemical properties between the membrane and the permeating components (Mulder M 1997, 14, 280).

The transport takes place as a result of the driving force acting on the components in the feed. The driving force can be a pressure difference, a concentration difference or an electrical potential difference (Mulder M, 1997, 280).

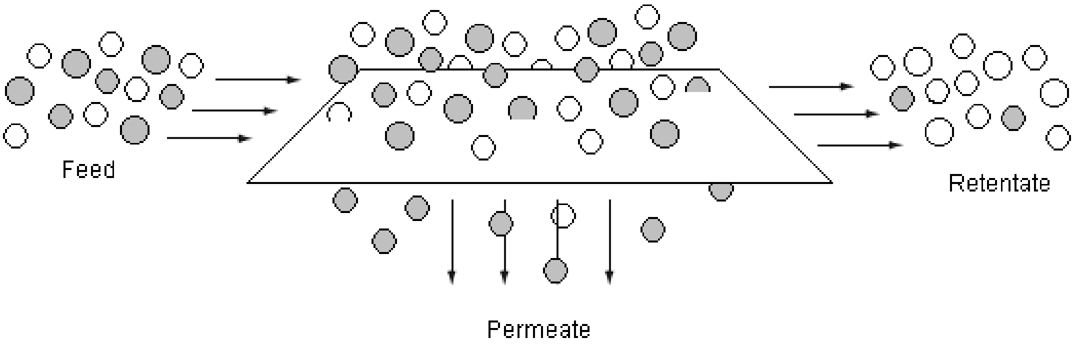

Figure 3. Schematic drawing illustrating the membrane process (Mulder M 1997, 7).

In pressure driven membrane processes, pressure is needed to achieve the permeation of the solvent and various solute molecules through the membrane, whereas other molecules or particles are rejected (Figure 3). As the size (or molecular weight) of the particle or molecules to be rejected by the membrane diminishes, the pore size in the membrane must become smaller. This implies that the resistance of the membrane to mass transfer increases and hence the applied pressure has to be increased to obtain the same flux (Mulder M 1997, 284-285).

The existing pressure driven membrane processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Table 1 summarizes a comparison of these different pressure driven processes (Mulder M 1997, 284-303).

Table 1. Comparison of various pressure driven processes (Mulder M 1997, 284-303).

Membrane process	Applied overpressure [MPa]	Pore size [nm]
Microfiltration (MF)	< 0.2	50–100000
Ultrafiltration (UF)	0.1–1	1–100
Nanofiltration (NF)	1–2	< 2
Reverse osmosis (RO)	2–10	< 2

Microfiltration is used in all kinds of analytical laboratories or in the sterilisation and clarification of beverages. Ultrafiltration is used for separating high molecular components from low molecular components in fields such as food, diary, textile or chemical industries. Both techniques are used in water treatment as well as nanofiltration and reverse osmosis which are used in desalination of brackish and seawater (Mulder M 1997, 284-303).

Processes that use concentration as the driving force are those that the substance diffuses spontaneously from a high to a low chemical potential through the membrane. Processes that use concentration driving force are gas separation, vapour permeation, pervaporation, dialysis, diffusion dialysis, carrier mediated processes and membrane contactors (Mulder M 1997, 307).

In processes, where electrical potential difference acts as the driving force, the ability of the charged ions or molecules to conduct an electrical current is used. When a potential difference is applied, the cations migrate to the cathode whereas the anions migrate to the anode. Uncharged molecules are not affected by this driving force and hence electrically charged components can be separated from their uncharged counterparts. The combination of an electrical potential difference and electrically charged membrane can be used in electrodialysis for desalination of water or production of salt, membrane electrolysis for the production of chlorine and caustic soda and bipolar membranes for the production of sulphuric acid and sodium hydroxide. In all the cases the charge membrane constitutes a selective barrier where the ions are either repelled or transported depending on the ionic charge and membrane charge (Mulder M 1997, 380-391).

4.1 Membrane module

In industrial scale, large areas of membranes are often required to perform the separation, thus it is necessary to have an efficient packaging. These packages are called membrane modules.

Different kinds of modules based in flat and tubular geometries are possible. Flat configuration includes plate-and-frame and spiral-wound modules whereas tubular, capillary and hollow fiber modules involve tubular membranes (Mulder M 1997, 465).

4.1.1 Flat membrane configuration

Plate-and-frame modules comprise a multiple flat sheet membrane in a sandwich arrangement consisting of the support plate, the membrane, and the channel spacer or separator. The modules can be pressure sealed with electrodialysis stacks, or be designed as cassettes. In the cassettes modules, membrane elements can be removed and replaced individually without the necessity of disassembling the whole module. In most of the flat plates system the feed flow is distributed among the different channels at one end of the device, and the retentate is collected at the opposite end (Judd & Jefferson 2003, 274; Zeman LJ et al. 1996, 336-338).

Spiral-wound module (Figure 4) is a plat-and-flame system wrapped around a central collection pipe (Mulder M 1997, 468). The membrane element consists in two membrane sheets separated by a permeable mesh, which defines the region of the permeate flow. Three of the membrane edges are sealed while the open side is attached to a central perforated tube, which collects the permeate product from inside the membrane element. The membrane is rolled up around the central tube to produce a spiral where feed solution is fed into one of the ends and the retentate is collected out of the other end (Zeman LJ et al. 1996, 339; Judd & Jefferson 2003, 27).

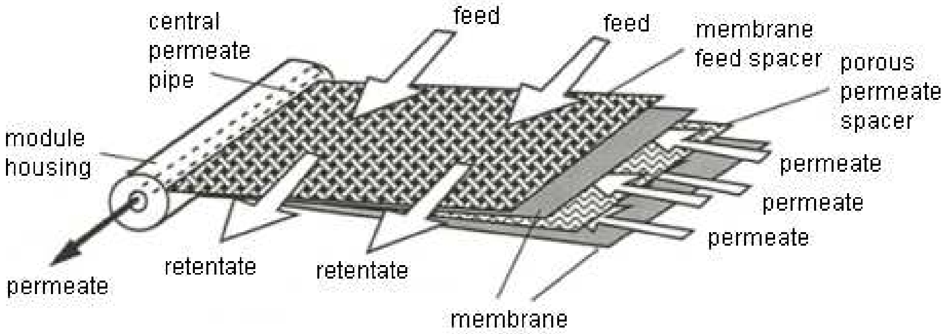

Figure 4. Scheme of a spiral-wound module (Mulder M 1997, 468).

4.1.2 Tubular configuration

Tubular membranes (Figure 4) are not self-supporting. Therefore, the membranes have to be placed inside a porous support tube made of fiber glass, ceramic, plastic, or stainless steel. The feed solution flows through the centre of the tubes, while the permeate flows radially outward through the porous support tube into the module housing, where it is collected. Mainly tubular or plate-and-frame modules are used in dairy applications (Zeman LJ et al. 1996, 334; Mulder M 1997, 469-474).

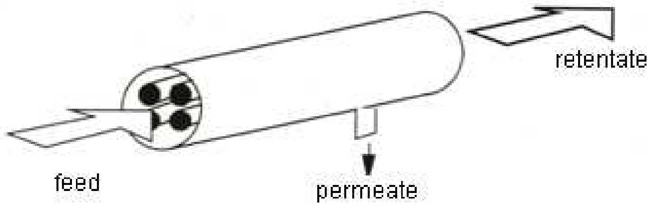

Figure 5. Scheme of a spiral-wound module (Mulder M 1997, 470).

Capillary modules consist of a large number of capillaries assembled together in a module and as the tubular membrane they are not self-supporting. In these modules two types of modules can be considered (see Figure 5). In the first one, the feed solution enters through the capillary and the permeate is collected outside of the membrane. In the second one, the feed solution enters through the shell side of the capillaries and the permeate passes into the fiber bore (Mulder M 1997, 470-471).

In hollow fiber modules the assembling of the module is the same as in the capillary modules. However, hollow fiber modules have the higher packing density and the lowest cost. As in the case of capillary modules, the feed solution can enter inside the fiber (inside-out) or on the outside (outside-in). In Figure 6 both types of modules are represented. This configuration is used as well as spiral-wound modules in seawater desalination, gas separation and pervaporation (Mulder M 1997, 472-474).

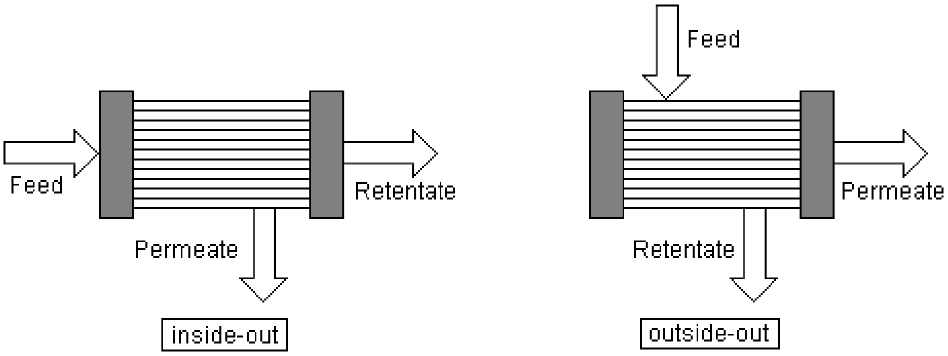

Figure 6. Schematic drawing of the two types of capillary module/hollow fiber module (Mulder M 1997, 471).

Despite being the most expensive configuration, the tubular module is well suited for applications with a high fouling tendency because of its good process control and ease of membrane cleaning. In contrast, hollow fiber modules are very susceptible to fouling and are difficult to clean. Therefore, pretreatment of the feed stream is important in hollow fiber systems (Mulder M 1997, 473).

4.2 Concentration polarisation and membrane fouling

Flux decline has a negatively influence on the economics of a given membrane operation, and for this reason measures must to taken to reduce it (Mulder M 1997, 417). The principal phenomena of flux decline are concentration polarisation and membrane fouling.

Figure 7 displays the concentration profile in concentration polarisation. Concentration polarisation is the term used to describe the tendency of the solute to accumulate at the membrane-solution interface within a concentration boundary layer, or liquid film. This layer contains a near-stagnant liquid where the only mode of transport within this layer is diffusion. Diffusion is slower than convective transport (Judd & Jefferson 2003, 36).

The membrane has a certain retentivity for the solute while the solvent can permeate more or less freely. The retained solutes can accumulate at the membrane surface where their concentration will gradually increase. Such a concentration build-up will generate a diffusion back-flow to the bulk of the feed, and after a given period of time steady-state conditions will be established. The convective solute flow to the membrane surface will be balanced by the bulk and the diffusive flow from the membrane surface to the bulk. So as a consequence of the flux decline, steady-state is reached when the convective transport of solute to the membrane is equal to the sum of the permeate flow and the diffusive back transport of the solute (Mulder M 1997, 418-419).

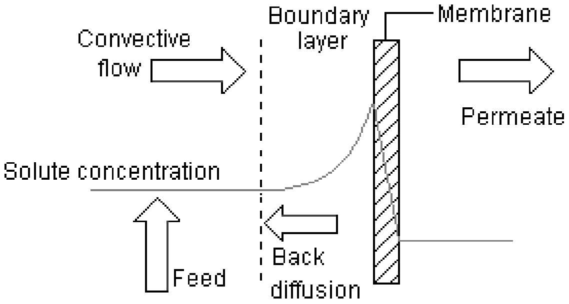

Figure 7. Concentration profile under steady-state conditions in concentration polarisation (Judd S 2003, 36).

Membrane fouling may be defined as the (ir)reversible deposition of retained particles, colloids, emulsions, suspensions, macromolecules, salts, etc. on or in the membrane. That retention may occur due to adsorption, pore blocking, precipitation and cake formation (Mulder M 1997, 448).

The accumulation of foulants onto the membrane surface (Figure 8) becomes in a fouling layer, which hinders the pass of the ions through the membrane. As a consequence, the performance of the membrane decreases over the time. Besides flux reduction it entails additional cost due to the membrane cleaning and replacement (Wang LK et al. 2011, 5).

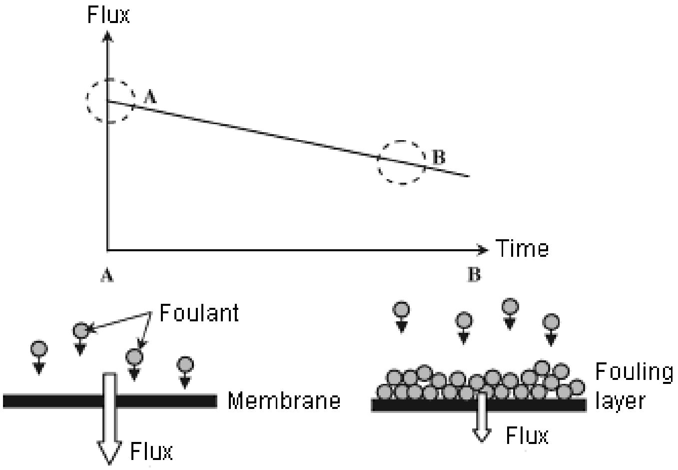

Figure 8. Decline of permeate flux with fouling development on membrane surface (Wang LK et al. 2011, 104).

Membrane fouling is a very complex phenomenon, which depends on physical and chemical properties such as concentration, pH, ion strength and component interactions; the nature of the membrane such as hydrophobicity, pore size, porosity; and operating conditions as temperature or cross-flow velocity (Mulder M 1997, 448; Wang LK et al. 2011, 5).

Because of the complexity of the phenomenon, the methods for reducing fouling can only be described very generally. Fouling reduction can be achieved by a proper pretreatment method such as heat treatment, pH adjustment or addition of complexing agents. It can also be reduced with a change of the membrane for an appropriate one or with an optimum cleaning (Mulder M 1997, 454).

4.3 Membrane technology for preconcentration

Membrane processes are designed to carry out physical or physicochemical separation. Water and wastewater treatment processes are the applications for membranes since they offer three clear advantages over conventional techniques. It is possible to separate the metal ions without requiring a phase change. Normally there is no need to regenerate the cycles since it can operate continuously due to no accumulations in the process. Finally, usually no chemical addition is required (Judd & Jefferson 2003, 7-9).

Membrane processes within industrial sectors are widely used and well established in many cases. For example, reverse osmosis and ultrafiltration are essential for providing ultrapure water in pharmaceutical industry, in semiconductor fabrication plants and for polishing the rise water. It is also used, although less established, for the treatment of industrial effluents for discharge (Judd & Jefferson 2003, 9-1).

Membrane methods for separation have generally been associated with industrial and technological developments such as in recycling wastewater treatment processes employing electrodialysis. However, they have also gained considerable interest as a means of samples preparation in analytical chemistry since they are used as a preconcentration technique prior to the determination of trace elements (Pyrzynska K 2006).

Various membrane preconcentration methods are considered, namely, liquid membrane techniques, solid phase extraction, micellar-enhanced ultrafiltration, liquid phase polymer based retention/polymer-enhanced ultrafiltration and Donnan dialysis.

In membrane technology the efficiency of the separation and the preconcentration is describe by the enrichment factor (EF) and the recovery factor (RF), which can be calculated as follows (Güell R et al. 2008; Pyrzynska K 2006):

$$\mathrm{EF} = \frac{C_i}{C_0} \tag{1}$$

where C_i is the (receiver) concentration of the analyte i [mg/dm^3] and

C_0 is the initial (feed) concentration of analyte i [mg/dm^3].

$$\mathrm{RF} = \left(1 - \frac{C_t}{C_0}\right) \cdot 100 \tag{2}$$

where C_t is the (feed) concentration at time t [mg/dm^3] and

C_0 is the initial (feed) concentration of analyte i [mg/dm^3].

4.3.1 Liquid membrane techniques

Liquid membrane technique is an alternative to the conventional heavy metals preconcentration processes which combines solvent extraction and a stripping process in a single step. In this case, two aqueous phases are separated by an immiscible liquid membrane. Preconcentration and separation is achieved when the permeate membrane, containing the specific extracting agent, is in contact with the feed solution (Aouarram A et al. 2007; Granado-Castro MD et al. 2004a).

Three basic liquid membrane systems can be use: bulk liquid membrane (BLM), supported liquid membrane (SLM) and emulsion liquid membrane (ELM).

4.3.1.1 Supported liquid membrane extraction (SLM)

Supported liquid membrane (Figure 9) is a separation method where an organic solvent is immobilized in a thin, macroporous, hydrophobic membrane and interposed between two aqueous phases. One of the aqueous phases is the feed solution containing the metal ion to be removed and the other one is the receiving solution where the metal ion will be retained. The organic solvent, alone or containing a complex agent selective towards the target metal, must have weaker affinity towards the heavy metal than the complex agent on the receiving solution. The use of much higher feed solution volumes than the receiving solution volume leads to higher enrichment factors (Fontàs C et al. 2005; Güell R et al. 2008).

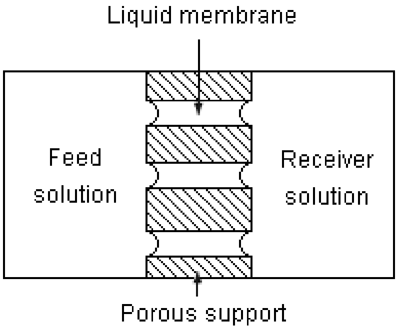

Figure 9. Schematic drawing illustrating the supported liquid membrane extraction (Mulder M 1997, 341).

The more extended configurations used in SLM extraction are flat-sheet and hollow fiber. This latter configuration allows separation and concentration of the target elements at the same time and high enrichment factors can be obtained. However, preconcentration factor may be insufficient for the analysis of some elements and the time required for achieving the maximum enrichment factor is rather long (Güell R et al. 2008; Parthasarathy N et al. 1997).

The efficiency of hollow fiber supported liquid membrane system has been studied for the removal and preconcentration of chromium at trace levels with very satisfactory results despite the long time needed in some cases. After 48 hours of experiment, a recovery of 72.6 % and an enrichment factor of 91 % have been achieved in a sample of 0.1 ppm of Cr (II) in a volume ratio of 100:1 between the feed and the receiver solutions. However, with a sample of 0.98 ppm of Cr (II) and a volume ratio of 10:1 just 9 % of the enrichment factor is achieved despite of 92.2 % of removal (Güell R et al. 2008).

Supported liquid membranes can be used for the recovery of metal ions from aqueous solutions, removal of contaminants from effluents, selective separation of biological species and gas separations. Despite its promising applications, it is very limited in industrial scale due to the low stability and short lifetime of the membrane (Zha FF et al. 1995).

4.3.1.2 Bulk liquid membranes (BLM)

Bulk liquid membrane is one of the simplest liquid membrane technique designs. It has been studied for pre-concentration and separation of different metal ions with a variety of liquid membrane phases (Zhanga W et al. 2009).

As illustrated in Figure 10, the device is divided in two parts; a common part, containing the membrane liquid and a second part, in which the feed and the receiving solutions are separated by a solid impermeable barrier or with a relatively thick layer of immiscible fluid without any means of support. The latter is kept apart from the external phases only by means of its immiscibility. The liquid membrane is in contact with the two other liquids and allows analyte to transfer from the feed to the receiving solution (Krieg HM et al. 2000; Nabieyan B et al. 2007).

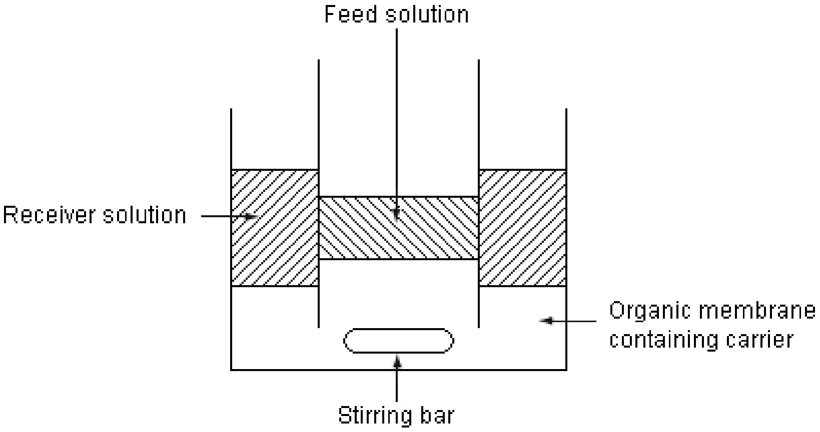

Figure 10. Schematic drawing illustrating the bulk liquid membrane (Reddy et al. TR 2010).

Bulk liquid membranes offer important advantages such as simplicity, reproducibility, economy and they enable the elimination of matrix interferences. However, it is not environmentally friendly due to the use of organic solvents in the membrane such as toluene. Studies show that cadmium and copper from natural waters can be effectively separated and preconcentrated with this method with the preconcentration factor of 17.9 and 17.87, respectively. Nonetheless, long time was required, around 6 and 8 hours, to achieve these values (Granado-Castro MD et al. 2004a; Granado-Castro MD et al. 2004b).

4.3.1.3 Emulsion liquid membranes

In an emulsion liquid membrane a water-in-oil emulsion of the receiving phase is prepared and dispersed into a feed phase containing the metal to be extracted. A thin film of oil is formed between two immiscible phases. The metal extraction agent is in the oil phase and the stripping reagent is in the aqueous receiving phase. This film serves as a membrane through which the metal ions diffuse. The process is completed when the purified aqueous phase is separated from the inner emulsion and the concentrated solution is separated from the oil phase (Sznejer G et al. 1999; Hu X et al. 2005).

Figure 11 shows a schematic drawing of the emulsion liquid membrane.

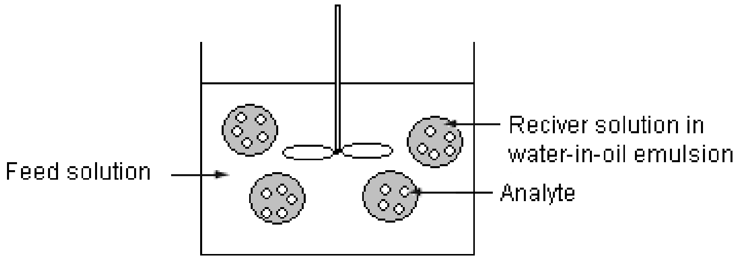

Figure 11. Schematic drawing illustrating the emulsion liquid membrane (Mulder M 1997, 341).

The method has high efficiency due to the large interfacial area between the phases involving availability for mass transfer. It consumes relatively small amount of energy compared to other separation processes and it has a simple design concept of contacting device. However, long-term stability and possibility of breakage of the liquid membrane is an important issue that limits the commercialization of the liquid membrane technology (Hu X et al. 2005).

Separation and preconcentration of citric acid by emulsion liquid membrane from a diluted solution has been studied. Under the optimum conditions up to 97 % of the citric acid was extracted and a 14-15-fold preconcentration was achieved in 20 minutes (Yordanov B et al. 2004).

This process has been used for the removal and recovery of various heavy metals such as copper, zinc, nickel, cadmium, uranium from different media, acids and bases, and pharmaceutical separations. This technique has also been used for the treatment of industrial wastewaters containing a wide range of toxic contaminants such as phenol, chlorophenol and nitrophenol (Fouad EA et al. 2008).

4.3.2 Solid phase extraction

Solid phase extraction is one of the widest techniques used for preconcentration of analytes in environmental waters because of its advantages of high enrichment factor, simplicity, and minimal costs due to low consumption of reagents, environmental friendliness and the ability to be used in combination with different detection techniques. However, the extraction efficiency of this technique is strongly dependent on the solid sorbent used (Zang Z et al. 2010; Arbab-Zavar MH et al. 2011; Sadeghi S et al. 2009).

In solid extraction, a liquid phase containing the sample matrix is in contact with a solid phase membrane which behaves as a sorbent. As illustrated in Figure 12, the method consist of passing the liquid sample through a column, a cartridge, a tub or a disk containing adsorbent that retains the analytes. After all of the samples have been passed through the sorbent, an eluent with a greater affinity for the analytes is used for the recovery of the ions (Camel V 2003; Huck CW et al. 2000).

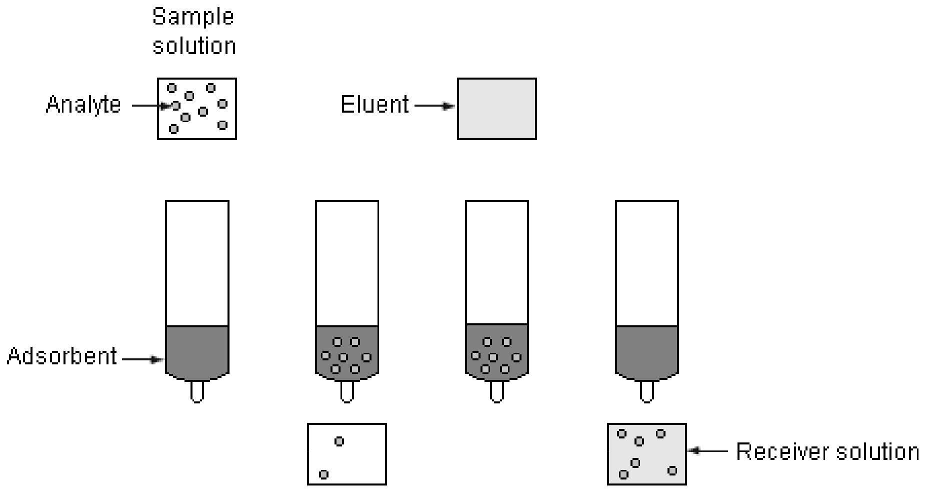

Figure 12. Schematic drawing illustrating the solid phase extraction process (Camel V 2003).

Solid phase extraction has been used for the analysis of numerous different classes of compounds in a variety of matrices. Solid phase extraction using silica gel modified with murexide has been studied for the extraction of uranium (IV) ions from water samples. The study achieved a recovery of 92 % within first five minutes and a preconcentration factor of 400 (Sadeghi S et al. 2009).

Although this method is used for preconcentration and removal of analytical samples it is also used for the determination of trace amounts of pesticides or organic contaminants in water, for analysis of industrial wastewater and for isolation of organic compounds from ground water (Huck CW et al. 2000).

4.3.3 Micellar-enhanced ultrafiltration (MEUF)

Micellar-enhanced ultrafiltration is an effective separation technique which involves the addition of surfactants to an aqueous solution in order to promote the removal and preconcentration of the metal ions. The aggregated surfactant forms large micelles in concentrations above its critical micelle concentration (CMC). The metal ions can be trapped by micelles in the outer part of the micelles due to electrostatic interactions. The metals are retained by the ultrafiltration membrane, which has pore size small enough to block the passage of micelles, which contain the metal ions, through the membrane (Tung C et al. 2002; Danisa U et al. 2009).

Figure 13 shows the principle of micellar-enhanced ultrafiltration.

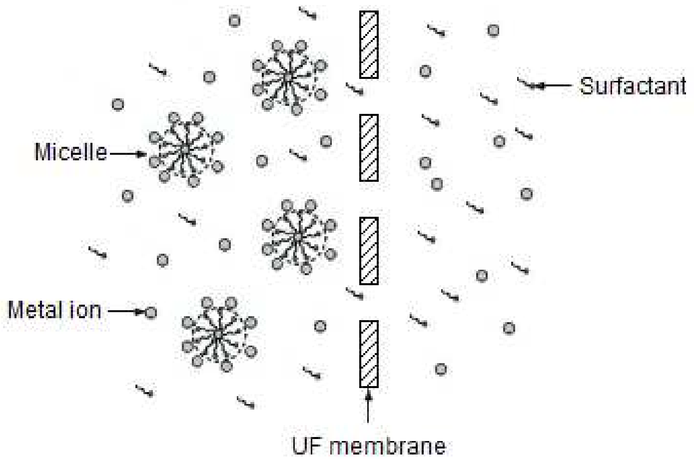

Figure 13. Schematic drawing illustrating the principle of micellar-enhanced ultrafiltration (Samper E et al. 2009).

The main advantages of the technique are simple operation, high removal efficiency, low-energy requirement and pollutant recovery, besides a great deal of cost effectiveness. Micellar-enhanced ultrafiltration has been successfully employed. However, its major drawback is the leakage of surfactant monomers with lower molecular weight than the molecular weight cut-off of the membrane (Danisa U et al. 2009).

De la Guardia et al. studied the application of micellar-enhanced ultrafiltration for the preconcetration of aluminium from aqueous media with a recovery factor up to 98 % (De la Guardia M et al. 1993).

4.3.4 Liquid phase polymer based retention (LPR)/Polymer-enhanced ultrafiltration

Polymer-enhanced ultrafiltration is a method, in which a water soluble polymer is added to bound metals and to form macromolecular complexes. The large polymer-metal complexes can be retained by the ultrafiltration membrane in the retentate stream, while the none-complex ions pass through the membrane into the permeate stream. Thus, target metal ions are separated from the rest of the solution (Müslehiddinoğlu J et al. 1998; Uludag Y et al. 1997).

Figure 14 shows the principle of polymer-enhanced ultrafiltration.

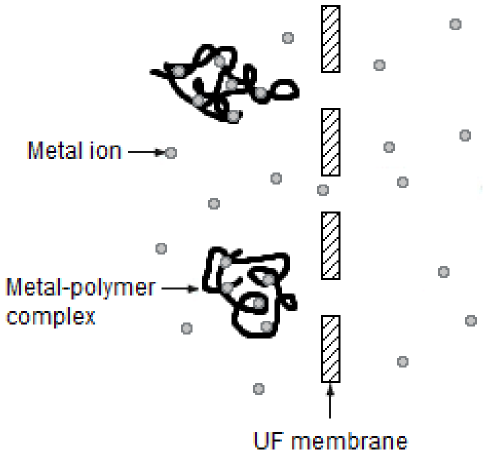

Figure 14. Schematic drawing illustrated the principle of polymer-enhanced ultrafiltration.

The main advantages are the lack of mass-transfer limitations, interface reactions and membrane instability often observed in a multiphase separation process. In addition, the process requires a small amount of energy involved in ultrafiltration or the favorable cost compared with classical method. However, some polymers such as polyethylenimine have the drawback of needing very low pH values to get the complex breakage (Uludag Y et al. 1997; Llanos J et al. 2008).

LPR has been applied as a method for the concentration of heavy metals prior to an analytical technique and for the removal of heavy metals in the treatment of water effluent, sewage water, underground water or with radionucleides (Llanos J et al. 2008).

Polymer-enhanced ultrafiltration has been successfully used successfully used as a preconcentration method previous to the determination of mercury, calcium and cadmium by atomic absorption spectrophotometry (AAS) (Müslehiddinoğlu J et al. 1998).

5 Donnan dialysis

5.1 Principle of Donnan dialysis

Donnan dialysis is an ion-exchange membrane separation process in which ions of the same electrical charge are exchanged between two solutions though an ion-exchange membrane (Strathman H. 2004, 215). An ionic–strength gradient across the membrane establishes the potential that allows ions to possess a charge opposite to the charge of the membrane to pass though the membrane (Pyrzynska K 2006).

The ion-exchange membrane is composed of a water-insoluble polymer with fixed ionogenic groups. According to the ionogenic groups fixed on the matrix of the membrane, the membranes can be cation-exchange membranes with negatively charge groups, mainly sulfonic group, or anion-exchange membranes with positively charge groups such as tetraalkylammonium (Pyrzynska K 2006; Strathman H 2004, 4).

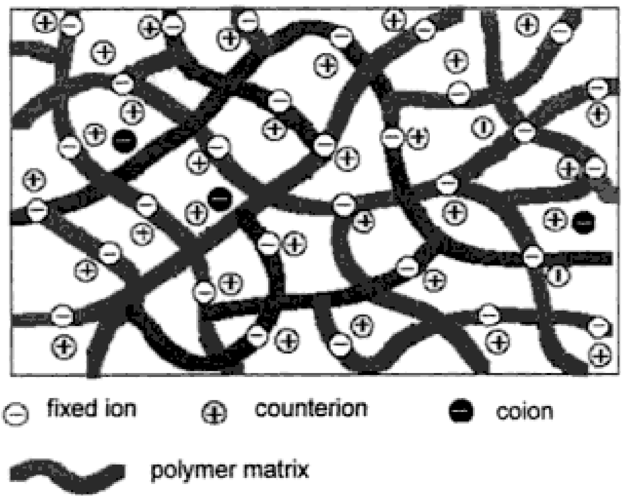

Figure 15. Structure of a cation-exchange membrane (Strathman H. 2004, 4-5).

Figure 15 shows the schematic structure of a cation-exchange membrane. The mobile anions are called co-ions and mobile cations are referred to as counter-ions. The latter ones are in the interstices of the polymer and are in electrical equilibrium with the fixed negative charge. Co-ions are more or less completely excluded from the polymer matrix because of their electrical charge which is identical to that of the fixed ions. This exclusion is called

Donnan exclusion. For this reason the cation-exchange membrane permeates only the transfer of cations. In an anion-exchange membrane the opposite occurs and the membrane permeates anions (Strathman H 2004, 4-5).

In order to lead to a counter-ion transport in opposite direction, an electroneutrality requirement is needed. Since the exchange membrane excludes co-ions from permeating the membrane, the two solutions achieve the necessary electronegativity when identical number of counter-ions is transported in opposite directions through the membrane.

In Figure 16 a schematic drawing illustrates an example of the principle of Donnan dialysis. The solution with the higher concentration is called stripping or receiving solution and in this case is represented with NaCl solution. The lower concentration solution is called feed solution and is represented with $CaCl_2$ solution.

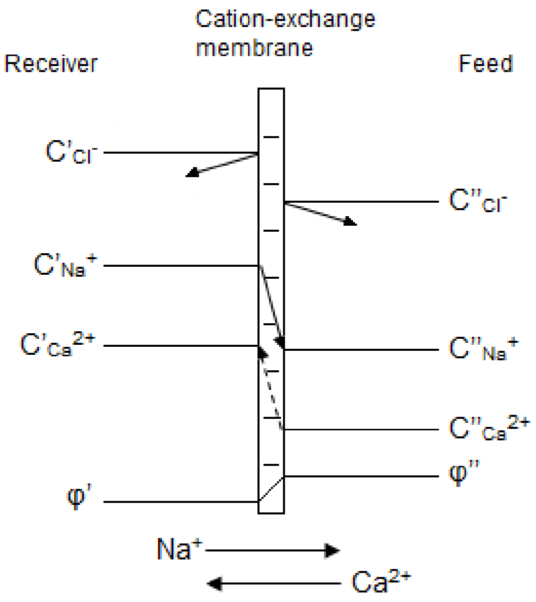

Figure 16. Illustration of the principle of Donnan dialysis with NaCl in the stripping and $CaCl_2$ in the feed solution (Strathmann 2004, 215).

The difference in concentration between both solutions acts as the driving force for the exchange of Ca^{2+} and Na^+-ions, but this is only possible when the same number of charges are transported in opposite directions. Cl^--ions acts as the co-ions thus they cannot permeate the cation-exchange membrane.

Equilibrium is achieved when the electrochemical potential is equal between the receiving and the feed solution and it is referred as Donnan equilibrium (Strathmann 2004, 215-216).

5.2 Mass transport in Donnan dialysis

In Donnan dialysis, mass transport is calculated by the transport of the counter-ions through the membrane and the flow velocity of both solutions across the membrane. For a strictly permselective ion-exchange membrane the flux of co-ions is 0 and the sum of the electrical charges carried by the counter-ion flux is also 0 due to the electroneutrality requirement. In addition, as there is no applied external electrical potential, there is no net transport of electrical charge and thus, the conservation of charge requires:

$$\sum_i z_i J_i = 0 \tag{3}$$

where J is the flux of counter-ions through the membrane [mol $m^{-2}s^{-1}$] and
z is their valance [eq mol^{-1}].

Equilibrium between the two solutions separated by the membrane is achieved when the electrochemical potential of all the ions in both solutions is equal. In equilibrium:

$$\eta_i^1 = \eta_i^2 = RT \ln a_i^1 + z_i F\varphi^1 = RT \ln a_i^2 + z_i F\varphi^2 \tag{4}$$

where η is the electrochemical potential [J mol^{-1}],
R is the gas constant [J °K^{-1} mol^{-1}],
T is the temperature [°K],
F is the Faraday constant [A s eq^{-1}],
a is the activity [mol m^{-3}],
φ is the electrical potential [V],
z is the valance [eq mol^{-1}],
$_i$ refers to the ions,

^{1} refers to the feed solution and

^{2} refers to the receiver solution.

When the two solutions are in equilibrium, the activity difference of the ions results in an electrical potential difference which is referred to as Donnan potential:

$$\varphi_{Don} = \varphi_2 - \varphi_1 = \frac{RT}{F} \ln \left(\frac{a_i^1}{a_i^2} \right)^{\frac{1}{z_i}} \qquad (5)$$

where φ is the electrical potential [V],

R is the gas constant [J °K^{-1} mol^{-1}],

T is the temperature [°K],

F is the Faraday constant [A s eq^{-1}],

a is the activity [mol m^{-3}],

z is the valance [eq mol^{-1}],

$_i$ refers to the ions,

^{1} refers to the feed solution and

^{2} refers to the receiver solution.

There is no applied external electrical potential and no net flux of electrical charge, thus there is no potential difference between the two solutions. So this:

$$\sum_i \left(\frac{a_i^1}{a_i^2} \right)^{\frac{1}{z_i}} = 0 \qquad (6)$$

where a is the activity [mol m^{-3}],

z is the valance [eq mol^{-1}],

$_i$ refers to the ions,

^{1} refers to the feed solution and

^{2} refers to the receiver solution.

If the system is composed of two electrolytes, as indicated in Figure 16, NaCl in the receiver side and $CaCl_2$ in the feed side, and it is assumed that the activity can be expressed by the concentration, the Donnan equilibrium is given by:

$$\frac{[\mathrm{Na}^+]^{\mathrm{r}}}{[\mathrm{Na}^+]^{\mathrm{f}}} = \left(\frac{[\mathrm{Ca}^{2+}]^{\mathrm{r}}}{[\mathrm{Ca}^{2+}]^{\mathrm{f}}}\right)^{\frac{1}{2}} \tag{7}$$

where $[Na^+]$ is the concentration of Na^+ [mol dm^{-3}],
$[Ca^{2+}]$ is the concentration of Ca^{2+}[mol dm^{-3}],
^{r} refers to the receiver solution and
^{f} refers to the feed solution.

This equation determines the maximum amount of a component that can be removed from the solution for a given initial concentration of the receiver and the feed solution. To design a Donnan dialysis system for a given application it is necessary to determine the required membrane area, the feed and receiver solution flow rate, and the process path length for a given cell geometry, and the initial and final concentration in the feed and receiver solution (Strathmann 2004, 216-218).

5.3 Process and applications

Donnan dialysis is an energy saving process, compared to the similar process such as electrodialysis, since it does not use electrical current. It is also a continuous process of ease operation. Because of its weak driving force, it is necessary to use large membrane areas to maintain the output of the process and thus the system is not economical at big scale. So far, there are no industrial applications of Donna dialysis, and the technique has only been investigated in laboratories (Tanaka 2007, 495).

Donnan dialysis has generally been applied in analytical procedures where recovery or the enrichment of valuable metal ions and removal of undesirable metal ions from wastewater is necessary. Donnan dialysis has been used to eliminate matrix effects prior to analyses by inductivity coupled plasma atomic emissions spectroscopy (ICP-AES) and atomic absorption spectrometry (AAS). In addition, it has also been applied as an interface in an optical sensor for Cr(VI) monitoring and for fractionation of heavy metal ions in natural waters and sample preparation prior to chromatographic analysis. (Pyrzynska K 2006) According to Donnan equilibrium principle, the preconcentration of metal ions is achieved as long as the receiver volume is much smaller than that of the sample (Pyrzynska K 2006).

The effectiveness of this method has been investigated and reported. It was demonstrated that the effective recovery of metal ions such as zinc, copper, nickel and iron from processing electroplatining rinse solution. It was also successfully removing titanium from red mud solutions, as well as cadmium, nickel, copper and chromium from wastewater effluents. Recovery of aluminium and iron from coagulants sludges has been conducted obtaining a recovery value of 70 % (Wang Q et al. 2010). It has also been reported to be an efficient technique for the separation of cyanide complexes of copper, gold and silver using several compartments (Pyrzynska K 2006; Wang Q et al. 2010).

In Donnan dialysis the preconcentration and recovery of metals from mixtures of different ions with almost the same charge can be obtained, but without any preference within the metals. Hence, to achieve the separation towards a desired metal a complex agent is needed. For this purpose, the complex agent can be added both in the receiving side as well as in the feed side.

The disadvantage of adding a complexing agent is that the enhancement of the selectivity decreases the transport flux of the counter-ions due to a reduction of the driving force, i.e., the concentration gradient diminishes. Consequently, the addition of a complex agent into the process is only a laboratory scale measure because it becomes economically impractical with large volumes processes.

EDTA, oxalic, citric and maloic acids have been used as complex agents in the feed solution in order to enhance the separation of a multicomponent solution of Cu(II), Ni(II) and Fe(II) (Pyrzynska K 2006). The addition of the complex agent in the receiving solution can enhance both the flux of the metal ions and the selectivity of the process. Free metal ions form complexes after passing through the membrane and when they are in contact with the complex agent. Therefore, the concentration gradient can be maintained constant. The stability of the complex compounds determines the effectiveness of the method. It has been reported that Cu(II) and Ni(II) fluxes were more significant with EDTA than using polyetyleimine, due to the higher stability of their complex compounds (Pyrzynska K 2006).

EXPERIMENTAL PART

6 Aims

Iron is an essential metal for the survival and the health of humans, however, at certain trace concentrations it may be toxic. Even the sensitiveness and selectivity of analytical techniques, direct determination of these low concentrations is not always possible and thus, a prior preconcentration step is needed.

The main purpose of this research was to study the applicability of Donnan dialysis for the preconcentration of iron from synthetic wastewaters. Magnesium and calcium were added to the feed solution in order to evaluate the competition between these ions with iron.

In multicomponent solutions as in this research, there is not a marked preference toward one metal. Therefore, a complex agent was added to the receiver side in order to evaluate the enhancement of the process selectivity towards iron.

The experiments were performed in a laboratory scale with a dialysis cell, according to an experimental design created with the MODDE 8.0 software also used for modelling the process.

7 Materials and methods

7.1 Membrane equipment

The Donnan dialysis set up consists of a dialysis cell, a cation exchange membrane, two peristaltic pumps, two beakers of different size and feed and receiver tubes. Both feed and receiver solutions were circulated back to their respective beakers in order to have a continuous system. The preconcentration could be achieved since the feed solution was of 1 dm^3 and the receiver solution volume was 10 cm^3.

Figure 17 shows a schematic drawing of the experimental process.

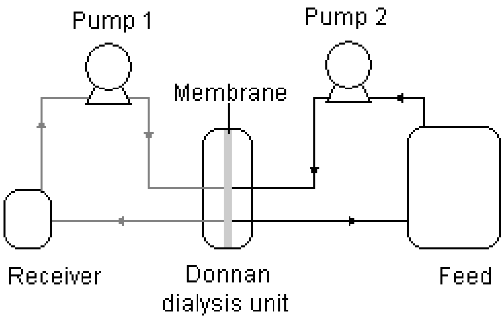

Figure 17. Donnan dialysis process.

The dialysis cell (Metrohm, model reference 6.2729.100) consists in two detachable compartments made with plexiglass which have a spiral channel in contact with the membrane (Figure 18). From the inlet to the outlet opening, the cell contains an approximately volume of 240 µl and a contact area of 8 cm^2. Between these compartments, a cation exchange membrane was inserted

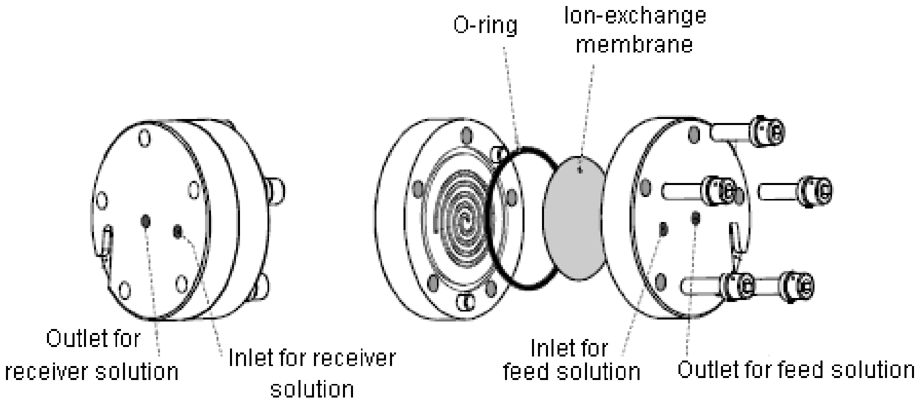

Figure 18. Assembling the dialysis cell (Metrohm, 16).

The membrane used for this study was a flat sheet cation exchange membrane (CMI-7000) provided by Membranes International Inc. from the United States. The polymer structure of the membrane was gel polystyrene cross linked with divenylbenzene and the negatively charge group fixed on the membrane were sulfonate ions. In addition, the efficiency of CMI-7000 was compared with the cation exchange membrane (RALEX CM PP) provided by MEGA a.s. from Czech Republic. RALEX CM PP, which contains polyethylene binder and polypropylene textile fibers and sulfonate ions as the ion group. The thickness of both membranes was 45 mm.

Two different peristaltic pumps were used for pumping the feed and the receiver solutions through the tubes. The pump used in the receiver side was a Watson Marlow 101 U and the feed pump was a Gilson Miniplus 3.

Feed tubes were made of silicon and the receiver tubes were Tygon ST of PVC provided by Metrhon. The latter ones were used to pump hydrochloric acid and thus, the material of these tubes was more resistant than the material of the feed tubes.

7.2 Chemicals used in the experiments

The salts used for the study were chosen is order to have the highest purity and to avoid interferences of impurities in the analyses. The chemicals used are presented in the Table 2.

Table 2. Chemicals used in the experiments.

Chemicals	Molecular weight [g/mol]	Purity [%]	Supplier
$FeCl_2 \cdot XH_2O$	55.847 (anhy)	99.5	Alfa Aesar
$MgCl_2 \cdot 6H_2O$	203.30		J.T. Baker
$CaCl_2$	110.99	≥ 98	Merck
$CuCl_2 \cdot XH_2O$	134.45	99	ACROS Organics
EDTA ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2$)	372.24	99	Oy FF-Chemicals Ab
HCl	36.46	36-38	Baker
NaCl	58.44	99.5	Merck
HNO_3		65	

All the feed and receiver solutions were prepared using deionized water (Milli Q water). Feed solutions, which had a volume of 1 dm^3, were prepared from $FeCl_2$, $MgCl_2$ and $CaCl_2$. $CuCl_2$ was used to prepare feed solutions of copper instead of iron in order to compare the behaviour of the membrane with another metal.

Moreover, HCl and EDTA were used to prepare the receiver solution. The preconcentration of metals by Donnan dialysis is achieved as long as the volume of the receiver solution is smaller than the feed solution. Therefore, the volume of the receiver solution was 10 cm^3.

For the preconditioning and cleaning of the membrane different solutions of hydrochloric acid (3.8 %) and sodium chloride (2 mol dm^{-3} and 0.5 mol dm^{-3}) were used. Finally, the equipment was cleaned with nitric acid (5 %) to remove any ions remaining in sample tubes.

7.3 Analytical methods

7.3.1 Atomic absorption spectroscopy (AAS)

Iron, magnesium, calcium and copper concentrations were determinate from the feed and receiver solutions using atomic absorption spectroscopy (AAS).

Atomic absorption spectroscopy (AAS) is a widely used method for the determination of element concentration in clinical and biology samples or in environmental, geochemistry and petrochemistry analyses. The method is specific and robust, and has a high detection power with an accuracy of 0.01 mg/ dm^3.

The sample is an aqueous solution which is supplied to a thermal atomizer where it is atomized. The concentration of the analyte is determined by absorption of resonant radiation with calibration to an aqueous standard solution which contains only a known amount of the element (Wizemann HD 2008).

The analyses were made in the Department of Process and Environmental Engineering at the University of Oulu which used two different analyzers. The first one was PerkinElmer AAS 4100 which uses a flame method for atomizing the sample and the second one, PerkinElmer AAnalyst 600, which uses the graphite method.

PerkinElmer AAS 4100 was used for the determination of most of the samples since it can detect all the elements used in this study. Due to some mechanical problems with this equipment, some of the samples were analyzed with PerkinElmer AAnalyst 600. In this case cadmium and magnesium were not possible to be analyzed by the PerkinElmer AAnalyst 600.

7.3.2 Focused ion beam and scanning electron microscope (FIB-SEM)

Different samples of the CMI-7000 cation exchange membrane were analyzed with FIB-SEM equipment in order to evaluate if the iron was absorbed in the membrane causing membrane fouling. The analyses were made in The Center of Micro- and Nanotechnology at the University of Oulu.

The samples analyzed by FBI_SEM were a new CMI-7000 membrane without pretreatment as the reference membrane, both sides of the regenerated CMI-7000 membrane after being used for all the experiments and, a new CMI-7000 membrane with and without regeneration used in an experiment with high concentration of calcium and magnesium.

Focused ion beam (FIB) can be used in analysis and imaging of samples. Imaging can be done by using the ion beam, but usually the electron microscope like SEM is used. The FIB-SEM device used for the imaging of the membrane samples was FEI Helios NanoLab 600**,** a dual beam system which contains both of a Focused Ion Beam (FIB) and a Scanning Electron Miscroscope (SEM). The electron and ion beams intersect at a coincident point (52 degree angle), allowing immediate SEM imaging of the FIB-milled surface.

The samples were first attached to sample holding stubs using carbon tape and coated with platinum via sputtering. The thickness of the coating was approximately 100 nm. A cross-section from the surface was then milled using FIB and the cross-section was imaged by SEM.

7.4 Experimental design

Design of experiments is based in the process of planning, designing and analyzing a set of experiments in order to extract a maximum amount of relevant information and thus a valid and objective conclusion can be formulated. With the fewest number of experimental runs possible, a carefully selected set of experiments is chosen in which all relevant factors are varied simultaneously and then connected by means of mathematic empirical model. The model is used to find the main factors affecting the response selected, and to evaluate how the factors interact in influencing the response. The empirical model developed can also be used for prediction and optimization.

There are three primary experimental objectives which can be solved with the design of experiments. The first one is screening, used to identify the most influence factors with the fewest experiments, and for determining the ranges in which theses should be investigated. The second experimental objective is optimization, which defines the optimal operating conditions, however, it requires more experiments. Finally, the third one is robustness testing which determines the sensitivity to small changes in the factor setting (Eriksson L et al. 2008, 2).

In this study, a screening design was performed in order to determinate the main factors affecting the preconcentration of iron by Donnan dialysis. In addition, the importance of the factor interactions was also evaluated.

MODDE 8.0 software provided by Umetrics Inc. was used in this study as a tool for the experimental design.

7.4.1 Factor levels

The factors are variables which, due to changes in their levels, will exert an influence on the system or the process. Many substances are present in wastewaters as well as many factors could influence the final objective of the preconcentration of iron. In this study, the factors to be studied were the feed concentrations of calcium, magnesium and, iron and the concentration of EDTA as the complexing agent in the receiver side (Eriksson L et al. 2008, 33).

Table 3 shows all the factor levels studied for the preconcentration of iron by Donnan dialysis.

Table 3. Factors and the levels studied with the respectively concentration.

Substance	Low level (-)	Central point (0)	High level (+)
Ca	0 mg/ dm^3	10 mg/ dm^3	20 mg/ dm^3
Mg	0 mg/ dm^3	2.5 mg/ dm^3	5 mg/ dm^3
EDTA	0 mg/ dm^3	77.5 mg/ dm^3	155 mg/ dm^3
Fe	Constant = 0.15 mg/ dm^3		

Iron concentration was maintained constant at 0.15 mg dm^{-3}. The concentration of iron was fixed based on a previous work conducted by M.Sc. Junkal Landaburu, were it was concluded that Donnan dialysis is more efficient for diluted feed metal systems (Landaburu J 2010).

Magnesium and calcium were selected as factors in order to study the competition between both metals with iron in the preconcentration process. For this study, the high level of the concentration value was selected in order to have hard waters conditions, which contain about 20 mg/ dm^3 of Ca^{2+} and 5 mg/ dm^3 of Mg^{2+} (Deleebeecka NME et al. 2009) .

Juang et al. have added polyethilenimine (PEI) and ethylenedinitrilo-tertaacetic acid (EDTA) in the receiver solution in order to enhance the metal ion flux. This review shows that the enhancement is more significant with EDTA than PEI. (Juang R et al. 2001) Further, EDTA has higher stability constants to form ferric ion complexes (Perrin DD et al. 1979, 764-765). Therefore, in this study, EDTA was chosen as the complexing agent to be added in the receiver side. The higher level concentration value was 155 mg dm^{-3}, which means that the Fe/EDTA molar ratio used was 1:200.

7.4.2 Responses

The efficiency of the separation and preconcentration of compounds by Donnan dialysis is described by the enrichment factor (EF). EF of iron was used as the measured response and it was calculated as shown in Equation (1).

7.4.3 Experimental design

Two levels full factorial design, denoted as 2^3, was chosen for the experimental design of this study. In the construction of full factorial design, each factor had a low (-) and a high (+) level and therefore, 8 experiments ($2^3 = 8$) were conducted (from experiment N1 to experiment N8). Furthermore replicate experiments were carried out as center points (0) in order to evaluate the reproducibility of the process and to evaluate the curvature of the linear model. (Eriksson L 2008, 56)

The empirical model was fitted with multiple linear regression (MLR), which estimates the coefficient terms in the model, and the confidence level used was 95 %.

The experiments were conducted randomly and it is possible to see the order of each experiment in the Table 4.

Table 4. Run order and variation of calcium, magnesium and EDTA.

Experiment name	Run Order	C(Ca) [mg/ dm^3]	C(Ca) [mg/ dm^3]	C(EDTA) [mg/ dm^3]	C(Fe) [mg/ dm^3]
N1	1	-	-	-	Cnt.
N2	4	+	-	-	Cnt.
N3	5	-	+	-	Cnt.
N4	7	+	+	-	Cnt.
N5	10	-	-	+	Cnt.
N6	9	+	-	+	Cnt.
N7	6	-	+	+	Cnt.
N8	3	+	+	+	Cnt.
N9	2	0	0	0	Cnt.
N10	11	0	0	0	Cnt.
N11	8	0	0	0	Cnt.

7.4.4 Model validity

When fitting a regression model the most important diagnostic tools are R^2 and Q^2, which are included in the summary of fit plot with the model validity and reproducibility bars.

Response variation percentage explained by the model (R^2) is a measure of how well the regression model can be made to fit the raw data. Response variation percentage predicted by the model (Q^2) estimates the predictive power of the model.

Model validity reflects whether the model chosen at the beginning is appropriate or not. The higher the numerical value the more valid the model is. A value above 0.25 is interpreted as good and valid model with no lack of fit.

Reproducibility is the variation of the response under the same conditions (pure error), often at the center points, compared to the total variation of the response. The replicate error is small when reproducibility bar is high whereas, if the value of the reproducibility bar is small there is a large pure error and poor control of the experimental procedure (Eriksson L et al. 2008, 77-78).

Another useful tool as a diagnostic test is the analysis of variance, ANOVA, which is concerned with estimating different types of variability in the response data, and then comparing such estimates with each other by means of F-tests. The first test assesses the significance of the regression model and the second test, or lack of fit test, compares the model error and the replicate error (Eriksson L et al. 2008, 88).

A good tool for finding deviating experiments (outliers) is the normal probability plot of residuals. This plot displays the residuals on a double Log scale. If the residuals are random and normally distributed, the normal probability plot of the residuals has all the points lying on a straight line between -4 and +4 standardized standard deviation.

The factor effects in the final model are shown in a coefficient plot, which makes the coefficients comparable by scaling the data. The size of the coefficient represents the change in the response when a factor varies from 0 to 1 while the other factors are kept at their average. When there is an interaction effect, the effect of one factor depends on the level of another factor and this fact can be seen in an interaction plot.

7.5 Donnan dialysis procedure

For conducting all the experiments, eleven different samples of synthetic wastewater were prepared. The synthetic wastewater contained various concentrations of magnesium, calcium, EDTA and iron. The effect of magnesium, calcium and EDTA on the preconcentration of iron by Donnan dialysis was studied.

7.5.1 Preparation of feed and receiver solutions

Previously to the realization of the feed solution, concentrated solutions of the metal ions were prepared. 2.769 g of magnesium salt were dissolved in deionized water in a 250 cm^3 volumetric flask. This results in a concentration solution of 1 g/dm^3 of Mg^{2+}. The same procedure was used to prepare 4 g/dm^3 concentrated solution of Ca^{2+} dissolving 2.0914 of $CaCl_2$. A standard iron concentrated solution of 1.5 g/dm^3 was also used.

Feed solutions were prepared using the standard solutions made previously. According to the different experimental runs, 100 µl of iron and different amounts of calcium and magnesium were mixed with deionized water in 1 a dm^3 volumetric flask. Appendix 1 summarises all the volumes and calculations done in order to prepare the feed solutions used in this study.

For the receiver solutions three different solutions were needed depending on the complex amount. Appendix 1 shows the masses and volumes used in each case. In this case HCl was mixed with deionized water and/or EDTA in a 100 cm^3 volumetric flask.

7.5.2 Pretreatment of a membrane

The membrane was preconditionated by immersing it in a 3.8 % HCl solution for one hour and then, it was properly washed with deionized water. Next, it was immersed in a 2 M NaCl solution for 2 hours more, and then washed properly with 0.5 M NaCl solution. The membrane was stored in 0.5 M NaCl solution. The same preconditioning procedure was conducted by Tanaka et al. (Tanaka Y. 2007, 17).

7.5.3 Performance of Donnan dialysis

The feed and the receiver rates were maintained constant at 2 cm^3/min and 0.4 cm^3/min, respectively. These values were based on the previous experiments conducted in the Heat and Mass Transfer Process Laboratory at the University of Oulu by M.Sc. Junkal Landaburu for preconcentration of iron by Donnan dialysis. The flow rates were fixed before starting the experiments by adjusting the velocity of the peristaltic pumps.

The membrane, which was in 0.5 M NaCl solution, was inserted in the dialysis cell after cleaning it with deioniszed water and drying it with hand paper. At the same time, the o-ring was inserted in the appropriated recess in the bottom compartment of the cell. Both compartments inside the membrane were assembled with screws.

The tubs were fitted to the dialysis cell with special capillary screws provided by Metrohm to avoid possible stress cracks. The feed entry tube was connected to the pump and to the inlet opening of the top part of the cell. The other part of the tub was inserted to the feed solution. The feed outlet tube was connected to the outlet opening of the top part of the cell and the other part of the tube was inserted to the feed solution. As a consequence, a closed circuit was created. The same procedure was done in the receiver side but the tubes were connected to the bottom part of the cell (See Figure 18).

After switching the peristaltic pumps on, the experiments were conducted for five hours. During the conduction of the experiment some sample were taken to be analyzed by AAS. After each experiment the membrane and the entire device was cleaned.

7.5.4 Sample taking

During the conduction of the experiments five samples of 15 cm^3 were taken from the feed solution. Removal of samples from the feed solution did not vary significantly the total volume since a 6 % of the total volume was modified. The samples were taken 0h, 2h, 3h, 4h and 5h after the experiment had started. They were collected in Falcon-tubes where they were mixed. In this case, it was possible to analyze all the ions because of the larger amount of samples.

Receiver solution contained only a volume of 10 cm^3 thus three samples from the receiver side were taken 1h, 3 h and 5 h after the experiment had started. Each sample contained 1 cm^3 of the solution and was collected in test tubes where it was diluted with deionized water to 5 cm^3. This amount of sample supposed an alteration of 20 % of the total volume which may cause a small false increase in the final ion concentration. These 50 times diluted samples were used to analyze the iron concentration.

From the main receiver solution, 5 cm^3 were taken as the initial sample and once the experiment was concluded the final volume was used as the final sample. Both samples were used to analyze iron, calcium and magnesium.

The collected samples were analyzed with AAS to see the evolution of the iron concentration and to evaluate if Donnan dialysis was a good method for the preconcentration of iron from the synthetic samples.

7.5.5 Membrane cleaning

In order to regenerate the membrane and prepare it for the next use, the membrane was cleaned with abundant deionized water and dried carefully with a paper. Then it was immersed in a 3.8 % HCl solution during half an hour and then, it was properly washed with deionized water and dried it with a paper. Next, it was immersed in a 2 M NaCl solution for half an hour more, and washed properly with 0.5 M NaCl solution. Finally it was immersed in the same 0.5 M NaCl solution at least for one night. This process was based on the literature (Tanaka Y 2007, 17).

7.5.6 Dialysis cell cleaning

Once the membrane was out of the dialysis cell, this was assembled again and air was introduced to take all the liquid away. To take all impurities away from the tubes, deionized water and HCl were passed through the feed and receiver tubes, respectively. After the tubes were cleaned, the dialysis cell was disassembled, cleaned with desionised water and dried with hand paper.

7.5.7 Disposal of the wastewater

Wastewater was collected after the experiments using different canisters for the receiver and the feed solutions. They were sent to the Chemistry Department at the University of Oulu, where the right treatment for the wastewater is conducted.

8 Results and Discussion

8.1 Empirical model for the preconcentration of iron

Table 5 shows all the experiments conducted for the preconcentration of iron by Donnan dialysis and the enrichment factors achieved.

Table 5. Factors and responses of the preconcentration experiments.

Experiment number	Factors				Response
	C_{Ca} [mg/dm^3]	C_{Mg} [mg/dm^3]	$C_{complex}$ [mg/dm^3]	C_{Fe} [mg/dm^3]	EF
1	0	0	0	0.15	4.52
2	20	0	0	0.15	1.28
3	0	5	0	0.15	2.49
4	20	5	0	0.15	1.65
5	0	0	155	0.15	2.66
6	20	0	155	0.15	0.57
7	0	5	155	0.15	4.09
8	20	5	155	0.15	2.14
9	10	2,5	77,5	0.15	2.51
10	10	2,5	77,5	0.15	1.94
11	10	2,5	77,5	0.15	1.04
12	0	0	0	0.15	3.55
13	0	0	0	0.15	4.33

After fitting the model to the experimental data (Table 5) the summary of fit was evaluated (Figure 19). In this plot the model validity, reproducibility, response variation explained by the model (R^2) and response variation percentage predicted by the model (Q^2) are represented.

The response variation percentage explained by the model, R^2 was 0.856. Large R^2 is a necessary condition for a good model, but it is not sufficient. The model validity is a measure of the validity of the model and had a value of 0.723 which means that there was no lack of fit since the bar was larger than 0.25.

The reproducibility of the experiments was 0.751. This is the variation of the response under the same conditions (pure error), in this study calculated with the centre points, compared to the total variation of the response.

Finally a useful model should have a large Q^2. In this study, the first empirical model developed showed a Q^2 below 0, thus data processing had to be conducted for improving the model.

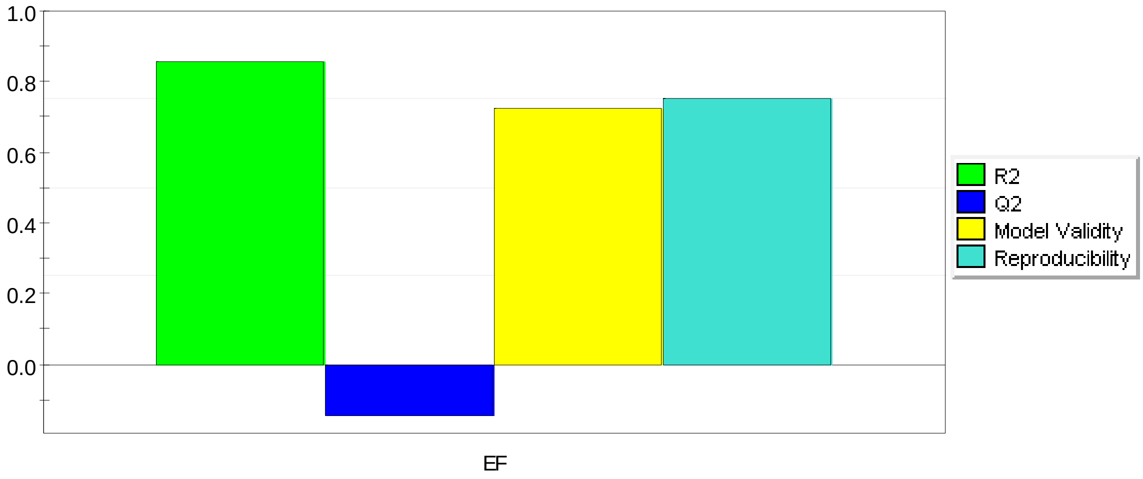

Figure 19. Summary of fit without any modification.

In order to detect if there were outliers a normal probability plot of residuals was made (Figure 20). This plot displays the residual on a double Log scale. If the residuals are random and normally distributed, the normal probability plot of the residuals has all the points lying on a straight line between -4 and +4 standardized standard deviation. In this case no outliers can be observed. However experiment 11 was deleted since it was far from the other values.

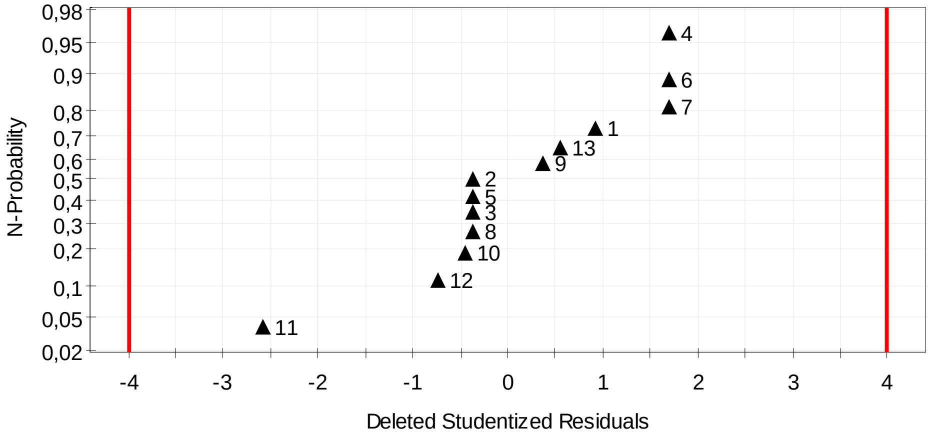

Figure 20. Normal probability plot of residuals.

After excluding the experiment N11, the new summary of fit (Figure 21) was not substantially improved. R^2 column arrived almost to the value of 1, which was very satisfactory. Model validity and reproducibility were improved respect to the other model but it was not yet satisfactory. Poor Q^2 can be due to a poor reproducibility, poor control over the experimental error or/and model validity and to insignificant terms in the model. Therefore, the model can be improved by removing insignificant terms. The identification of the insignificant terms can be conducted by evaluating the coefficient plot of the model (Figure 22).

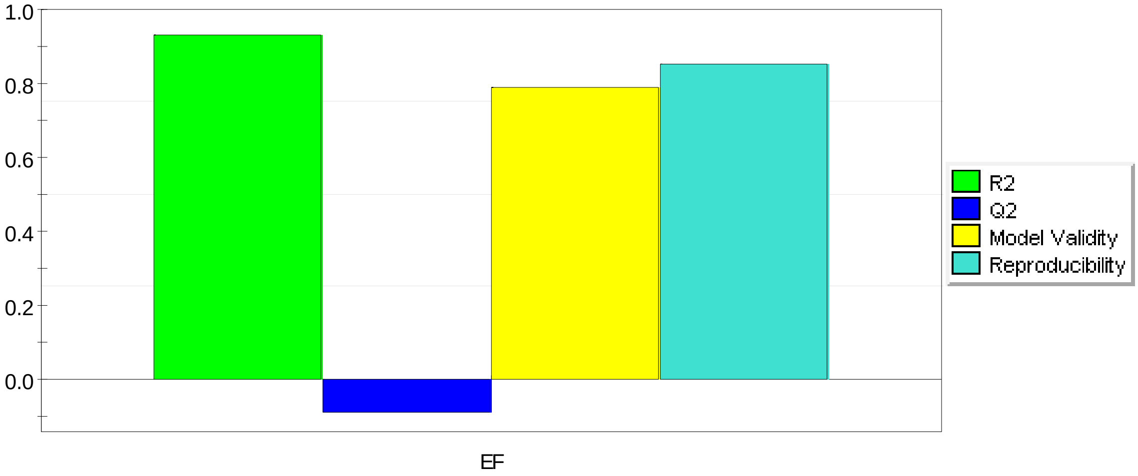

Figure 21. Summary of fit without N11.

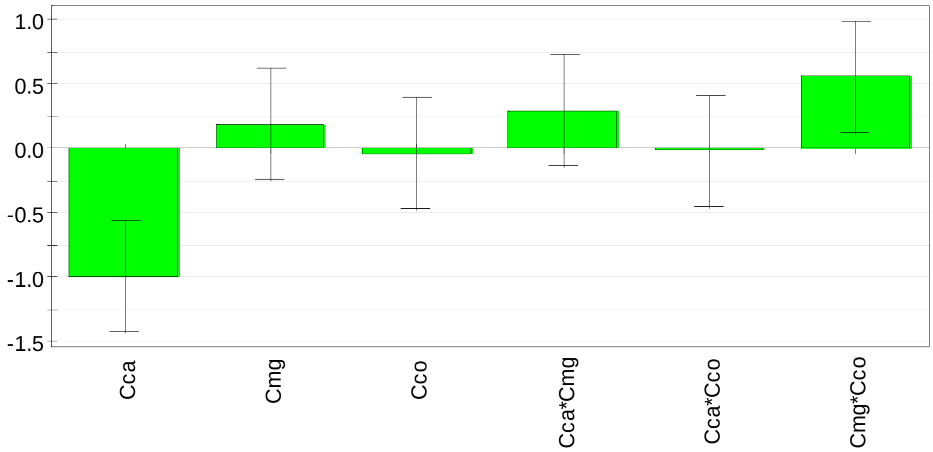

Figure 22. Coefficient results plot.

The size of the coefficient represents the change in the response when a factor varies from 0 to 1 while the other factors are kept at their average. The coefficient is significant when the confidence interval does not cross zero. In this study the most insignificant term was C_{Ca}*C_{Co} and it was removed from the model.

8.1.1 Final model

This summary of fit of the improved and final model is illustrated in Figure 23. In this study, the response variation predicted by the model, Q^2, was 0.597 and the response variation percentage predicted by the model, R^2, was 0.929. According to the literature (Eriksson L et al. 2008, 78) a model can be concluded to be good when Q^2 is higher than 0.5 and the difference between R^2 and Q^2 is lower than 0.2-0.3. Moreover, model validity and reproducibility has to be higher than 0.25 and 0.5, respectively. In this study, the difference between R^2 and Q^2 is 0.332 and therefore, it can be concluded to be a good model.

As Figure 23 shows, model validity was 0.865 and reproducibility was 0.853. Both columns were above 0.8, and consequently the model can be concluded to be a good model.

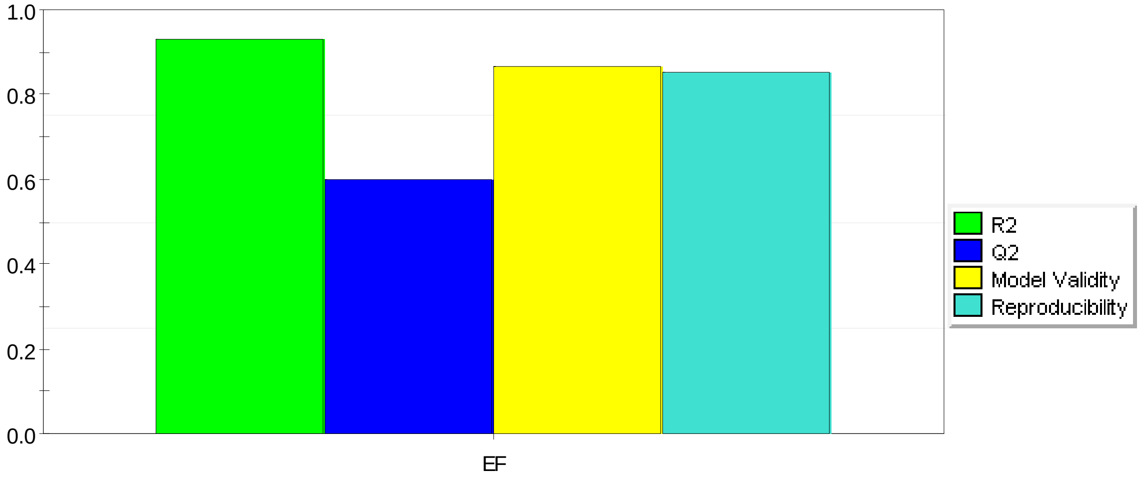

Figure 23. Final summary of fits.

When evaluating the validity of the fitted model with the analysis of variance (ANOVA) results (Table 6) show that $p < 0.05$. Therefore, the regression model is statistically significant with 95 % confidence level in the range studied. In addition, the lack of fit is not significant with a 95 % confidence level ($p > 0.05$).

Table 6. ANOVA table for preconcentration of iron.

Source of variation	DF	SS	MS	F_{value}	Probability (p)	SD
Total Corrected	11	17.22	1.57			1.25
Regression	5	15.99	3.20	15.71	**0.002**	1.79
Residual	6	1.22	0.20			0.45
Lack of Fit	3	0.53	0.18	0.77	**0.58**	0.42
Pure Error	3	0.69	0.23			0.48

8.2 Effects of factors on the enrichment factor of iron

The main factors affecting the enrichment factor of iron can be evaluated by displaying the coefficient plot of the model. In this plot the coefficients are significant, different from the noise, when the confidence interval does not cross zero.

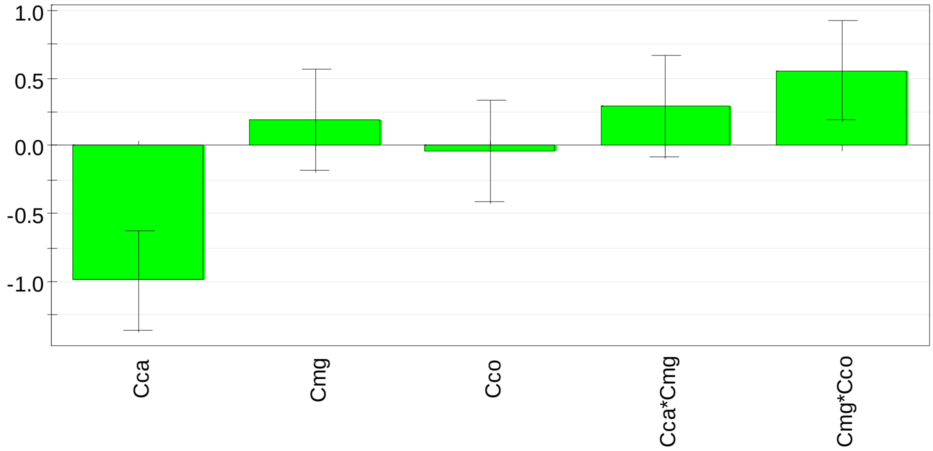

Figure 24. Coefficient for enrichment factor.

As illustrated in Figure 24, the presence of calcium showed a statically significant effect on the enrichment factor of iron. In addition, the presence of magnesium did not show a statistical significant effect on the enrichment factor of iron. It has been reported in the literature (Wiśniewski J et al. 2007) that calcium and magnesium, causing the water hardness, can be efficiently exchanged by Donnan dialysis. Wiśniewski et al. obtained after 2.5 hours, 87 % of the removal of both ions. Moreover, they reported that the removal efficiency of calcium and magnesium is similar, but in the initial phase of the process the Ca^{2+} flux is evidently higher than that of Mg^{2+} ions. This can be explained by the difference in size of both cations since the Ca^{2+} ion has smaller hydrated ionic radius (0.412 nm) than the Mg_{2+} ion (0.429 nm). Moreover, calcium shows lower electronegativity than magnesium. As a consequence, Wiśniewski reported that the attraction of the Ca^{2+} ion by the negatively charged ion-exchange groups inside the membrane is stronger than that observed in the case of the Mg^{2+} ion (Wiśniewski J et al. 2007).

In this study, the Ca^{2+} flux is evidently higher than the Mg^{2+} flux (see Table 1 in Appendix 2). This fact and the presence of high concentration of calcium caused a competition between Ca^{2+} and Fe^{2+}, i.e., the presence of calcium affects negatively the system decreasing the enrichment factor of iron.

Despite the good affinity of Mg^{2+} ions with sulfate group, the presence of magnesium did not affect as much as calcium. This might be due to the low feed concentration of magnesium and to the lower flux in the initial phase.

The addition of complexing agents to the receiver solution can enhance both flux and selectivity although the selectivity enhancement is generally less than when adding the anionic ligands to the feed solution. EDTA is a significant complex agent because it has a stronger binding ability with metal ions and it readily forms stable complexes with most heavy metals in a 1:1 molar ratio. (Juang R et al. 2001) According to Juang et al., EDTA increased the flux of copper in single copper systems and in binary systems of copper and nickel, enhancing also the enrichment factors. However, in the present study the complex agent, EDTA with a 1:200 molar ratio, showed an insignificant effect and did not improve the enrichment factor. The high concentration of EDTA might have affected the analyses made with AAS since burning of the iron-EDTA complex with the flame might have not been efficient. Therefore, lower concentrations of iron should be used to obtain more efficient burning of the complex by the flame of AAS and to detect the real amount of iron. Other authors reported analytical problems when analysing metal complexes with EDTA. Wang et al. reported that when analyzing samples by capillary electrophoresis with indirect ultraviolet detection, excessively high concentrations of EDTA should be avoided. Otherwise, alkaline-earth metal ion peaks detected with this technique would be long and the limits of detection would be high (Wang T et al. 1995).

Figure 25 shows the statistically significant effect of the interaction between magnesium and EDTA, which has a statistical significant effect on the enrichment factor of iron. When an interaction effect is significant, the effect of one factor depends on the level of another factor. This indicates that the effect of magnesium on the enrichment factor is dependent on the complex agent concentration used and vice versa.

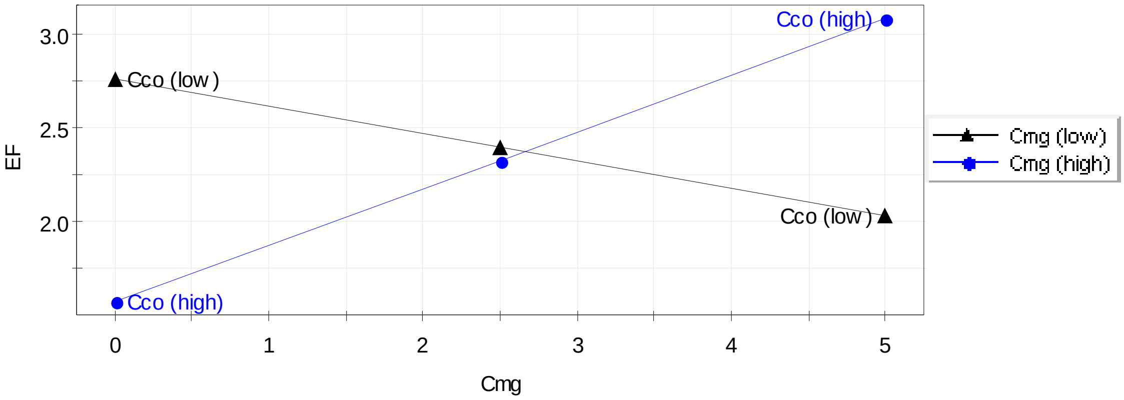

Figure 25. Interaction plot for Cmg*Cco respect enrichment factor.

As seen in Figure 25, an increase in the concentration of magnesium in the presence of complexing agent caused an increase in the enrichment factor of iron. After passing though the membrane, Fe^{2+} was immediately complexed with EDTA. Moreover, the stability of complexing iron compounds was higher than magnesium compounds. Therefore, Fe^{2+} flux was enhanced and the enrichment factor of iron increased. However, an increase in the concentration of magnesium without EDTA had the opposite effect, i.e. when there was no complexing agent in the receiver side, increasing the magnesium feed concentration decreased the enrichment factor of iron. Despite the lower Mg^{2+} flux, there was a competition between magnesium and iron. Therefore, the final enrichment factor decreased.

8.2.1 Enrichment factor of calcium and magnesium

As it can be seen in Table 1 in Appendix 2, calcium and magnesium were also preconcentrated by Donnan dialysis. With the exception of one experiment (N7), the enrichment factor increased as follows: $EF_{Mg}>EF_{Ca}>EF_{Fe}$. The competition between iron, magnesium and calcium may have caused the situation where the final preconcentration of iron was lower than expected. Donnan dialysis could be a better method to preconcentrate magnesium or calcium than iron.

8.3 Membrane fouling

The reproducibility of the membrane CMI-7000 was not as good as expected. As it can be seen in Table 5 the enrichment factor at the center points varied significantly from each other. Furthermore, by conducting mass balance calculations (Table 2 in Appendix 3) it could be observed that the initial mass of iron in the feed solution was not equal to the sum of the mass of iron in the receiver and the feed solution after the experiment. Therefore, it could be possible that iron was absorbed by the membrane reducing also the reproducibility of the process and the membrane. This theory is also supported by the fact that according to the supplier of the membrane (Membrane International from United States) the most likely cause of fouling of the CMI-7000 membrane is iron.

Membrane fouling could have been caused due to an insufficient regeneration of the membrane. Concentration of the solutions used for regeneration and time of regeneration depends on the type of foulant. Strongly bonded ions need higher concentrated solutions and longer times. It might be that the steps taken in this work for the regeneration might have not been sufficient, decreasing the reproducibility of the process.

The Center of Micro- and Nanotechnology at the University of Oulu made a study of the membranes, with a focused ion beam and scanning electron microscope, in order to check if there was membrane fouling. The analyses were made in the first layer of the membrane of 10 µm.

Appendix 4 shows all the images taken for this purpose. Below, some spectrums of the membrane are shown in order to evaluate the composition of the membrane samples.

The first membrane studied was a new CMI-7000 cation exchange membrane sample without pretreatment and without any experiment. This study was used as the reference membrane.

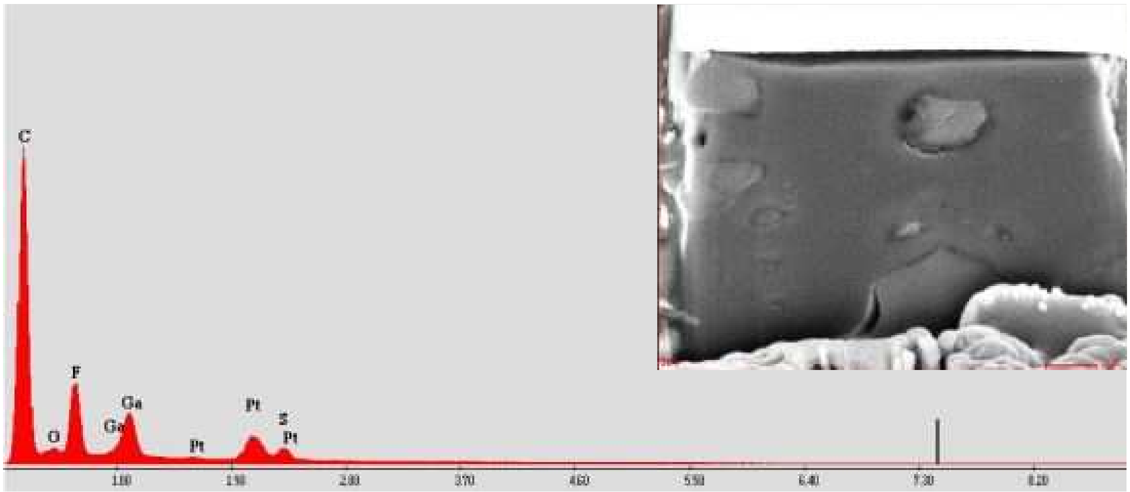

Figure 26. Spectrum and image of the membrane before any modification.

The reference membrane spectrum (Figure 26) shows the presence of five different substances. As expected, the polymeric membrane contains carbon (C) at high levels as well as sodium (Na). The presence of sulfur (S) and oxygen (O) can be explained since the membrane used for this purpose had sulphonic acid group (R-SO_3^-) as the ion-exchange group. Platinum (Pt) and Gallium (Ga) were added in the preparation stage of the samples before the analyses. In addition, according to the spectrum, the membrane also contains fluor (F). The energy of F is 0.667 keV and iron is 0.705 keV so the F peak could also be considered as iron.

Iron was added in one of the samples (bottom side of the membrane used in the main experiments) in order to confirm if fluor peak was actually iron. As it can be observed in Figure 27, fluor was inside the range between the two blue lines corresponding to the iron, thus the membrane contained iron in the structure instead of fluor.

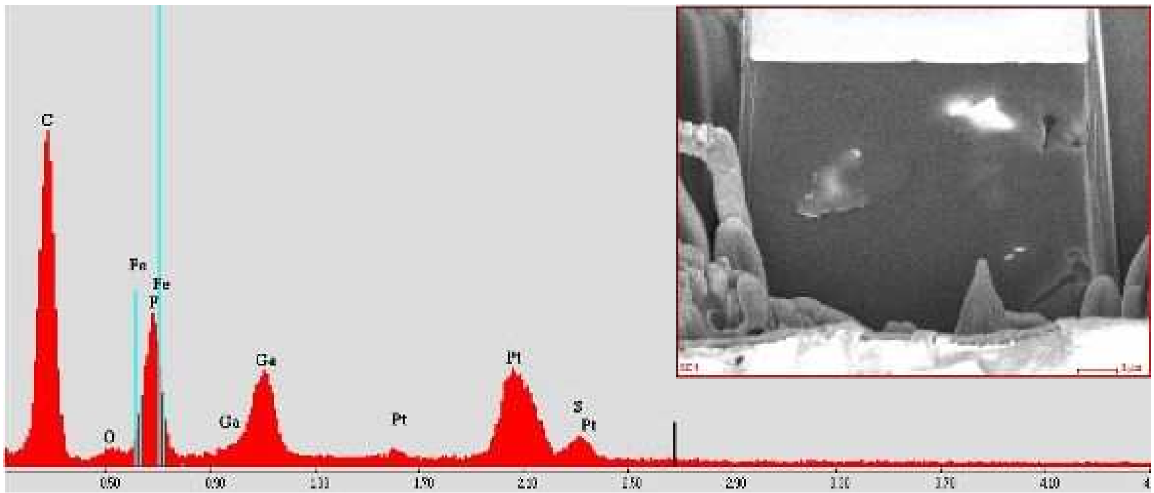

Figure 27. Spectrum and image of the second point of the membrane in the bottom side with an addition of iron.

The second study was to evaluate the amount of iron absorbed by the membrane due to the conduction of an experiment. A new CMI-7000 membrane was pretreated and used for the preconcentration of iron in an experiment with high concentration of calcium and magnesium. The imaging was made before the regeneration of the samples and in two different points of the sample.

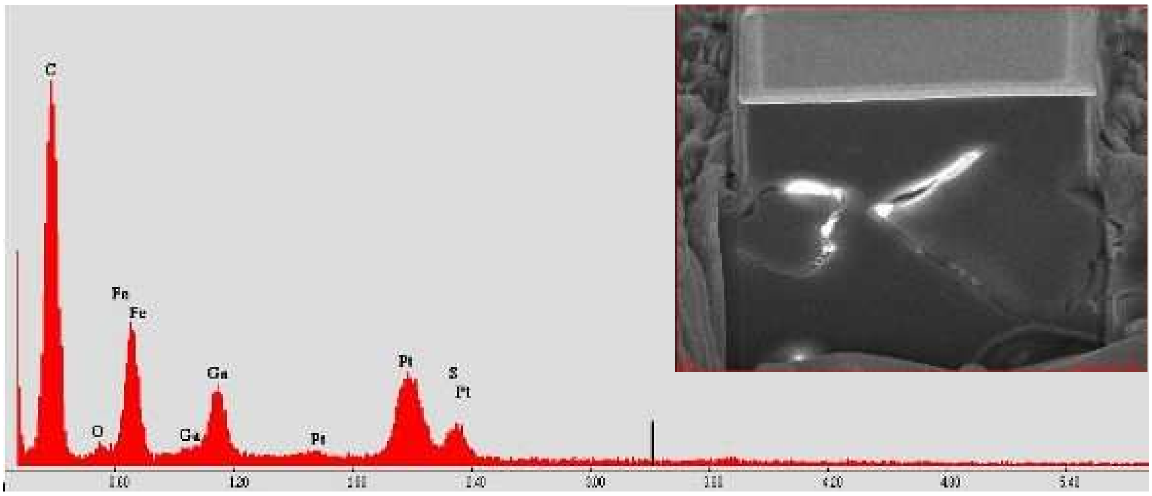

Figure 28. Spectrum and image of the first point of the membrane after one experiment.

In the spectrum of Figure 28 the presence of different elements on the membrane can be observed. As in the reference spectrum carbon (C) as well as sodium (Na) were present from the polymer structure of the membrane and sulfur (S) and oxygen (O) provided from the sulphonic acid group (R-SO_3^-) which acted as the ion-exchange group. Platinum (Pt) and Gallium (Ga) were added for the preparation of the samples before the analyses. In this spectrum iron (Fe) has a higher peak than in the spectrum of the reference membrane, hence it can be concluded that the iron was absorbed by the membrane structure.

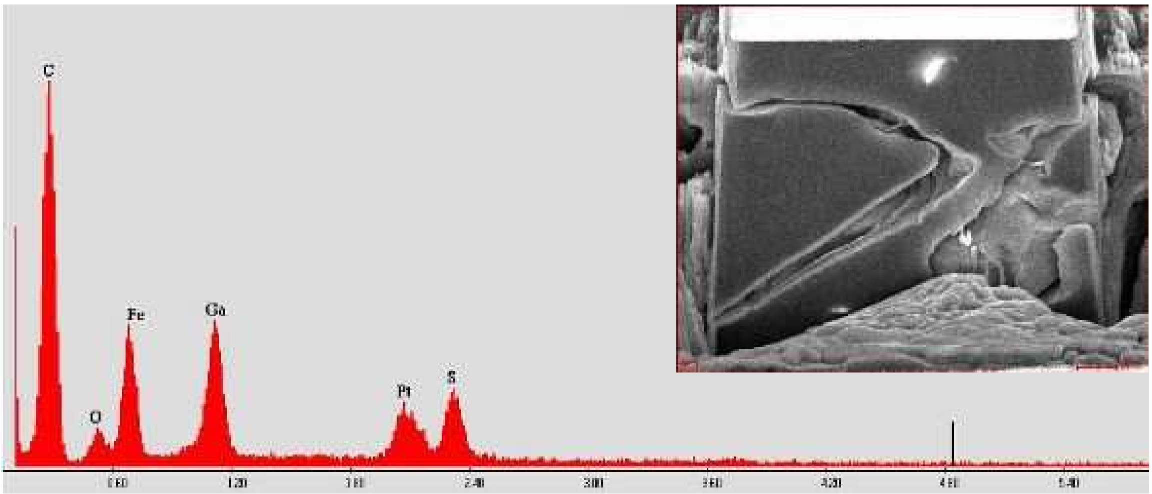

Figure 29. Spectrum and image of the second point of the membrane after one experiment.

The spectrum shown in Figure 29 corresponds to a different point on the membrane. As it can be observed in Figure 26 and Figure 28, both spectra are very similar and, the peaks of iron have approximately the same size, therefore, the presence of iron in the samples can be concluded to be the same in all the contact area of the samples.

In order to see the efficiency of the regeneration presented in this study, half of the CMI-7000 membrane used for the experiment was regenerated. The imaging was made in two different points of the sample.

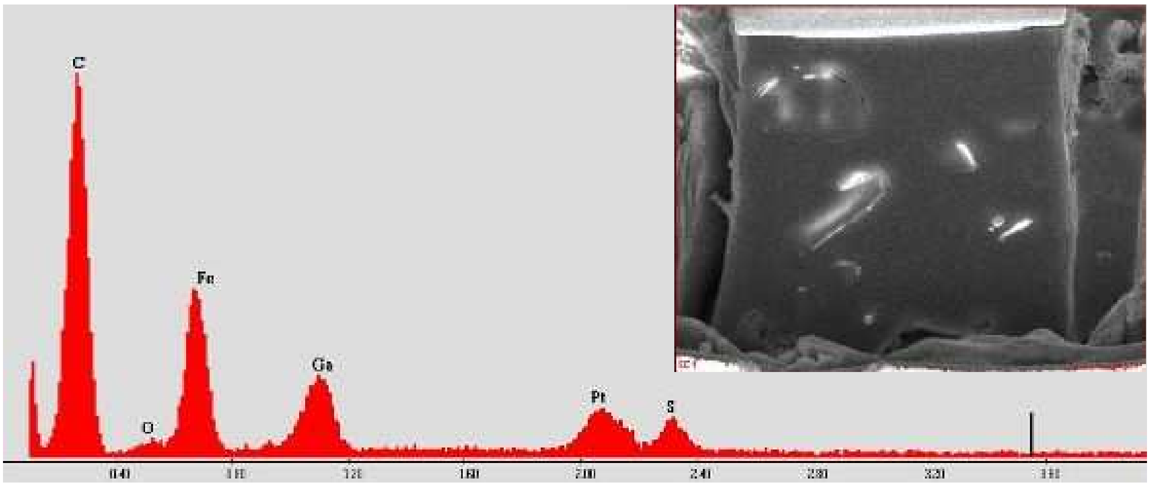

Figure 30. Spectrum and image of the first point of the membrane after regeneration.

In the spectrum of Figure 30, the characteristics elements of the membrane are present. In addition, the presence of iron has been observed. The high iron peak supports the theory that the regeneration done was not sufficient to eliminate adsorbed iron.

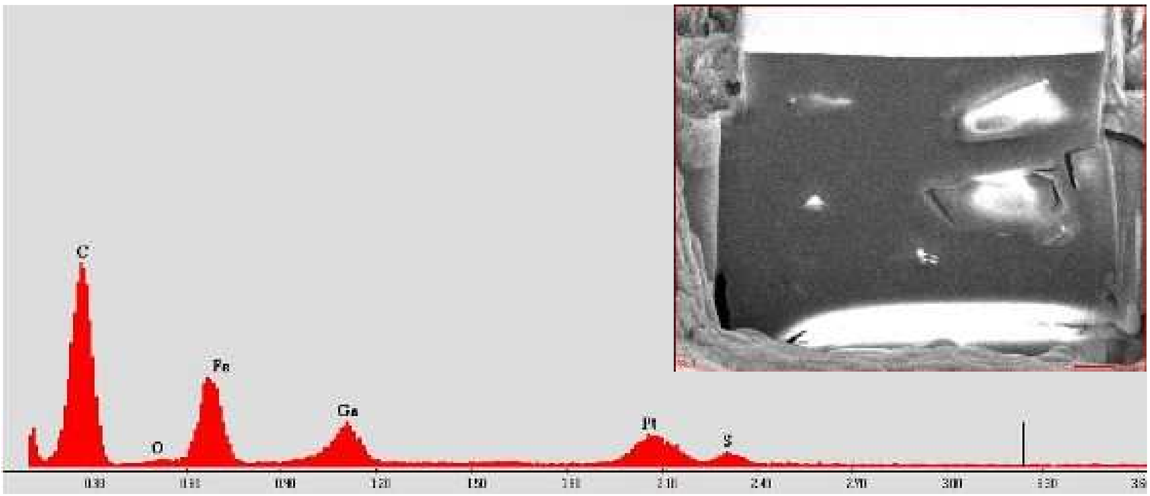

Figure 31. Spectrum and image of the second point of the membrane after regeneration.

In this second spectrum (Figure 31) corresponding to the second point of the membrane, the same elements have been observed than in the spectrum of the first point (Figure 30). At this point the regeneration works better than in the first point since the iron peak of the spectrum of Figure 31 is lower than in Figure 30. The conclusion that could be reached was that the membrane fouling due to iron was eliminated partially with the regeneration.

The last study was to evaluate the CMI-7000 membrane used in all the experiments since the reproducibility of the experiments using this membrane was not as satisfactory as expected. The membrane was analyzed after finalising the set of experiments conducted using the statistical design of experiments and after regeneration. Two points in both sides of the membrane were analyzed.

Fig. 32, Fig. 33 and Fig. 34 show the spectra of this last study.

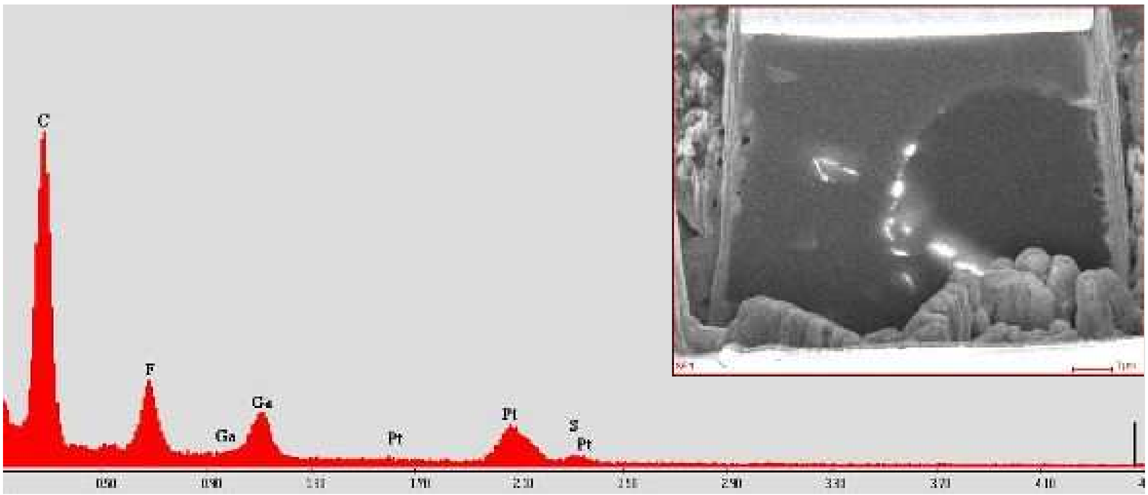

Figure 32. Spectrum and image of the first point of the membrane in the bottom side.

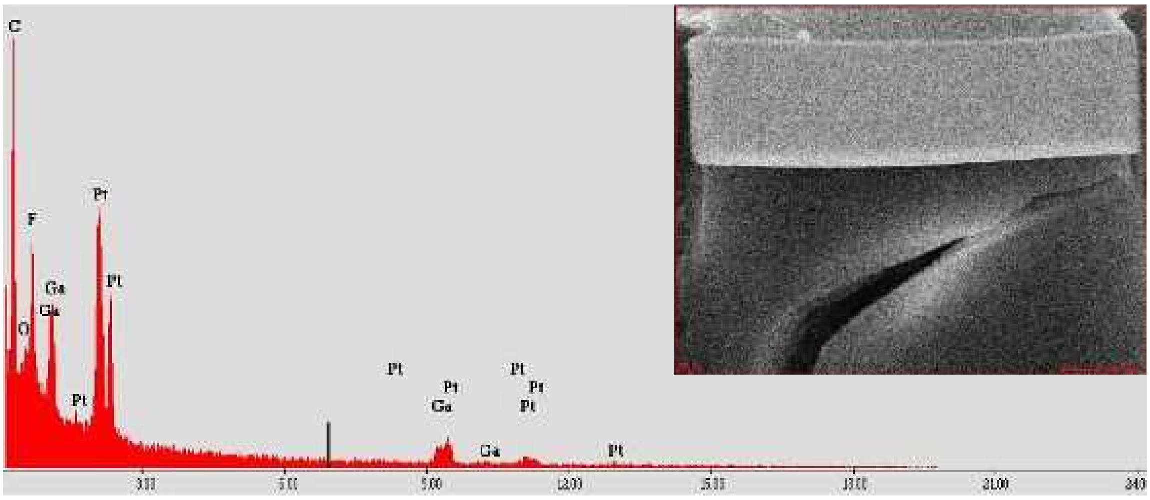

Figure 33. Spectrum and image of the first point of the membrane in the top side.

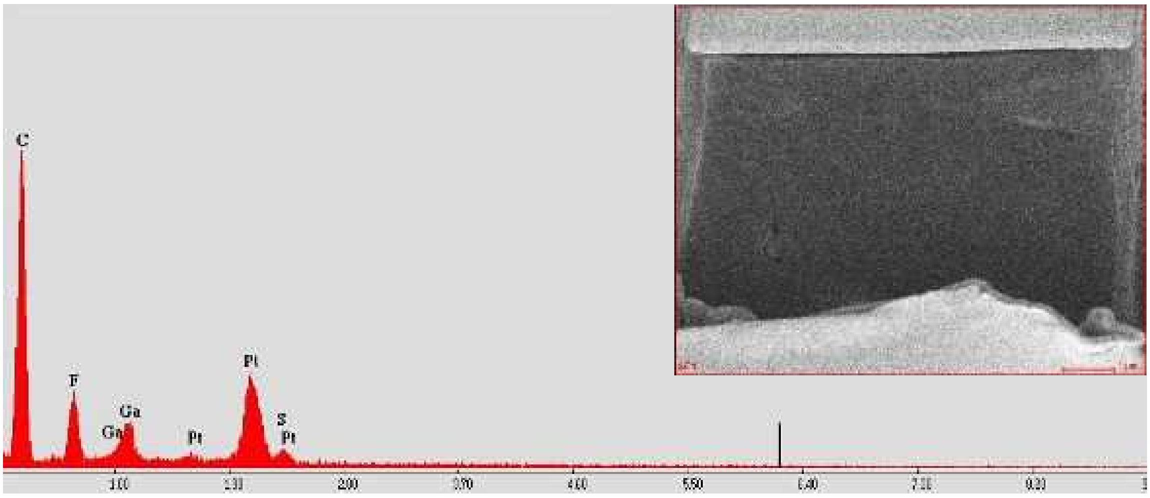

Figure 34. Spectrum and image of the second point of the membrane in the top side.

In the spectra in Figures 32, 33 and 34 the presence of the same elements that appear in the reference spectra can be observed. As explained before, the peak of fluor is representing the presence of iron. The iron peak in Figure 34 is approximately as in the spectrum of the reference membrane (Figure 26), however it is lower than in Figure 30 or 31. Therefore, the regeneration worked differently in each case, having a partial regeneration of the membrane. This fact could explain the bad reproducibility of the membrane.

8.4 Comparison between different membranes

The efficiency of the CMI-7000 cation exchange membrane (Membranes International inc.) towards the preconcentration of iron was compared with the membrane RALEX CM-PP (RALEX a.s.). For this purpose two extra experiments were conducted where the iron feed concentration was 0.15 mg/dm^3 and with and without EDTA in the receiving solutions.

Table 7. Factors and responses of preconcentration experiments with different membranes.

Experiment number	Factors					Response
	Membrane	C_{Ca} [mg/dm^3]	C_{Mg} [mg/dm^3]	$C_{complex}$ [mg/dm^3]	C_{Fe} [mg/dm^3]	EF
1	CMI-7000	0	0	0	0.15	4.52
5	CMI-7000	0	0	155	0.15	2.66
14	RALEX CM-PP	0	0	0	0.15	2.75
15	RALEX CM-PP	0	0	155	0.15	2.76

As it can be observed in Table 7, the enrichment factors obtained with the RALEX CM-PP membrane provided by RALEX were the same with and without the complexing agent, achieving enrichment factor of 2.75. When comparing these results with the results obtained using the CMI-7000 membrane (Membrane International), it can be observed that without the presence of EDTA in the receiver side the CMI-7000 membrane was more efficient than the RALEX CM-PP membrane, obtaining higher enrichment factors.

Cengeloglu et al. obtained recovery factors of iron up to 15 % in samples of red mud. This value was reached after three hours of experiment using a cation exchange membrane with a thickness of 0.15 mm. In the same study, the comparison of different membranes with different thicknesses showed that the thicker the membrane the lower the recovery factor was (Cengeloglu Y et al. 2003). When the membrane thickness increases, the diffusion of the ion through the membrane decreases. Consequently, the flux of the ion decreases obtaining lower enrichment factors (Akretche D et al. 2000).

The CMI-7000 and RALEX CM-PP membranes used in this study had relatively high thickness, which is around 3 times higher than the ones used in the literature. Therefore, it can be concluded that longer experimental time or membranes with more appropriated thickness should be used in order to increase the ion flux though the membrane and consequently to improve the enrichment factor of iron.

8.5 Preconcentration of copper

The purpose of this specific study was to compare the efficiency of Donnan dialysis for the preconcentration of another metal such as copper.

Two experiments were conducted with copper instead of iron. The experiments contained 0.15 mg/dm^3 of Cu^{2+} in the feed solution and no complexing agent was added in the receiving solution. The first experiment was performed with the membrane provided by Membrane International (CMI-7000) and in the second one the membrane was provided by MEGA a.s (RALEX CM-PP).

Table 8. Factors and responses of preconcentration experiments of copper with different membranes.

Experiment number	Factors				Response	
	Membrane	$C_{complex}$ [mg/dm^3]	C_{Fe} [mg/dm^3]	C_{Cu} [mg/dm^3]	EF_{Fe}	EF_{Cu}
1	CMI-7000	0	0.15	0	4.52	
16	CMI-7000	0	0	0.15		3.22
14	RALEX CM-PP	0	0.15	0	2.75	
17	RALEX CM-PP	0	0	0.15		4.44

As it can be observed in Table 8, the enrichment factor of copper was 3.22 and 4.44 with the CMI-7000 membrane and RALEX CM-PP membrane, respectively. However, preconcentration of iron with the CMI-7000 membrane (4.52) resulted in a higher efficiency than with the RALEX CM-PP membrane (2.75).

Wiśniewski et al. (Wiśniewski J et al.) reported that the attraction of the Ca^{2+} (31.39 eV) ion by the negatively charged ion-exchange groups inside the membrane is stronger than that observed in the case of the Mg^{2+} ion as a consequence of the difference in the electronegativity (16.2 eV). As the electronegativity of Fe^{2+} and Cu^{2+} are similar, 23.4 eV and 28.5 eV, respectively (Person RG 1988), the behaviour of these metals with the ionic exchange membrane is also similar and therefore, it is understandable that the range of the enrichment factors was the same.

9 Conclusions

In this study the preconcentration of iron by Donnan dialysis has been achieved, obtaining enrichment factors up to 4.52. Therefore, Donnan dialysis has been proved to be a feasible technique to preconcentrate trace elements such as iron from wastewater sample. However, this study has also shown that the metal competition can be a relevant disadvantage on the Donnan dialysis process.

The effect of the presence of magnesium and calcium in the feed solution and the addition of EDTA as a complexing agent in the receiver solution were analysed with the MODDE software. The study showed that calcium decreased the enrichment factor of iron due to the competition between Ca^{2+} and Fe^{2+}.

Magnesium did not show any significant effect on the enrichment factor of iron. However, a significant flux of magnesium through the membrane was observed, achieving higher enrichment factors of magnesium than iron. It was observed that the enrichment factors increased as follows: $EF_{Mg}>EF_{Cu}>EF_{Fe.}$ The enrichment factor of iron was also affected by the magnesium and EDTA interaction, which enhanced the iron preconcentration when adding both substances in the process.

The presence of EDTA in the receiver side did not affect the enrichment factor of iron. The molar ratio used in this study (1:200) decreased the detection limit avoiding the detection of Fe^{2+}, therefore the enrichment factors were low. It can be concluded that in order to enhance the selectivity of the Donnan dialysis towards iron, a molar ratio of 1:1 should be used.

The membrane fouling was studied by taking microscope images of four different samples of membranes. The fouling theory was confirmed as a consequence of the high presence of iron in the membrane after an experiment. Moreover, it was possible to see iron in the membrane after regeneration. This means that the membrane cleaning was not efficient enough to remove all impurities, and consequently, the reproducibility of the membrane was lower than expected.

The results obtained using CMI-7000 for the preconcentration of iron and using statistical design of experiments were compared using another membrane (RALEX CM-PP) and also with another metal, i.e. copper. In all the comparisons, the results were very similar.

The metal enrichment factors obtained in this study were lower than expected. It was concluded that the low iron flux achieved were due to the high thickness of the membrane. In this study, the experiments were conducted for 5 hours. It can be concluded that longer experimental time is needed in order to achieve higher enrichment factors with the membranes used in this study.

10 Summary

In the present study, the applicability of Donnan dialysis for the preconcentration of iron from a synthetic wastewater was investigated. Heavy metals are of great concern because of their extreme toxicity, even at low traces. Even with the sensitivity and selectivity of extracting analytical techniques, the direct determination is not always possible due to the low concentration of the ions. For this reason there is a great necessity for preconcentration of heavy metals prior to their determination.

In the theoretical part of the study some hazardous metals were studied, focusing on their characteristics such as possible harm to the human system, the untaken limits permitted and the sources of the metals. Operating principles, advantages and disadvantages, and other applications of conventional preconcentration techniques were compared. The same characteristics were studied for membrane technology for preconcentration. Donna dialysis was studied in more detail.

In the experimental part of the work the preconcentration of iron from synthetic water samples by Donnan dialysis was studied. The samples were synthetic wastewater which included iron as the metal to be preconcentrated and magnesium and calcium to simulate more realistic conditions in natural waters. EDTA as a complexing agent was also added in the receiver solution in order to improve the final enrichment factor of iron. The results were analyzed with the MODDE 8.0 experimental design software.

Extra experiments were conducted in order to study the efficiency of Donnan dialysis at different conditions. One of the studying was focused on comparing the efficiency of different membranes (CMI-7000 and RALEX CM-PP) to concentrate iron by Donnan dialysis and the other study was focused on comparing the efficiency of Donnan dialysis when preconcentrating different metals (iron and copper).

Microscope images of the membranes were taken for the study of the membrane structure before and after experiments and after regenerations. These images helped to verify the presence of iron in the membrane due to the absorbance and the insufficient regeneration of the membranes.

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The Appendices

Preparation of feed solutions

Preparation of Fe^{2+} 0.15 ppm

$$1\,\mathrm{dm}^3 \cdot \frac{0.15\ \mathrm{mg\ Fe}^{2+}}{1\,\mathrm{dm}^3} \cdot \frac{1\,\mathrm{g}}{1000\ \mathrm{mg}} \cdot \frac{1\,\mathrm{dm}^3\ \mathrm{Fe}^{2+}}{1.5\ \mathrm{g\ Fe}^{2+}} \cdot \frac{1000\ \mathrm{cm}^3}{1\,\mathrm{dm}^3} = 0.1\,\mathrm{cm}^3\ \mathrm{Fe}^{2+}$$

Preparation of Ca^{2+} 4g/dm^3 from $CaCl_2$

$$250\ \mathrm{cm}^3 \cdot \frac{1\,\mathrm{dm}^3}{1000\ \mathrm{cm}^3} \frac{4\ \mathrm{g\ Ca}^{2+}}{1\,\mathrm{dm}^3} \cdot \frac{1\,\mathrm{mol\ Ca}^{2+}}{40.078\ \mathrm{g}} \cdot \frac{1\,\mathrm{mol\ CaCl}_2}{1\,\mathrm{mol\ Ca}^{2+}} \frac{110.99\ \mathrm{g\ CaCl}_2}{1.5\ \mathrm{mol\ CaCl}_2} = 2.091\,\mathrm{g\ CaCl}_2$$

Preparation of Ca^{2+} 20 ppm

$$1\,\mathrm{dm}^3 \cdot \frac{20\ \mathrm{mg\ Ca}^{2+}}{1\,\mathrm{dm}^3} \cdot \frac{1\,\mathrm{g}}{1000\ \mathrm{mg}} \cdot \frac{1\,\mathrm{dm}^3\ \mathrm{Ca}^{2+}}{4\ \mathrm{g\ Ca}^{2+}} \cdot \frac{1000\ \mathrm{cm}^3}{1\,\mathrm{dm}^3} = 5\ \mathrm{cm}^3\ \mathrm{Ca}^{2+}$$

Preparation of Ca^{2+} 10 ppm

$$1\,\mathrm{dm}^3 \cdot \frac{10\ \mathrm{mg\ Ca}^{2+}}{1\,\mathrm{dm}^3} \cdot \frac{1\,\mathrm{g}}{1000\ \mathrm{mg}} \cdot \frac{1\,\mathrm{dm}^3\ \mathrm{Ca}^{2+}}{4\ \mathrm{g\ Ca}^{2+}} \cdot \frac{1000\ \mathrm{cm}^3}{1\,\mathrm{dm}^3} = 2.5\ \mathrm{cm}^3\ \mathrm{Ca}^{2+}$$

Preparation of Mg^{2+} 1g/dm^3 from $MgCl_2$

$$250\ \mathrm{cm}^3 \cdot \frac{1\,\mathrm{dm}^3}{1000\ \mathrm{cm}^3} \frac{1\,\mathrm{g\ Mg}^{2+}}{1\,\mathrm{dm}^3} \cdot \frac{1\,\mathrm{mol\ Mg}^{2+}}{24.305\ \mathrm{g}} \cdot \frac{1\,\mathrm{mol\ Mg}^{2+}_{\mathrm{comercial}}}{1\,\mathrm{mol\ Mg}^{2+}} \frac{203.3\ \mathrm{g\ Mg}^{2+}_{\mathrm{comercial}}}{1\,\mathrm{mol\ Mg}^{2+}_{\mathrm{comercial}}} = 2.769\ \mathrm{g\ Mg}^{2+}_{\mathrm{comercial}}$$

Preparation of Mg^{2+} 5 ppm in 1 dm^3

$$1\,\mathrm{dm}^3 \cdot \frac{5\ \mathrm{mg\ Mg}^{2+}}{1\,\mathrm{dm}^3} \cdot \frac{1\,\mathrm{g}}{1000\ \mathrm{mg}} \cdot \frac{1\,\mathrm{dm}^3\ \mathrm{Mg}^{2+}}{1\ \mathrm{g\ Mg}^{2+}} \cdot \frac{1000\ \mathrm{cm}^3}{1\,\mathrm{dm}^3} = 5\ \mathrm{cm}^3\ \mathrm{Mg}^{2+}$$

Preparation of Mg^{2+} 2.5 ppm in 1 dm^3

$$1\ \mathrm{dm}^3 \cdot \frac{2.5\ \mathrm{mg\ Mg}^{2+}}{1\ \mathrm{dm}^3} \cdot \frac{1\ \mathrm{g}}{1000\ \mathrm{mg}} \cdot \frac{1\ \mathrm{dm}^3\ \ \mathrm{Mg}^{2+}}{1\ \mathrm{g\ Mg}^{2+}} \cdot \frac{1000\ \mathrm{cm}^3}{1\ \mathrm{dm}^3} = 2.5\ \mathrm{cm}^3\ \ \mathrm{Mg}^{2+}$$

Preparation of receiver solutions

Preparation of HCl 1M

$$100\ \mathrm{cm}^3 \cdot \frac{1\ \mathrm{dm}^3}{1000\ \mathrm{cm}^3} \cdot \frac{1\ \mathrm{mol\ HCl}}{1\ \mathrm{dm}^3} \cdot \frac{36.46\ \mathrm{g\ HCl}}{1\ \mathrm{mol\ HCl}} \cdot \frac{1\ \mathrm{cm}^3}{1.19\ \mathrm{g\ HCl}} \cdot \frac{100}{38} = 8.06\ \mathrm{cm}^3\ \ \mathrm{HCl}$$

Preparation of EDTA 155 ppm

$$100\ \mathrm{cm}^3 \cdot \frac{1\ \mathrm{dm}^3}{1000\ \mathrm{cm}^3} \cdot \frac{155\ \mathrm{mg\ EDTA}}{1\ \mathrm{dm}^3} \cdot \frac{1\ \mathrm{g}}{1000\ \mathrm{mg}} \cdot \frac{1\ \mathrm{mol\ EDTA}}{292.246\ \mathrm{g\ EDTA}} \cdot \frac{1\ \mathrm{mol\ EDTA}_{\mathrm{comercial}}}{1\ \mathrm{mol\ EDTA}} \cdot$$
$$\cdot \frac{372.24\ \mathrm{EDTA}_{\mathrm{comercial}}}{1\ \mathrm{mol\ EDTA}_{\mathrm{comercial}}} = 0.0197\ \mathrm{g\ EDTA}_{\mathrm{comercial}}$$

Preparation of EDTA 77.5 ppm

$$100\ \mathrm{cm}^3 \cdot \frac{1\ \mathrm{dm}^3}{1000\ \mathrm{cm}^3} \cdot \frac{77.5\ \mathrm{mg\ EDTA}}{1\ \mathrm{dm}^3} \cdot \frac{1\ \mathrm{g}}{1000\ \mathrm{mg}} \cdot \frac{1\ \mathrm{mol\ EDTA}}{292.246\ \mathrm{g\ EDTA}} \cdot \frac{1\ \mathrm{mol\ EDTA}_{\mathrm{comercial}}}{1\ \mathrm{mol\ EDTA}} \cdot$$
$$\cdot \frac{372.24\ \mathrm{EDTA}_{\mathrm{comercial}}}{1\ \mathrm{mol\ EDTA}_{\mathrm{comercial}}} = 0.0099\ \mathrm{g\ EDTA}_{\mathrm{comercial}}$$

Table 1. Analysis of all the experiments performed with AAS. N5, N6, N14, N15, N16, N17 were analyzed by graphite method and the other ones by flame method.

Test	Sample	Fe [mg/dm^3]	Ca [mg/dm^3]	Mg [mg/dm^3]	EF_{Fe}	EF_{Ca}	EF_{Mg}
N1	F0	0.166					
	F2	0.168					
	F3	0.154					
	F4	0.148					
	F5	0.149					
	R0	0.169					
	R1	0.529					
	R3	0.6					
	R5	0.752					
	R	0.957					
					4.52		
N2	F0	0.100	16.490				
	F2	0.125	15.880				
	F3	0.119	15.580				
	F4	0.123	15.060				
	F5	0.123	14.490				
	R0	0.037	0.110				
	R1	0.097					
	R3	0.128					
	R5	0.128					
	R	0.174	37.530				
					1.28	2.28	
N3	F0	0.156		4.874			
	F2	0.158		4.616			
	F3	0.163		4.533			
	F4	0.156		4.527			
	F5	0.146		4.312			
	R0	0.087		0.006			
	R1	0.061					
	R3	0.140					
	R5	0.390					
	R	0.411		13.490			
					2.49		2.77
N4	F0	0.096	16.170	4.941			
	F2	0.110	15.150	4.757			
	F3	0.147	14.500	4.635			
	F4	0.108	14.300	4.507			
	F5	0.096	13.810	4.414			
	R0	0.044	0.044	0.014			
	R1	0.112					
	R3	0.103					
	R5	0.158					

Table 1. continues.

Test	Sample	Fe [mg/dm^3]	Ca [mg/dm^3]	Mg [mg/dm^3]	EF$_{Fe}$	EF$_{Ca}$	EF$_{Mg}$
	R	0.151	43.550	18.760			
					1.65	2.69	3.80
N5	F0	0.120					
	F2	0.126					
	F3	0.131					
	F4	0.127					
	F5	0.124					
	R0	0.075					
	R1	0.040					
	R3	0.063					
	R5	0.319					
	R	0.307					
					2.66		
N6	F0	0.085	-				
	F2	0.106	-				
	F3	0.094	-				
	F4	0.100	-				
	F5	0.111	-				
	R0	0.046	-				
	R1	0.048					
	R3	0.051					
	R5	0.048					
	R	0.049	-				
					0.57	-	
N7	F0	0.114		4.886			
	F2	0.124		4.705			
	F3	0.128		4.533			
	F4	0.127		4.433			
	F5	0.123		4.254			
	R0	0.017		0.010			
	R1	0.104					
	R3	0.201					
	R5	0.465					
	R	0.485		15.170			
					4.09		3.10
N8	F0	0.133	19.250	4.971			
	F2	0.140	18.430	4.730			
	F3	0.135	17.860	4.576			
	F4	0.134	17.290	4.497			
	F5	0.172	16.910	4.372			
	R0						
	R1	<20					
	R3	<20					

Table 1. continues.

Test	Sample	Fe [mg/dm^3]	Ca [mg/dm^3]	Mg [mg/dm^3]	EF_{Fe}	EF_{Ca}	EF_{Mg}
	R5	<20					
	R	<20	68.800	21.720			
					2.14	3.57	4.37
N9	F0	0.142	9.461	2.480			
	F2	0.146	9.243	2.348			
	F3	0.146	8.918	2.260			
	F4	0.141	8.579	2.182			
	F5	0.132	8.350	2.102			
	R0	0.067	0.052	0.006			
	R1	0.046					
	R3	0.142					
	R5	0.356					
	R	0.403	29.430	9.745			
					2.51	3.11	3.93
N10	F0	0.149	7.638	2.329			
	F2	0.148	7.312	2.231			
	F3	0.130	7.128	2.110			
	F4	0.132	6.874	2.060			
	F5	0.135	6.627	2.009			
	R0	0.089	0.203	0.059			
	R1	0.139					
	R3	0.194					
	R5	0.288					
	R	0.289	21.010	7.831			
					1.94	2.75	3.36
N11	F0	0.123	7.542	2.334			
	F2	0.122	7.347	2.221			
	F3	0.129	7.130	2.183			
	F4	0.122	7.067	2.143			
	F5	0.128	6.747	2.076			
	R0	0.022	0.078	0.006			
	R1	<20					
	R3	<20					
	R5	0.128					
	R	0.184	12.560	4.570			
					1.04	1.67	1.96
N12	F0	0.167					
	F2	0.158					
	F3	0.149					
	F4	0.152					
	F5	0.145					
	R0	0.133					
	R1	-					

Table 1. continues.

Test	Sample	Fe [mg/dm^3]	Ca [mg/dm^3]	Mg [mg/dm^3]	EF_{Fe}	EF_{Ca}	EF_{Mg}
	R3	0.337					
	R5	0.593					
	R	0.643					
					3.55		
N13	F0	0.185					
	F2	0.228					
	F3	0.168					
	F4	0.174					
	F5	0.176					
	R0	-					
	R1	0.349					
	R3	0.538					
	R5	0.556					
	R	0.802					
					4.33		
N14	F0	0.148					
	F1	0.150					
	F2	0.149					
	F4	0.143					
	F5	0.150					
	R0	0.079					
	R1	0.135					
	R3	0.228					
	R5	0.406					
	R	0.421					
					2.75		
N15	F0	0.153					
	F2	0.169					
	F3	0.155					
	F4	0.141					
	F5	0.147					
	R0	0.024					
	R1	0.071					
	R3	0.170					
	R5	0.424					
	R	0.448					
					2.76		
N16	F0	0.142					
	F2	0.138					
	F3	0.128					
	F4	0.129					
	F5	0.124					
	R0	0.005					

Table 1. continues.

Test	Sample	Fe [mg/dm^3]	Ca [mg/dm^3]	Mg [mg/dm^3]	EF_{Fe}	EF_{Ca}	EF_{Mg}
	R1	0.037					
	R3	0.174					
	R5	0.458					
	R	0.488					
					3.22		
N17	F0	0.152					
	F2	0.149					
	F3	0.145					
	F4	0.143					
	F5	0.134					
	R0	0.005					
	R1	0.019					
	R3	0.244					
	R5	0.677					
	R	0.814					
					4.44		

where F_i is feed solution of the experiment i,

R_i is receiver solution of the experiment i, and

R is the leftover receiver solution.

Table 2. Mass balance of iron.

Test	Initial m_{feed} [mg]	Final m_{feed} [mg]	$m_{receiver}$ [mg]	$m_{feed+receiver}$ [mg]
N1	0.1663	0.1402	0.0060	0.1462
N2	0.0997	0.1279	0.0010	0.1289
N3	0.1562	0.1374	0.0031	0.1405
N4	0.0960	0.0903	0.0013	0.0916
N5	0.1201	0.1162	0.0026	0.1188
N6	0.0852	0.1042	0.0004	0.1046
N7	0.1137	0.1152	0.0037	0.1189
N8	0.1332	0.1617	0.0023	0.1640
N9	0.1419	0.1245	0.0028	0.1273
N10	0.1485	0.1273	0.0023	0.1296
N11	0.1226	0.1199	0.0010	0.1209
N12	0.1672	0.1410	0.0052	0.1462
N13	0.1854	0.1720	0.0064	0.1784
N14	0.1477	0.1412	0.0032	0.1444
N15	0.1532	0.1381	0.0034	0.1415
N16	0.1422	0.1165	0.0037	0.1202
N17	0.1521	0.1263	0.0054	0.1317

where m_{feed} is the mass of the feed solution [mg],

$m_{receiver}$ is the mass of the receiver solution [mg] and

$m_{feed+receiver}$ is the sum of the mass in the feed and receiver solution [mg].

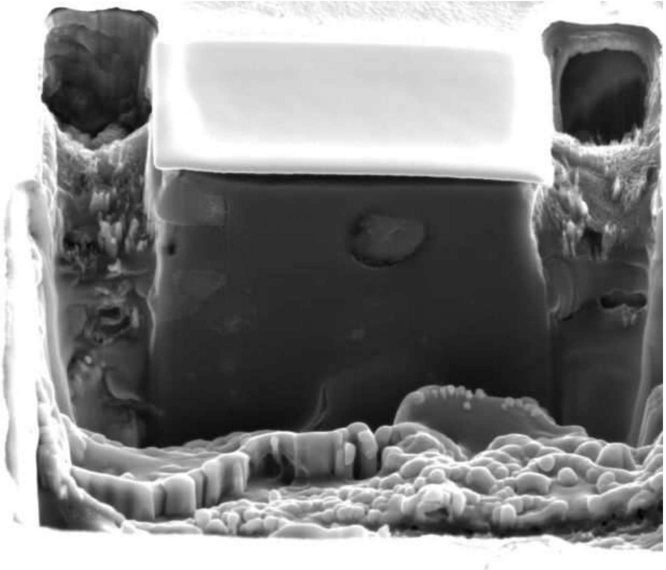

Figure 1. Image of 10 µm area of the reference membrane.

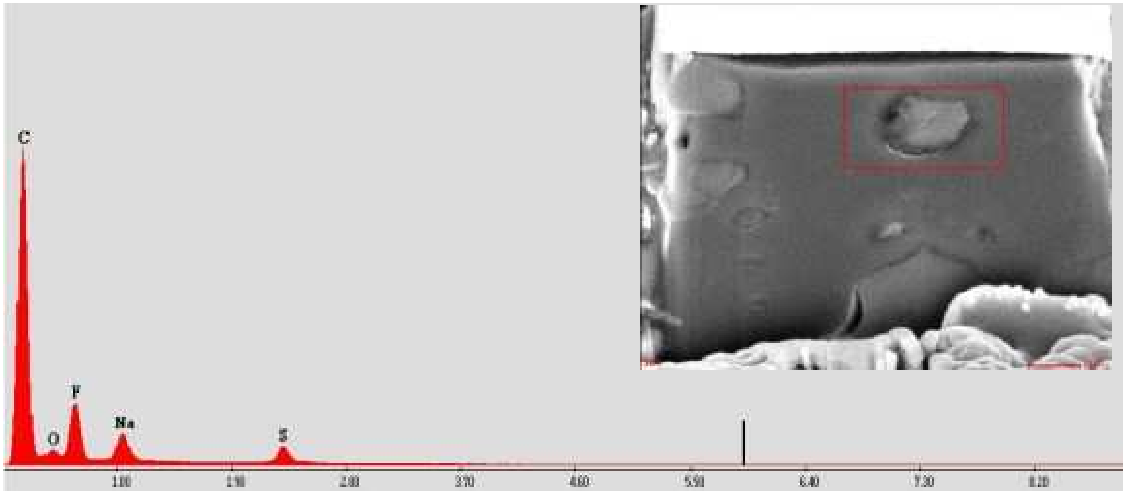

Figure 2. Spectrum of a partial area of Figure 1.

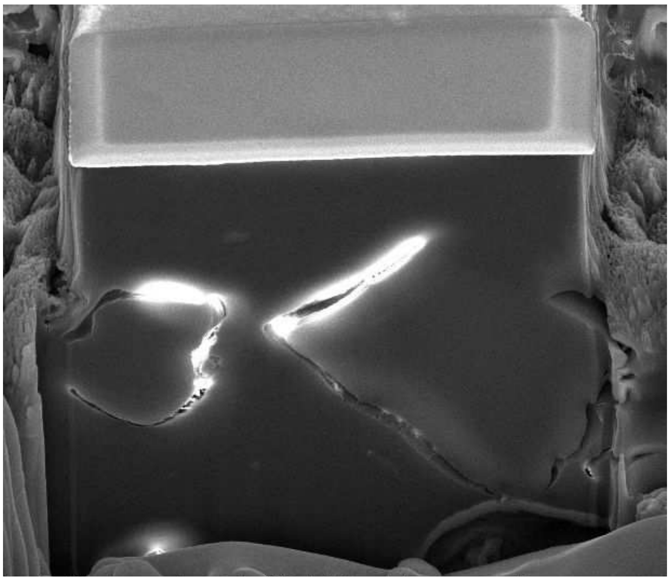

Figure 3. Image of 10 µm area of the membrane after an experiment in the first point.

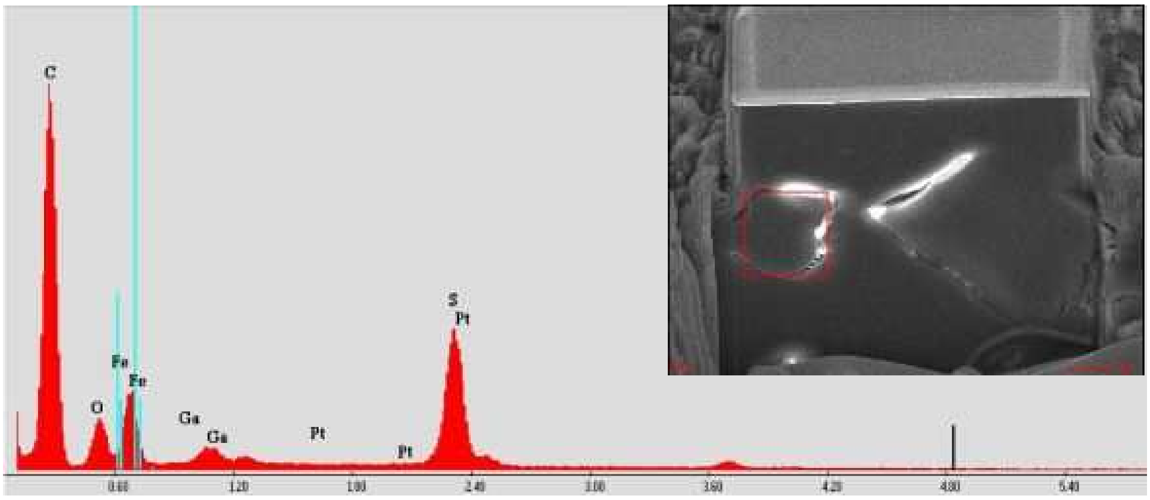

Figure 4. Spectrum of a partial area of Figure 3.

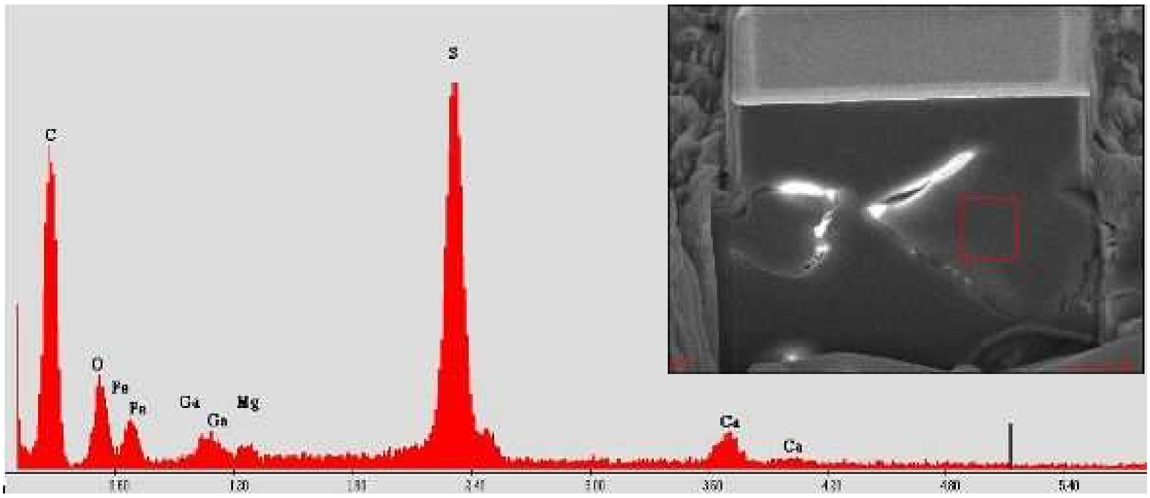

Figure 5. Spectrum of a partial area of Figure 3.

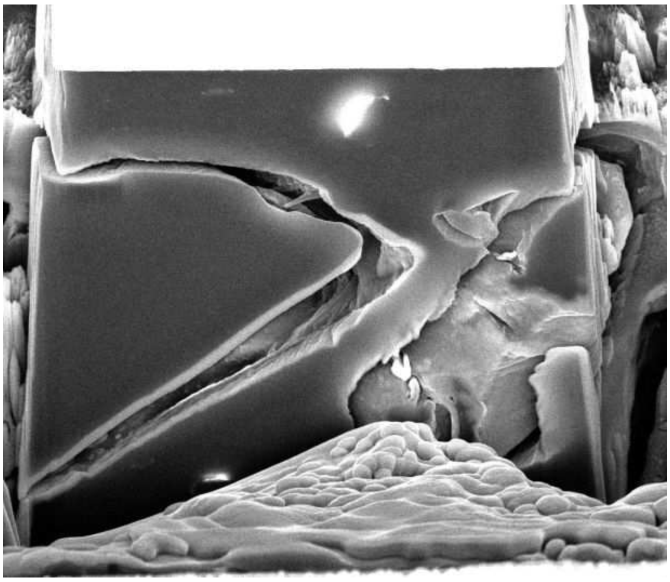

Figure 6. Image of 10 µm area of the membrane after an experiment in the second point.

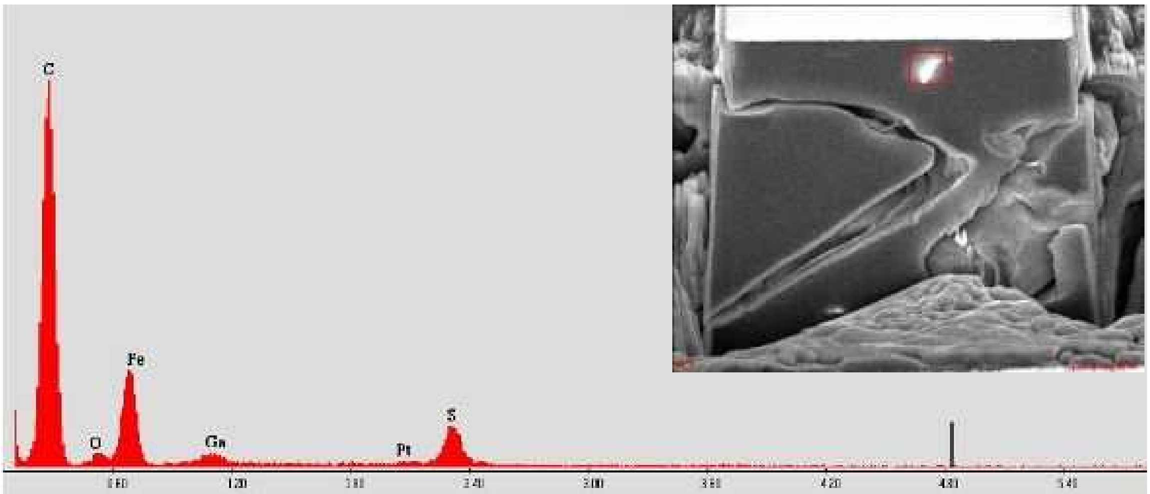

Figure 7. Spectrum of a partial area of Figure 6.

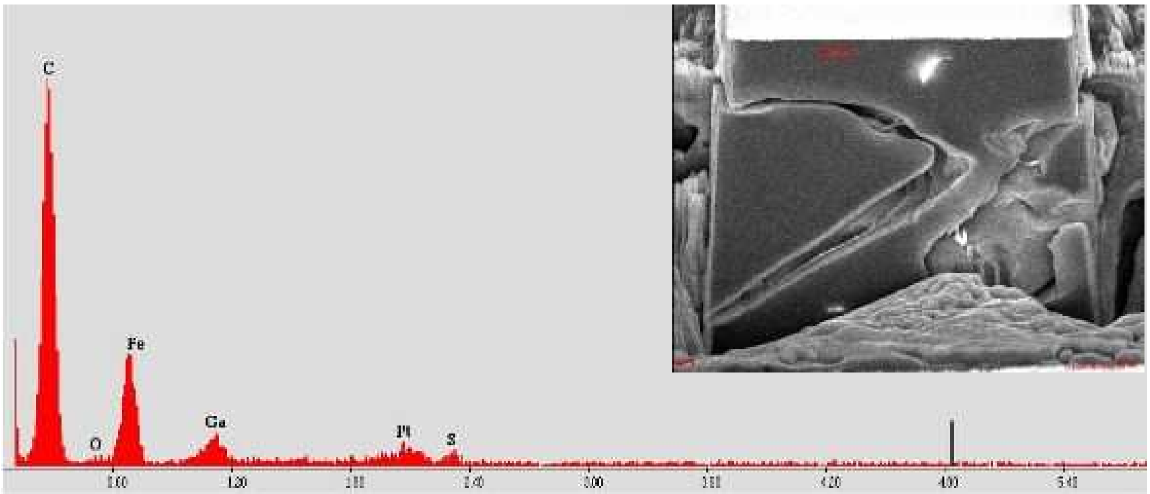

Figure 8. Spectrum of a partial area of Figure 6.

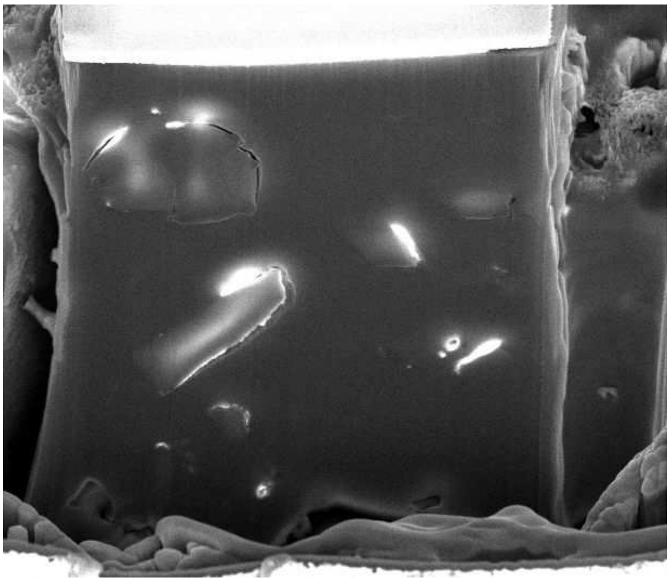

Figure 9. Image of 10 µm area of the membrane after regeneration in the first point.

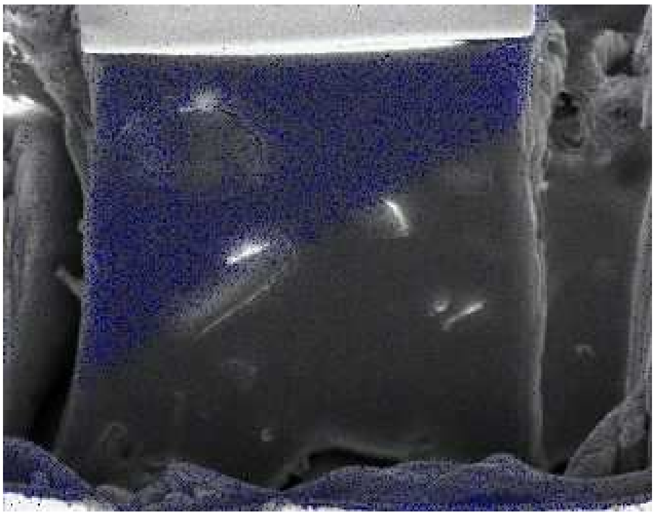

Figure 10. Figure 9 with a mapping test to illustrate the location of Fe (dark blue).

Figure 11. Image of 10 µm area of the membrane after regeneration in the second point.

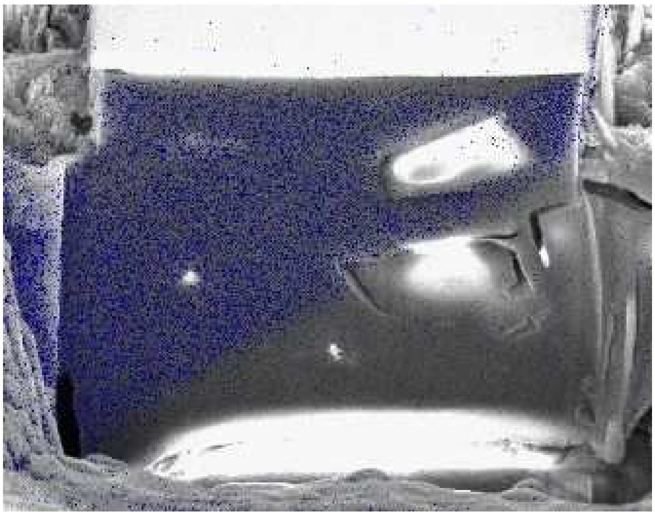

Figure 12. Figure 11 with a mapping test to illustrate the location of Fe (dark blue).

Figure 13. Image of 10 µm area of the membrane used in the main experiments. First point of the bottom side.

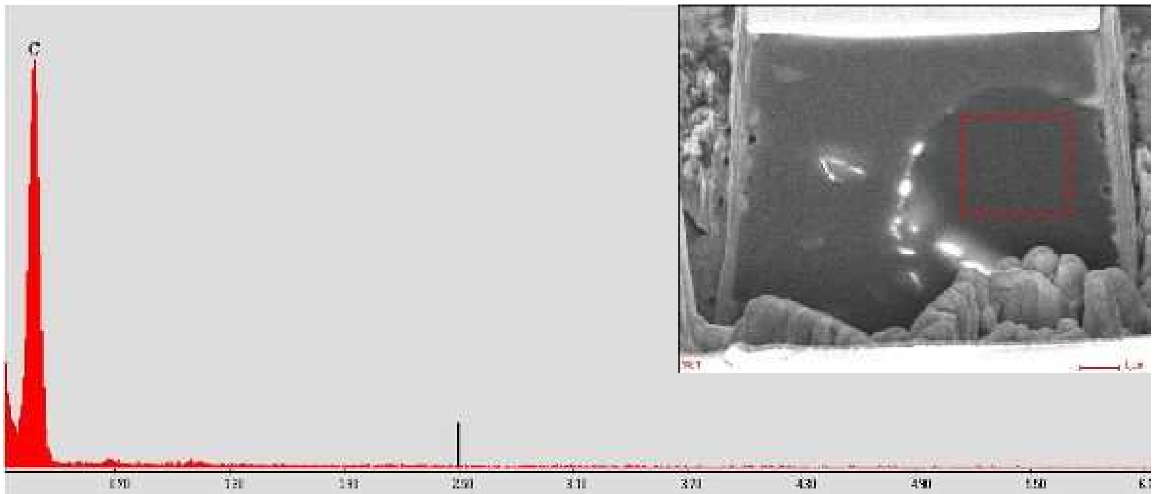

Figure 14. Spectrum of a partial area of Figure 13.

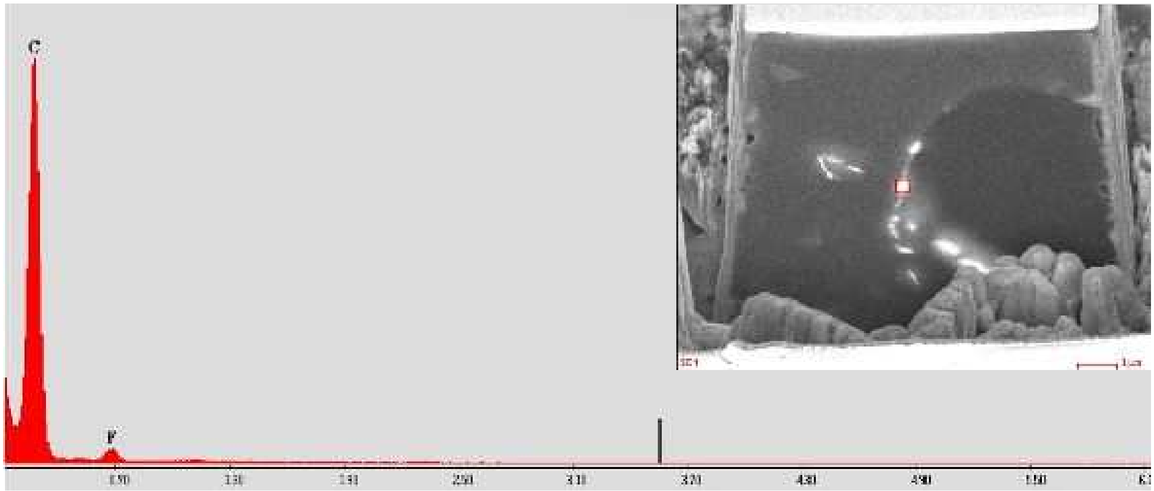

Figure 15. Spectrum of a partial area of Figure 13.

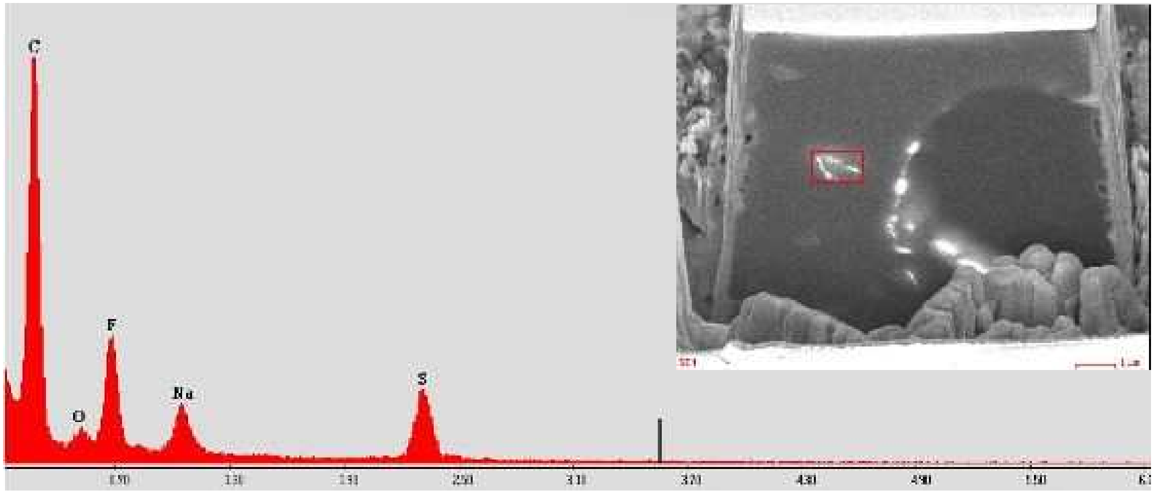

Figure 16. Spectrum of a partial area of Figure 13.

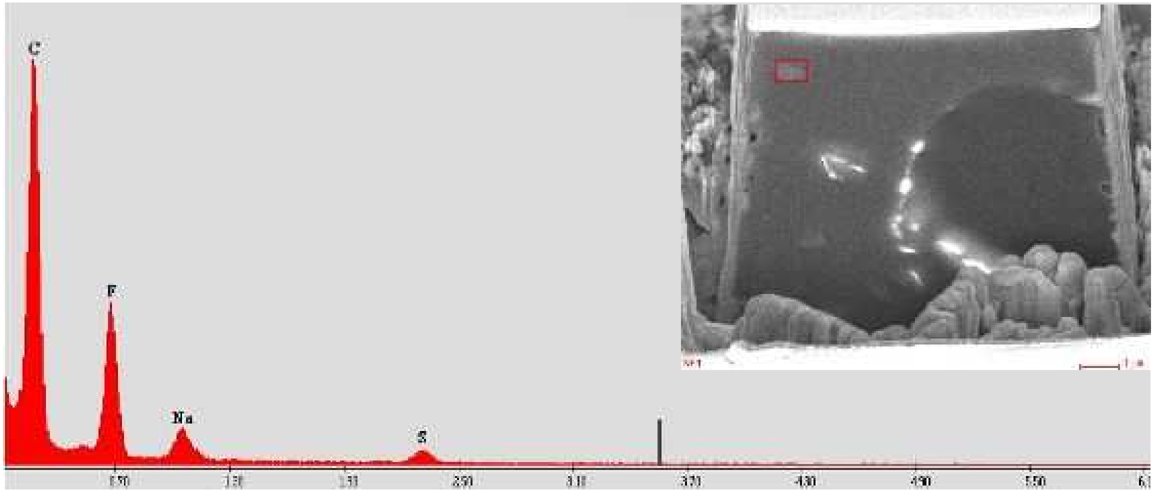

Figure 17. Spectrum of a partial area of Figure 13.

Figure 18. Image of 10 µm area of the membrane used in the main experiments. Second point of the bottom side.

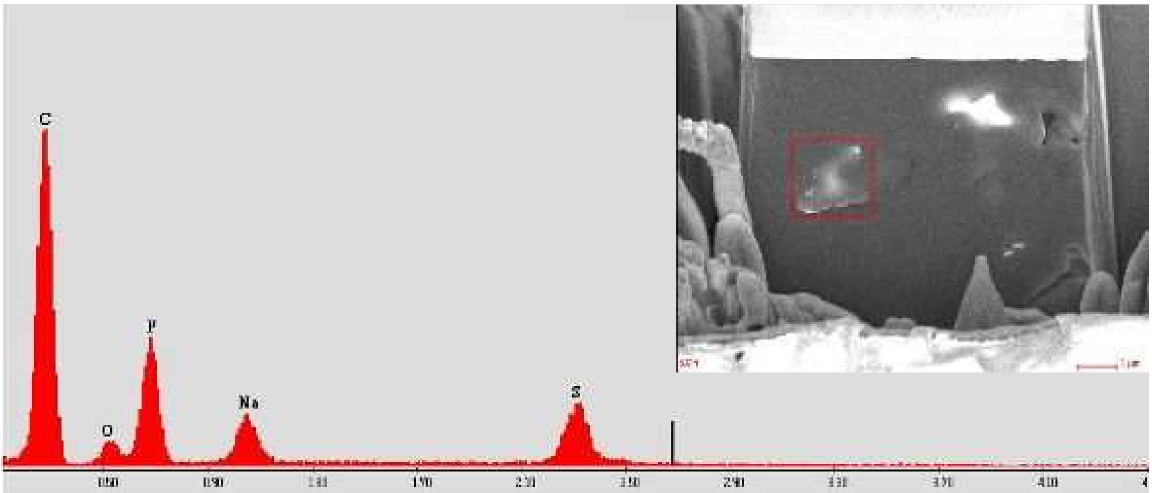

Figure 19. Spectrum of a partial area of Figure 18.

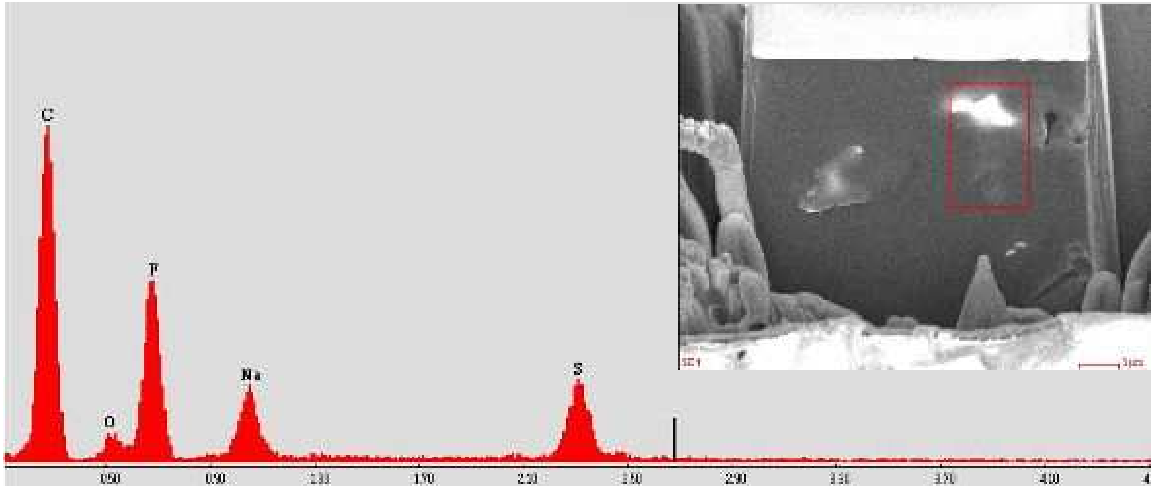

Figure 20. Spectrum of a partial area of Figure 18.

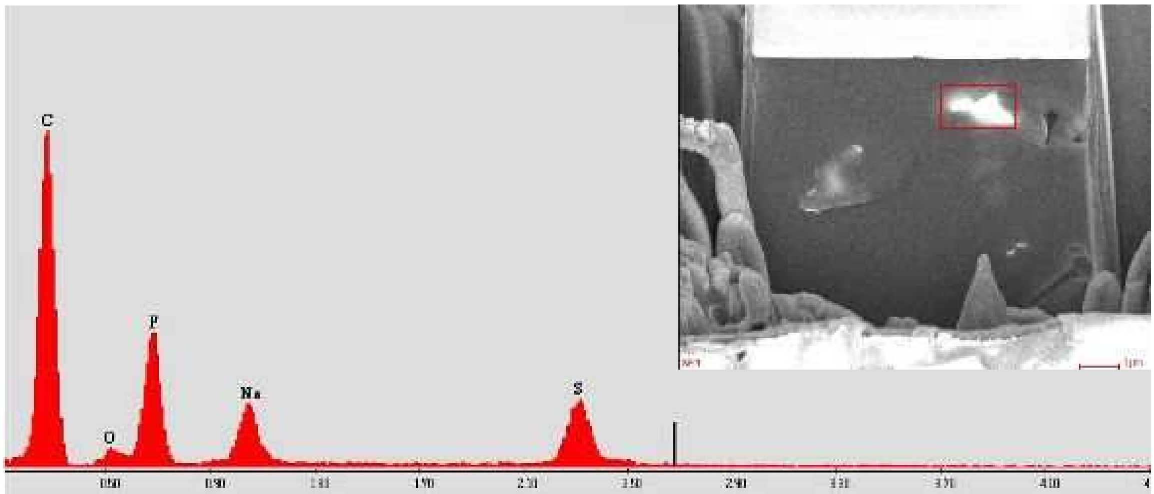

Figure 21. Spectrum of a partial area of Figure 18.

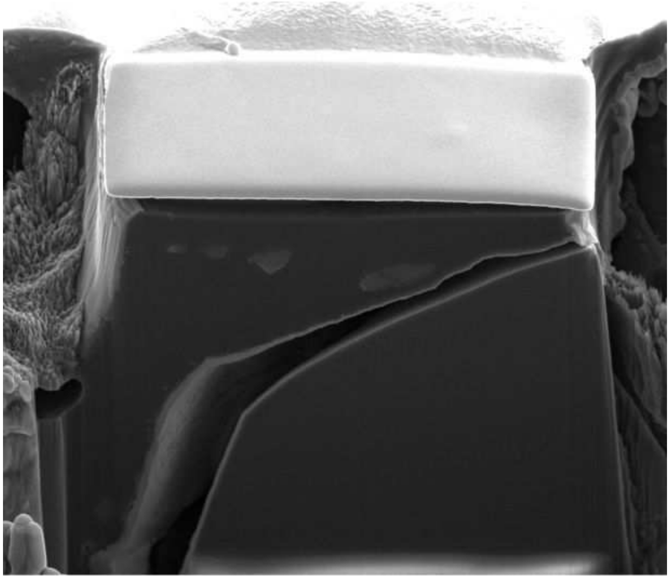

Figure 22. Image of 10 μm area of the membrane used in the main experiments. First point in the top side.

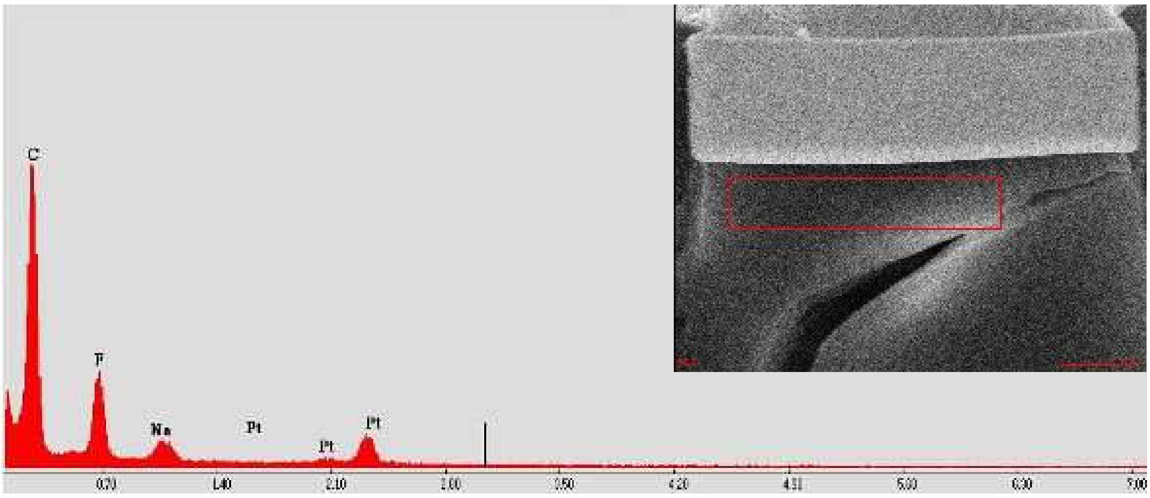

Figure 23. Spectrum of a partial area of Figure 22.

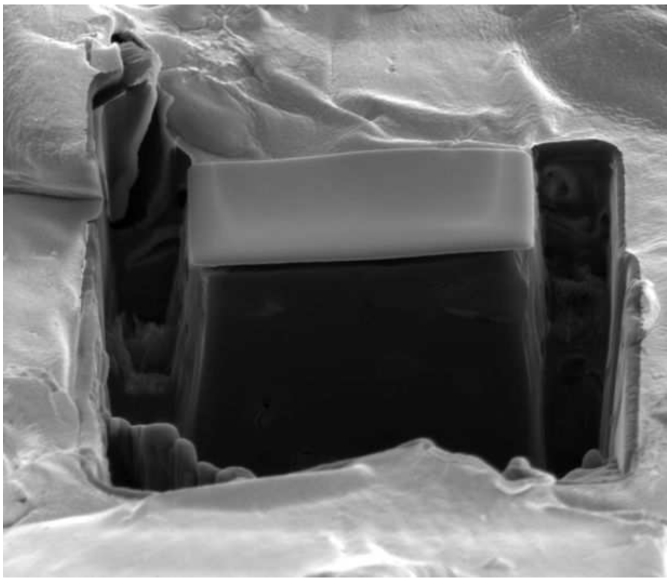

Figure 24. Image of 10 µm area of the membrane used in the main experiments. Second point in the top side.

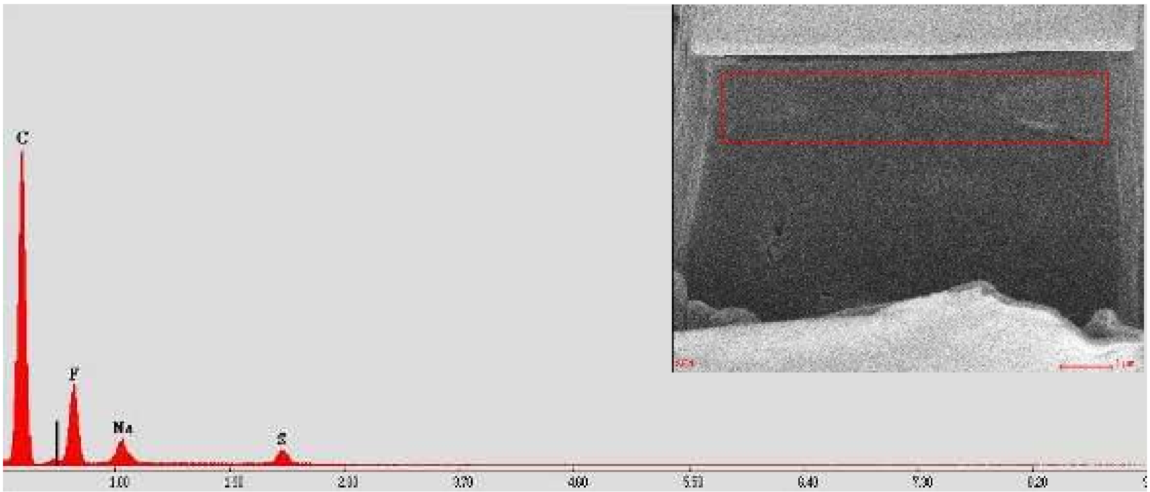

Figure 25. Spectrum of a partial area of Figure 24.