Junkal Landaburu-Aguirre

MICELLAR-ENHANCED ULTRAFILTRATION FOR THE REMOVAL OF HEAVY METALS FROM PHOSPHOROUS-RICH WASTEWATERS

FROM END-OF-PIPE TO CLEAN TECHNOLOGY
JUNKAL LANDABURU-AGUIRRE

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Abstract

Fertilizer industry often generates phosphorous rich wastewaters containing heavy metals. While phosphorous is a valuable compound for the industry, heavy metals hinder the recovery of phosphorous due to their detrimental effects on human health and the environment. Consequently, heavy metals must be removed from the wastewaters. In this study the use of micellar-enhanced ultrafiltration (MEUF) was evaluated for the removal of cadmium, copper, zinc and nickel from phosphorous rich wastewaters.

This study has been conducted following a systematic methodology from single metal synthetic wastewaters to more complex synthetic and real wastewaters. The experimental work was conducted in a laboratory scale stirred cell using 3, 5 and 10 kDa regenerated cellulose membranes and in a cross flow semi-pilot scale equipment using a 10 kDa spiral wound polyethersulphone membrane. Statistical design of experiments was used as the research methodology to evaluate the effect of factors on the MEUF process performance as well as for finding optimal conditions. The factors studied were heavy metal, phosphorous and surfactant feed concentrations, pH, membrane nominal molecular weight limits, transmembrane pressure and cross flow velocity. The membrane performance was characterized by the heavy metal retention/rejection coefficients and the permeate flux.

The experimental results showed that the removal of heavy metals from single synthetic wastewaters by MEUF is more efficient for more diluted systems. In complex systems containing phosphorous, simultaneous removal of heavy metals was successfully achieved obtaining rejection coefficients up to 80%. Phosphorous was not retained by the membrane showing the potential applicability of MEUF to purify phosphorous rich wastewaters. The study of metal complex formation and heavy metal competition has been shown to be very important in order to predict the MEUF results. Concentration polarization phenomenon was insignificant in the synthetic wastewaters but it was more severe when applying MEUF to real wastewaters. In addition, with real wastewaters SDS leakage was insignificant. This study has provided new and valuable knowledge regarding the applicability of MEUF to industrial wastewater treatment.

Keywords: clean technologies, heavy metals, membrane technology, micellar-enhanced ultrafiltration, phosphorous, statistical design of experiments, wastewater


Asiasanat: fosfori, jätevesi, kalvoerotustechnikka, miselliaviusteinen ultrasuodatus, puhtaat teknologiat, raskasmetallit, tilastollinen kojesuunnittelu
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Oulu, August 2012

Junkal Landaburu-Aguirre
**List of original papers**

The thesis is based on the following publications:


Landaburu-Aguirre was the main and corresponding author of Papers I–IV. In Paper V, Landaburu-Aguirre’s contribution was the design of experiments, data analyses and co-writing the paper with the first author.
List of symbols and abbreviations

*Latin symbols*

A  membrane effective area (m$^2$)

$b_i$  linear coefficient

$b_{ii}$  quadratic coefficient

$b_{ij}$  interaction coefficient

$b_o$  constant coefficient

$C_b$  solute concentration value in the bulk (ppm or mM)

$C_{Cu}$  copper feed concentration (ppm)

$C_{Cd}$  cadmium feed concentration (ppm or mM)

$C_{fi}$  i compound concentration in the feed (ppm or mM)

$C_m$  solute concentration value at the membrane surface (ppm or mM)

$C_{Ni}$  nickel feed concentration (ppm)

$C_{pi}$  i compound concentration in the permeate (ppm or mM)

$C_{Phosph.}$  phosphorous feed concentration (g/dm$^3$)

$C_{ri}$  i compound concentration in the retentate (ppm or mM)

$C_{SDS}$  SDS feed concentration (mM)

$C_{Zn}$  zinc feed concentration (ppm or mM)

$f$  number of factors studied

$F_{tabulated}$  fisher test critical value

$F_{value}$  fisher test calculated value

$J_V$  permeate flux (dm$^3$/m$^2$h)

$n$  number of experiments of the central composite design

$n_a$  number of experiments of factorial design

$n_c$  number of star points

$n_o$  number of centred points, replicates

$p$  $p$-value, probability

$Q^2$  response variation percentage predicted by the model

$R$  rejection/retention coefficient (%)

$R^2$  coefficient of determination

$R^2_{ad}$  adjusted coefficient of determination

$R_{tot}$  total resistance (m$^{-1}$)

$R_m$  membrane resistance (m$^{-1}$)

$R_{cp}$  concentration polarization resistance (m$^{-1}$)
R_f  fouling resistance (m$^{-1}$)
S/M  surfactant to metal concentration ratio
$t$  time needed for collecting the permeate (h)
$V$  volume of permeate sample (dm$^3$)
$X_i$ factor coded level
$X_iX_j$ interactive variables
$Y$  predicted response

**Greek symbols**

$\alpha$  star point
$\Delta P$  transmembrane pressure (bar)
$\Delta \pi$  osmotic pressure difference across the membrane (bar)
$\mu$  viscosity of the permeate (kg/m s)

**Abbreviations**

AAS  atomic absorption spectroscopy
ANOVA  analysis of variance
BAT  best available technique
CCC  central composite design circumscribed
CCF  face centred composite design
CCI  inscribed central composite design
CMC  critical micelle concentration
EDL  electrical double layer
E-PRTR  European pollution release and transfer register
FF  full factorial
FrF  fractional factorial
ICP-OES  inductively coupled plasma-optical emission spectroscopy
IUPAC  international union of pure and applied chemistry
MEUF  micellar-enhanced ultrafiltration
MF  microfiltration
MLR  multiple linear regression
MWCO  molecular weight cut off
NF  nanofiltration
NMWL  nominal molecular weight limit
OECD  Organization for Economic Co-operation and Development
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>PPP</td>
<td>polluter pays principle</td>
</tr>
<tr>
<td>RO</td>
<td>reverse osmosis</td>
</tr>
<tr>
<td>RSM</td>
<td>response surface methodology</td>
</tr>
<tr>
<td>SDS</td>
<td>sodium dodecyl sulphate</td>
</tr>
<tr>
<td>TMP</td>
<td>transmembrane pressure</td>
</tr>
<tr>
<td>TOC</td>
<td>total organic carbon</td>
</tr>
<tr>
<td>UF</td>
<td>ultrafiltration</td>
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1 Introduction

During the industrial revolution, development of science and technology caused the growth of different industries where the use of chemicals became crucial (Morazé 1976). In this way, the chemical industry was born in the middle of the 18th century due to the demand of other industries for chemical products (Aftalion 2001).

During World War I, it was clear that the chemical industry was a critical component of State and military power and the development of new chemicals such as explosives became crucial (Travis et al. 2010). As the role of chemical warfare became more important, the demands for chemical compounds rapidly increased. During World War I, chemists investigated over 3000 chemical substances for potential use as weapons. (Coleman 2005). Further, introduction of new compounds such as polyamides in early 1938 increased the production of plastics to a yearly production of more than 50 million tonnes by 1980 (Förstner 1998). After World War II, policymakers saw the increase in food production as a priority and encouraged the growth of new agricultural technologies to increase food production dramatically (green revolution) (Reddy 2006). Production of fertilizers increased significantly between the 1950’s and the 1960’s with the increased application of phosphates by 75%, nitrates by 146% and pesticides by 300% (Förstner 1998).

The development of the chemical industry has been beneficial to our society. The chemical industry has improved the quality of life by producing healthcare products, has had an important role in the food security of many countries with the application of fertilizers and has contributed to the economic growth of many countries. However, it has also caused drawbacks since the implementation of new chemical processes and products has also introduced pollutants and environmental problems that were previously unknown.

In addition to the pollution from agricultural and municipal sources, water pollution has been accelerated by the direct discharge of industrial effluents into water bodies (Gottlieb 1995). Many processes produce wastewater effluents containing contaminants that can cause severe health problems and adversely impact the ecological cycle. Some examples of water pollution problems in the 20th century are eutrophication of waters due to nutrient overloading, organic micro-pollutants and heavy metal pollution (Förstner 1998).

The term “heavy metal” has been widely used in the scientific and industrial community as well as in environmental legislation. However, until the present,
the term “heavy metal” has never been defined by any authoritative body such as the International Union of Pure and Applied Chemistry (IUPAC). Over the last 60 years the term heavy metal has been defined based on the density, the atomic weight, the chemical properties and the toxicity of the metals. However, many of the definitions have lacked consistency and have often created confusion. As an example, different density limits (from 3.5 g/cm³ up to 7 g/cm³) have been used for characterizing what is a heavy metal. Some reports define heavy metals as compounds that have atomic weight higher than calcium and this includes zinc, which is also considered to be an essential metal. (Duffus 2002). Further, the existing environmental policies have also defined the term inconsistently, proposing lists that differ from regulation to regulation. The European waste catalogue (Directive 2000/532/EC) defines the term “heavy metal” as

“any compound of antimony, arsenic, cadmium, chromium (VI), copper, lead, mercury, nickel, selenium, tellurium, thallium and tin, including these metals in metallic form”.

In this definition, zinc is not classified as a heavy metal but metalloids such as arsenic are, most probably due to their potential harm to the environment. However, zinc is considered a heavy metal by the European Union in The European Pollutant Release and Transfer Register. The Baltic Marine Environmental Commission (Helcom recommendation 23/11 2002) classifies mercury, cadmium, copper, nickel, lead, chromium and zinc as heavy metals. Due to the wide range of definitions that can be found in the literature, it is important to specify that in this thesis, the term heavy metal has been used following the Helcom recommendation 23/11 (2002).

Heavy metals cannot be degraded or destroyed and once they reach the environment they bioaccumulate. In water bodies they accumulate in sediments and organisms from where they are transferred into the food chain. Due to the bioaccumulation and high toxicity of heavy metals, they constitute a great danger to human health and the environment (Dogra 2008, Kaur 2010). Table 1 summarizes the toxicity and symptoms of cadmium, copper, zinc and nickel, which are the heavy metals studied in this thesis.
Table 1. Heavy metal toxicity and symptoms in humans (Institute of Medicine 2001, Srivastava & Baslaas 2009).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Characteristics</th>
<th>Toxicity symptoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>Carcinogenic</td>
<td>Hypertension, severe nausea and vomiting, damage in renal and hepatic systems.</td>
</tr>
<tr>
<td>Copper</td>
<td>Nutrient, recommendation for adults &lt; 10 mg/day</td>
<td>Hypertension, nausea and vomiting, acute renal failure</td>
</tr>
<tr>
<td>Nickel</td>
<td>Carcinogenic, Nutrient, recommendation for adults &lt; 1 mg/day</td>
<td>Dermatitis, cyanosis, weakness and edema.</td>
</tr>
<tr>
<td>Zinc</td>
<td>Nutrient, recommendation for adults &lt; 40 mg/day</td>
<td>Abdominal pain, vomiting and diarrhea</td>
</tr>
</tbody>
</table>

Figure 1 and Figure 2 show the industrial sources of cadmium, copper, zinc and nickel in the EU-27 countries in 2009. According to The European Pollutant Release and Transfer Register (E-PRTR 2009) waste and wastewater management sector (mainly urban wastewater treatment plants) was the predominant sector releasing these heavy metals to water bodies (Figure 1). However, as Figure 2 shows, metal and chemical industries are the main industries transferring cadmium, copper, zinc and nickel to wastewaters.

Among the chemical industry, the fertilizer industry is one of the sectors generating wastewaters containing heavy metals. The main raw material for phosphate fertilizer production is phosphate rock, which naturally contains impurities such as heavy metals (Dogra 2008, Oosterhuis et al. 2000, Urtiaga et al. 2000). Consequently, the production of phosphate fertilizers often generates phosphorous rich wastewaters containing heavy metals. While phosphorous is a valuable compound for the fertilizer industry that can be further recovered, heavy metals are impurities that even at diluted concentrations limit the recovery of phosphorous. Consequently, heavy metals must be removed from the wastewaters. This thesis studies the removal of heavy metals from phosphorous-rich wastewaters using micellar-enhanced ultrafiltration (MEUF).
Fig. 1. Industrial sources of heavy metal discharge to waters in EU-27 countries in 2009 (E-PRTR 2009).

Fig. 2. Industrial sources of heavy metal transfer to wastewaters in EU-27 countries in 2009 (E-PRTR 2009).

1.1 Objectives and scope

The objectives of this thesis can be summarized as follows,

- To gain new knowledge on the removal of heavy metals from synthetic and real wastewaters by MEUF;
- To evaluate the feasibility of MEUF for the removal of heavy metals from real wastewaters
- To establish the applicability of MEUF for the purification of phosphorous rich wastewaters
- To apply statistical design of experiments as a research methodology for modeling and optimization of the MEUF process
- To gain new knowledge on the effect of factors on the MEUF process performance
- To gain new knowledge on the metal competition and heavy metal complex formation in complex systems.

The thesis consists of 5 refereed journal articles whose scope and contribution to the thesis are summarized in Figure 3.

Paper I and Paper II deal with the use of MEUF for the removal of heavy metals from single metal synthetic waters. In these papers the potential use of MEUF for the removal of heavy metals from low concentration systems is ascertained. In addition, statistical design of experiments is established to be an efficient research methodology for gaining a better understanding of the systems (effect of factors) and process optimization. Consequently, statistical design of experiments is also used in the following three articles.

Paper III deals with the simultaneous removal of heavy metals from complex systems containing phosphate electrolytes. Paper III is in line with the previous two papers by applying MEUF for the simultaneous removal of heavy metals at very low concentrations. In addition, the applicability of MEUF for purification of phosphorous-rich wastewaters is addressed.

In Paper IV the applicability of MEUF for the simultaneous removal of heavy metals from real wastewaters is studied and evaluated. In addition, the feasibility of MEUF for the purification of phosphorous-rich real wastewaters is evaluated. The experiments in the four first papers composing this thesis are conducted on laboratory scale. Paper V addresses a more realistic approach from the industrial point of view by focusing on the purification of phosphorous-rich wastewaters in a cross-flow semi-pilot scale.
Fig. 3. Scope and contribution of the refereed articles to the thesis.

**Simultaneous removal of diluted heavy metals from phosphorous rich synthetic waters by MEUF.**
**Paper III**
- Simultaneous removal of cadmium, copper, zinc and nickel by MEUF
- Modeling the rejection coefficients of cadmium and copper using statistical design of experiments
- Feasibility of MEUF for separating phosphates from heavy metals
- Study the effect of pH, the presence of phosphates and SDS feed concentration on the rejection coefficients of heavy metals
- Study the heavy metal competition

**Purification of P-rich real wastewater containing diluted heavy metals by MEUF.**
**Paper IV**
- Study the applicability of MEUF for the simultaneous removal of heavy metals from real wastewaters
- Study the feasibility of MEUF to purify phosphorous rich real wastewaters
- Study the effect of pH and SDS feed concentration on the rejection coefficients of cadmium and copper
- Understand the complex formation of the metals and its influence on the MEUF performance
- Finding optimal conditions for achieving maximum rejection coefficients
- Study the SDS leakage to the permeate

**Evaluation of MEUF for the removal of heavy metals from wastewaters**

**Removal of heavy metals from single metal systems by MEUF.**
**Papers I and II**
- Removal of zinc and cadmium from single metal systems by MEUF
- Modeling and optimization of the removal of heavy metals using statistical design of experiments
- Study the effect of surfactant and heavy metal feed concentration, pressure and NMWL on the rejection coefficient and permeate flux
- Establishment of MEUF applicability for heavy metals removal from diluted system
- Recovery of the surfactant (SDS)

**Semi pilot scale study of MEUF for low pH P-rich real wastewaters.**
**Paper V**
- Feasibility of more realistic module to evaluate the feasibility for industrial applications
- Modeling the permeate flux using statistical design of experiments
- Study the effect of surfactant feed concentration, transmembrane pressure and feed flow velocity on the permeate flux
2 Industrial wastewater management

Until the middle of the 20th century water pollution control policies had the main focus area of reducing waterborne diseases. Consequently, these policies focused on the remediation of municipal wastewaters by the application of primary and/or secondary treatment (Förstner 1998). In this framework, the water treatments used helped to eliminate the problem of waterborne diseases in the developed countries. Unfortunately, regarding industrial effluents, the only pollution control approach taken until 1960’s was the “dilution and disperse” strategy (Shi & Wen 2002).

It was only after catastrophic environmental events that policy makers started taking new pollution control measures. The first known case of heavy metal detrimental effect occurred in 1956 in Japan, where a company producing acetaldehyde discharged tonnes of mercury into the Minamata bay. Mercury entered the food chain and thousands of people whose normal diet included fish and shellfish developed symptoms of mercury poisoning, now called Minamata disease (Shi & Wen 2002). It was clear that the “dilution and disperse” approach did not really work and early environmental legislation in the 1960’s was introduced to solve this kind of specific and sometimes local pollution problem. Currently, heavy metals are strictly monitored and targeted by international environmental legislation. Table 2 shows the European Union environmental legislation regarding metals and metalloids.

With the design of new policies to establish discharge limits to water bodies (Gottlieb 1995) and in order to comply with the existing legislation, industries started to install purification units at the end of the production process (end-of-pipe technologies) (Shi & Wen 2002).
Table 2. European Union legislation regarding metals and metalloids.

<table>
<thead>
<tr>
<th>Priority substance</th>
<th>Priority hazardous substance</th>
<th>Polluting substance to water</th>
<th>Dangerous substances for the aquatic environment</th>
<th>Water discharge limits (mg/dm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0.2</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td>X</td>
<td>X</td>
<td>0.5</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td>X</td>
<td>X</td>
<td>2.0</td>
</tr>
<tr>
<td>Ni</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>1.0</td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td>X</td>
<td>X</td>
<td>–</td>
</tr>
<tr>
<td>Pb</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0.5</td>
</tr>
<tr>
<td>Hg</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0.05</td>
</tr>
<tr>
<td>As</td>
<td></td>
<td>X</td>
<td>X</td>
<td>–</td>
</tr>
<tr>
<td>Cr</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0.5; Cr(III)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1; Cr(VI)</td>
</tr>
</tbody>
</table>

2.1 End-of-pipe technologies

From the production system point of view, end-of-pipe technologies are clearly separated from the production process. Therefore, with the end-of-pipe approach a process plant is designed without considerations of water pollution abatement and by separately designing the wastewater facilities to treat the polluted waters (Ramalho 1977). Further, in end-of-pipe solutions the output is not usually used in the production and/or consumption process but released to the environment. The advantages of the end-of-pipe approach are as follows (Zotter 2004):

- they do not affect production because they are implemented after the production process and can be operated independently,
- they are mature technologies that have been used in the past,
- they have high degree of legal security because they are suggested and recognized by the official authorities.

The end-of-pipe approach has been successfully employed to control industrial pollution to some extent and to comply with the existing environmental legislation. However, the end-of-pipe approach is a reactive pollution control method, where the objective is to modify the residual products of a process to a less harmful residue for the environment (Zotter 2004). Therefore, they are focused on decreasing the negative consequences of the production line instead of
removing or reducing the environmental damage at the source. Another disadvantage is the formation of secondary pollution. The pollution problem is not eliminated but transformed into other kind of pollution like sludge or even more concentrated wastewater.

2.2 Clean technologies

Clean technologies are new industrial processes or modifications of the existing ones intended to reduce the impact of production activities on the environment, including reducing the use of energy and raw materials (European Commission 2003). Contrary to end-of-pipe technologies, clean technologies aim to reduce resource use and/or pollution at the source by using cleaner products and production methods (Frondel et al. 2004). Belis-Bergouignan et al. (2004) classified 4 types of clean technologies as follow,

- Substitution and savings in inputs. The production process is adapted in order to reduce the use of inputs or to use inputs that are less polluting
- Pollution prevention and control technologies. The goal is to integrate into the production process a new technology or a new type of equipment that enables the emissions to be reduced or treated
- Recovery or internal recycling. Integrating a process that involves recovery, recycling or regeneration of raw materials and/or certain substances, leading to a reduction at source of pollution
- Radically new clean process. There is a complete modification of production processes by adopting a cleaner process.

In order to encourage the application of environmental technologies towards a preventative technological approach authorities have implemented economic and regulatory instruments.

*Economic instruments: Polluter Pays Principle*

The use of economic instruments such as pollution charges has been stimulated from the Polluter Pays Principle (PPP) that states “whoever is responsible for damage to the environment should bear the costs associated with it” (Rogers 1995). In 1972 the Organisation for Economic Co-operation and Development (OECD council) mentioned for the first time on the international level the PPP stating:
“The principle to be used for allocating costs of pollution prevention and control measures to encourage rational use of scarce environmental resources and to avoid distortions in international trade and investment is the so-called Polluter Pays Principle.”

PPP is nowadays one of the fundamental principles of the European Community environmental policy and intends to encourage the parties concerned to take more precautions and to reduce pollution. In this way, The Treaty Establishing the European Community (Treaty 2010/C 83/01), under Title XX Environment, article 191.2 mentions the following,

“Community policy on the environment shall […] be based on the precautionary principle and on the principles that preventive action should be taken, that environmental damage should as a priority be rectified at source and that the polluter should pay”

Regulatory instruments

The implementation of the Water Framework Directive (Directive 2000/60/EC) establishes a framework for Community action in the field of water policy. In this way, the Water Framework Directive aims to promote sustainable water usage and environmental protection. Further, in order to improve the sustainable use of water resources the directive supports water pricing, including the environmental cost (cost of waste caused by water use in ecosystems) and resource cost (due to resource depletion leading to the disappearance of options for other users).

In the wastewater policy, the Environmental Liability Directive (Directive 2004/35/CE) establishes a framework for environmental liability based on the polluter pays principle, with a view of preventing and remediating environmental damage. The Directive is applied among others to the industrial and agricultural activities with a high pollution potential that requires a permit under the Industrial Pollution Prevention and Control, IPPC Directive (Directive 2008/1/EC). The permit is given only if certain environmental conditions are met such as the use of Best Available Techniques (BATs) and the prevention, recycling and disposal of the waste in the manner that creates the least pollution. In addition, the permits must contain specific requirements such as emission limit values for polluting substances (Directive 2008/1/EC).
2.3 **BATs for heavy metals and phosphorous containing wastewaters**

The strategy adopted by the European Union to minimize the environmental impact of wastewater is mainly based on four steps:

- effluent treatment should be applied to achieve water recycling or recovery, as well as to improve discharge quality
- clean technologies and clean raw materials should be applied to prevent waste from being discharged into the environment
- if complete prevention of waste is not practicable, the next step is waste minimisation, not only of volume, but also of impact caused by hazardous substances that might be replaced in the production process
- if all measures for minimisation are taken, the next step is controlling the inevitable discharge by implementing the most effective treatment system possible, so as to minimize the total environmental impact.

In this way, the best available techniques for the wastewaters in the chemical industry include:

- the methodology to prevent wastewater discharges, identify the need for and carry out improvement of emissions and find the best option for wastewater collection and treatment (effluent management)
- the identification of the best and most suitable treatment technologies.

### 2.3.1 BATs for heavy metals

As heavy metals are chemical elements that cannot be destroyed, the European Union states that their recovery and reuse are the only ways to prevent them being released into the environment. In this way, under the Industrial Emission Directive (Directive 2010/75/EU) and IPPC Directive (Directive 2008/1/EC), the Best Available Technique for heavy metals containing wastewater in the chemical industry is to (BREF 2003):

- segregate waste water containing heavy metal compounds as much as possible
- treat the segregated wastewater streams at source before mixing with other streams
- use techniques that enable recovery as widely as possible;
facilitate further elimination of heavy metals in a final wastewater treatment plant as a polishing step, with subsequent treatment of sludge, if necessary.

The appropriate techniques for the removal of heavy metals are recognized to be precipitation, crystallization, ion-exchange and nanofiltration/reverse osmosis (Table 3).

**Table 3. Recommended technologies for the removal of heavy metals from wastewater (BREF 2003).**

<table>
<thead>
<tr>
<th>Technology</th>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation</td>
<td>Separation by formation of insoluble heavy metal compounds (precipitate)</td>
<td>Simple, inexpensive and recovery of heavy metals is possible in principle</td>
<td>Ineffective in diluted heavy metal systems, sludge (secondary pollution)</td>
</tr>
<tr>
<td>Crystallization</td>
<td>Growth of heavy metal compounds on granular seed material (sand or mineral)</td>
<td>Used for the recovery of metals, no sludge production</td>
<td>Ineffective in diluted heavy metal systems</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>Replacement of heavy metals by other ions from the resins</td>
<td>High removal efficiency at diluted systems, fast kinetics, recovery of heavy metals is possible</td>
<td>Not efficient in high ionic strength solutions, regeneration of resins needed</td>
</tr>
<tr>
<td>NF/RO</td>
<td>Separation of heavy metals by membranes</td>
<td>High removal efficiency, do not require addition of chemicals, recovery of heavy metals is possible</td>
<td>High pressure, low flux, concentrate needs further treatment</td>
</tr>
</tbody>
</table>

**2.3.2 BATs for phosphorous**

Excess concentration of phosphorous in water bodies can cause environmental problems such as eutrophication. Eutrophication is an accelerated growth of algae on higher forms of plant life that induces an undesirable disturbance to the balance of organisms present in the water and to the quality of the water concerned. (Gomes Ferreira et al. 2007). Therefore, due to its detrimental environmental impact, strict environmental legislation restricts phosphorous discharge to the environment. Under the Industrial Emission Directive (Directive 2010/75/EU) and IPPC Directive (Directive 2008/1/EC), the European Commission (BREF 2007) specifies that the Best Available Technique for the wastewater treatment in the fertilizer production is that
“Wastewater that cannot be avoided is discharged after adequate treatment, e.g. biological wastewater treatment with nitrification/denitrification and precipitation of phosphorous compounds”.

### 2.3.3 Legislative limitation for clean technology practice

The prevailing legislation has helped to control industrial wastewater discharges better and therefore, the water quality has been improved. However, even the target of the IED and IPPC Directives is to promote a preventative pollution control approach through the application of clean technologies, often in the case that wastewater is already formed existing legislation does not go further than recommending wastewater treatment prior to discharge (end-of-pipe approach). Therefore, under the main objective of preventing environmental damage by pollutant discharge into the environment, the stringency of the environmental policy often favors the application of end-of-pipe technologies. This is often due to the fact that the legislation orders certain limits and standards that can only be achieved by applying end-of-pipe measures. (Frondel et al. 2004).

In the case of wastewaters containing heavy metals, BATs follows the criteria for clean technologies by prioritizing the segregation and further recovery of heavy metals from wastewaters and in this way, promoting the recycling of unavoidable waste. In the case of phosphorous containing wastewater, the requested precipitation of phosphorous from wastewater prior to discharge does not go further than following the end-of-pipe measures. The purification and recovery of phosphorous from phosphorus-rich wastewater would comply with the practice of clean technology and consequently with the prevention of pollution by

- minimizing the wastewater volumes;
- reducing the harm towards the environment by eliminating phosphorous discharges;
- improving resource efficiency of phosphorous.

In order to follow the principles of the clean technology concept, wastewater treatment technologies should not be limited for treating wastewater to reduce its pollutant content but should be applied beyond the end-of-pipe approach. Wastewater treatment technologies in the 21st century should have the purpose of reclamation and recovery of resources such as valuable compounds and the water itself. Membrane technology is a good example of wastewater treatment
technologies that can successfully be applied for reclamation of valuable compounds since it enables to fractionate the wastewaters onto valuable pure materials that can be subsequently reused as resources (Koltuniewicz & Drioli 2008). In this context, and in order to further promote the application of clean technologies in industry, legislation should evolve towards a new paradigm in viewing wastewater as a resource of valuable compounds instead of a source of pollutants.

2.4 MEUF for the removal of heavy metals from phosphorous-rich wastewaters

Phosphorous (P) is a fundamental nutrient for living organisms and for crop production (Shu et al. 2006). The “Green revolution” that occurred in the 1960’s, changed agriculture and obtained a tremendous increase in crop yields by applying inorganic fertilizer products. Nowadays, to sustain high crop yields, modern agriculture requires a steady supply of inorganic fertilizers such as phosphate fertilizers (Cooper et al. 2011). Most of the phosphate fertilizer production is achieved by processing phosphate rocks with sulphuric acid or nitric acid (Al-Shawi & Dahl 1999). Increase in population and request for meat and dairy-based diets and non-food crops like biofuel crops have increased the demand for phosphate fertilizers and consequently have increased phosphate rock production by 2% per year during 2004–2010 (Cooper et al. 2011, Cordell et al. 2009, IFA 2010, Schröder et al. 2009).

Phosphate rocks are a non-renewable source, whose occurrence in nature is limited. There is a concern that exploitation of this non-renewable source to meet current demands is not sustainable. Driver et al. (1999) reported that resources of phosphate rock could be depleted in 50 to 100 years. Further, taking into account that there are few countries in the world that have phosphate rock reserves, phosphorous exploitation is a sensitive geopolitical matter. In 2010 China, Morocco and The United States were the countries with the biggest share of world phosphate rock production (Cooper et al. 2011). China has already begun to safeguard its supplies and in 2008 increased the tariff on exports (U.S. Geological Survey 2009). Finland is the only West European country that has phosphate rocks reserves. Therefore, European phosphorous consumption is mainly based on imports (Schröder et al. 2009).

The concern about the use of renewable and non-renewable resources has been addressed by the European Commission that launched a thematic strategy on
the sustainable use of natural resources (Communication COM 670 2005). The aim of the strategy is to reduce the depletion and pollution of natural resources in a growing economy by integrating the concept of life cycle and impact of resources into the policies. Further, crucial resources are described not only as resources used in production of goods but also as the media used for absorbing emissions (air, water and land).

Under this context, in order to increase the life expectancy of the world’s phosphorus resources and to make fertilizer production more sustainable special attention has been given in the industrial and research communities towards the recovery and recycling of phosphorous from waste (Cordell et al. 2011, Shu et al. 2006). The constraint is that industrial waste sources often contain heavy metals that can put the further reuse of the recovered fertilizer product at risk. Therefore, heavy metals must be removed and separated from the phosphorous-rich waste streams before the recovered phosphorous can be used as a fertilizer. This thesis aims to establish the use of micellar-enhanced ultrafiltration as a potential purification technology for phosphorous-rich wastewaters containing heavy metals.

Research conducted with micellar-enhanced ultrafiltration has been addressed from the end-of-pipe technology approach, where wastewater is treated to remove toxic metals prior to discharge. However, MEUF can further be used as a clean purification technology for wastewaters containing valuable compounds. The purification of wastewaters containing valuable compounds allows their further recovery and reuse improving the use of resources. Further, the purification of phosphorous-rich wastewater can also promote wastewater reuse. Wastewater reuse benefits the industry by reducing freshwater consumption, which also is a scarce and a valuable resource (Van der Bruggen & Braeken 2006, Van der Bruggen 2010).
3 Membrane processes

3.1 General

Membrane technology is a generic term used for separation processes where a membrane is used. Further, membrane can be defined as a material through which one type of substance can pass more readily than others, thus presenting the basis of a separation process (Judd & Jefferson 2003). The substances that pass through the membrane are called permeate and the substances that do not pass through the membrane are called retentate.

The membrane separation processes can be applied for purposes such as (Mulder 1998)

- Concentration: the desired component is present at a low concentration and the solvent is removed
- Purification: undesired impurities are removed from the solution
- Fractionation: a mixture must be separated into two or more desired components
- Reaction mediation: combination of a chemical or biochemical reaction with a separation of substances.

Membrane processes can be classified according to the type of driving force required for the separation to occur. The driving force is the difference in chemical potential between the feed and the permeate sides that can be created by a difference in concentration (dialysis), electrical potential (electrodialysis), vapor pressure (pervaporation), temperature (membrane distillation) and hydrostatic pressure (pressure driven membrane processes).

In pressure driven membrane processes the difference in pressure varies depending on the membrane pore size. In this way, the pressure is applied in order to overcome the hydraulic resistance of the membrane for the mass transfer. Table 4 summarizes different pressure driven membrane processes and their characteristics. As it can be observed from Table 4, when the membrane pore size is bigger, the hydraulic resistance of the membrane will be smaller and consequently, the pressure difference needed for the separation to occur will be smaller. In addition, in some cases the osmotic pressure difference across the membrane can be significant and the pressure gradient across the membrane decreases, decreasing the driving force for the mass transfer. The osmotic pressure difference is usually significant in nanofiltration and reverse osmosis.
processes, whereas in microfiltration and ultrafiltration can be considered negligible.

Microfiltration (MF) and ultrafiltration (UF) membranes are porous membranes and the main separation mechanism is the size sieving. In reverse osmosis the membranes used are dense membranes (non-porous). Unlike in MF and UF, the separation mechanism in RO is not mainly based on size sieving but on the chemical affinity between solutes and the membrane. Nanofiltration membranes have the characteristics between reverse osmosis and ultrafiltration. In this way, in addition to the size sieving the separation mechanism also depends on the affinity of the solutes with the membrane. Further, in nanofiltration membranes the charge of the membrane plays an important role and the repulsive/attractive forces between the ionic solutes and the charged membrane can control the selectivity of the process (Donnan effect).

**Table 4. Pressure driven membrane processes and characteristics (Judd & Jefferson 2003, Mulder 1998).**

<table>
<thead>
<tr>
<th>Membrane process</th>
<th>Pressure range (bar)</th>
<th>Pore size (nm)</th>
<th>Separation mechanism</th>
<th>Retained solutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration (MF)</td>
<td>&lt;2</td>
<td>50–10,000</td>
<td>Size sieving</td>
<td>Suspended solids, fine particles</td>
</tr>
<tr>
<td>Ultrafiltration (UF)</td>
<td>1–10</td>
<td>1–100</td>
<td>Size sieving</td>
<td>Colloids, macrosolutes (&gt; 1000 Da)</td>
</tr>
<tr>
<td>Nanofiltration (NF)</td>
<td>10–25</td>
<td>&lt;2</td>
<td>Size sieving, chemical affinity, charge rejection</td>
<td>High molecular weight compounds (100–1000 Da), multivalent ions</td>
</tr>
<tr>
<td>Reverse osmosis (RO)</td>
<td>10–100</td>
<td>Dense</td>
<td>Chemical affinity</td>
<td>Virtually all dissolved solutes and suspended solids except the solvent (water)</td>
</tr>
</tbody>
</table>

### 3.2 Membrane process performance

The performance of a membrane process is determined by the selectivity of the membrane and by the permeate flux. Membrane selectivity is the ability of the membrane to separate different compounds from each other. In pressure driven membrane processes is characterized by the rejection/retention coefficient (Equations 1 and 2, respectively).
where $C_{pi}$, $C_{fi}$ and $C_{ri}$ are the concentrations of the i compound in the permeate, feed and retentate, respectively.

In addition, permeate flux is the amount of substance (volume, mass) that passes through the membrane per unit area and time. It can be calculated as,

$$J = \frac{V}{t \times A},$$

where $V$ is the volume of the permeate, $t$ is the time needed for collecting the permeate and $A$ is the membrane effective area. In addition, the permeate flux is described by the resistance in series model as follows,

$$J_v = \frac{\Delta P - \Delta \pi}{\mu \times R_{tot}} = \frac{\Delta P - \Delta \pi}{\mu \times (R_m + R_{cp} + R_f)},$$

where $\Delta P$ is the transmembrane pressure applied, $\Delta \pi$ is the osmotic pressure (considered to be negligible in MF and UF), $\mu$ is the viscosity of the permeate and $R_{tot}$, $R_m$, $R_{cp}$ and $R_f$ are the total, membrane, concentration polarization and fouling resistances, respectively. As it can be observed in Equation 4, in addition to the membrane hydraulic resistance the total resistance can be further increased by concentration polarization and/or by fouling decreasing the permeate flux.

### 3.2.1 Concentration polarization

Concentration polarization is the term used for describing the concentration profile of the solutes on the membrane-solution interface, within the boundary layer (Judd & Jefferson 2003). As it can be observed in Figure 4, in pressure driven membrane processes, the retained solutes can accumulate on the membrane surface where their concentration is increased. The concentration build up generates a diffusive flow back from the membrane surface to the bulk of the feed (Mulder 1998). The diffusive transport is around two orders of magnitude slower than the convective transport in the bulk region (Judd & Jefferson 2003). Consequently, a concentration profile is formed in the boundary layer where the concentration of the solutes increases towards the membrane side, achieving a
maximum concentration value at the membrane surface ($C_m$). The concentration built up increases the resistance towards the flux and consequently the flux declines. After certain time the convective transport is balanced by the diffusive back flow, achieving steady state flux values.

![Diagram of concentration polarization](image)

**Fig. 4. Concentration polarization in pressure driven membranes (based on Mulder (1998) and Judd & Jefferson (2003)).**

Control of concentration polarization can substantially affect the membrane performance by means of reducing flux decline. This is especially important for microfiltration and ultrafiltration, where concentration polarization is usually more severe than for nanofiltration and reverse osmosis. In microfiltration and ultrafiltration the convective flow is higher than in nanofiltration and consequently, the retained solutes will accumulate faster having a greater concentration profile. In addition, the diffusion coefficient of the retained solutes in microfiltration and ultrafiltration is relatively small and the accumulation on the membrane surface is therefore, more pronounced than in nanofiltration and reverse osmosis. (Mulder 1998).

Concentration polarization phenomena can be reduced by reducing the size of the boundary layer, which is entirely dependent on the process hydrodynamics (Judd & Jefferson 2003). The hydrodynamic conditions can be improved for example by an efficient mixing, increasing the cross-flow velocity and applying turbulence promoters. In addition, system design also plays an important role to reduce concentration polarization. Cross-flow operations tend to have less concentration polarization phenomena than dead-end operations. (Mulder 1998).
3.2.2 Fouling

Fouling is the (ir)reversible deposition of retained solutes on/in the membrane. In case of reversible fouling, the initial water flux can be restored after flushing the membrane with clean water. However, in the case that the fouling is irreversible chemical cleaning is needed to achieve the initial water flux. Membrane fouling can be caused by adsorption of solutes on the membrane surface or within the membrane pores, filling of pores with solids (pore clogging), deposition of solids on the membrane surface accompanied by crystallization and compaction of the membrane structure, chemical interaction between membrane material and solutes, and bacterial growth (Sablani et al. 2001).

As with concentration polarization, in cross-flow operations the fouling phenomenon is usually smaller than in dead-end operations (Mulder 1998). In addition, the degree of fouling is highly dependent on the physical and chemical characteristics of the solution being processed. Solution pH, temperature and ionic strength are some of the characteristics that play a key role in the fouling phenomena (Mulder 1998). The interaction between the solute and the membrane also has a crucial role in fouling. Properties such as hydrophobicity and charge of the membrane should be taken into account when investigating the fouling phenomena. There are different methods that can be applied for reducing fouling. Some examples are pretreatment of the solution to reduce the amount of potential foulants, pH adjustment of solution and choosing appropriate membranes (hydrophobicity, charge, pore size distribution, etc.). (Sablani et al. 2001).

3.3 Micellar-enhanced ultrafiltration (MEUF)

As the term micellar-enhanced ultrafiltration suggests, MEUF is a membrane separation process where the performance of ultrafiltration is enhanced by the formation of surfactant micelles. Figure 5 shows the schematic diagram of micellar-enhanced ultrafiltration (MEUF).
Fig. 5. Schematic diagram of MEUF.

In MEUF, surfactants (anionic, cationic or non-ionic) are added into the polluted water stream. The surfactant monomers aggregate and form micelles above the critical micelle concentration (CMC). The organic compounds are solubilized in the micelle interior and the ionic compounds such as metals get trapped in the outer part of the oppositely charged micelles by electrostatic interaction. Consequently, for the removal of heavy metals anionic surfactants must be used, whereas cationic surfactants are used for the removal of anionic compounds such as nitrates and phosphates. The micelles and the compounds trapped on the micelles are retained by the ultrafiltration membrane. The untrapped solutes and free surfactant monomers will readily pass through the membrane to the permeate side.

Surfactants play a very crucial role in MEUF and consequently, in order to understand the removal mechanism it is very important to understand what surfactants and their properties are.

3.3.1 Surfactants

Surface active agents (surfactants) have a characteristic amphiphilic molecular structure that consists of a molecular component that has small attraction towards the solvent (lyophobic group) and a molecular component that has a strong attraction towards the solvent (lyophilic group). When the solvent is water, the
Surfactant molecular components are called hydrophobic (tail) and hydrophilic (head) components. The hydrophobic tail is usually a long hydrocarbon chain or a siloxane chain, whereas the hydrophilic group is an ionic or highly polar group.

Depending on the nature of the hydrophilic group, surfactants are classified as anionic (negative charge), cationic (positive charge), zwitterionic (both positive and negative charges) and non-ionic (no apparent ionic charge). Table 5 shows the type of surfactants according to their hydrophilic groups. The hydrophobic tails can be among others natural fatty acids (CH₃(CH₂)ₙ), paraffins (CH₃(CH₂)ₙCH₃), olefins (CH₃(CH₂)ₙCH=CH₂), alkylbenzenes (CH₃(CH₂)ₙCH₂(C₆H₅), alklyphenols (CH₃(CH₂)ₙCH₂(C₆H₄OH)), fluorocarbons (CF₃(CF₂)ₙCOOH) and silicone (Myers 1999).

### Table 5. Type of surfactants according to their hydrophilic head groups (Myers 1999, Rosen 1978).

<table>
<thead>
<tr>
<th>Type of surfactant</th>
<th>Hydrophilic head group</th>
<th>Industrial uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxylic acid salts</td>
<td>R-CO₂M⁻</td>
<td>Toilet soap bars, degumming of silk</td>
</tr>
<tr>
<td>Sulfonic acid salts</td>
<td>R-SO₃M⁻</td>
<td>Detergents, cosmetics, dry cleaning soaps, oil/water emulsion stabilizers, wetting agents in paints, printing inks and textiles</td>
</tr>
<tr>
<td>Sulfuric acid ester salts</td>
<td>R-OSO₃M⁺</td>
<td>Detergents, toothpaste, food and cosmetic</td>
</tr>
<tr>
<td>Phosphoric acid esters</td>
<td>R-OPO₃₂M²⁺</td>
<td>Emulsifying agent in pesticides and emulsions, textile wetting</td>
</tr>
<tr>
<td>Cationic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amines and their salts</td>
<td>R₁H₂N¹'R₂H₂N¹'R₃H³'X</td>
<td>Emulsifying agent, corrosion inhibitor for metal surface</td>
</tr>
<tr>
<td>Quaternary ammonium salts</td>
<td>R₁H₂N¹'X</td>
<td>Textile softener, hair conditioners, emulsifying agents, germicides and disinfectants</td>
</tr>
<tr>
<td>Quaternized polyoxyethylenated long chain amines</td>
<td>RN(CH₃)ₙ(CH₂CH₂O)ₓH⁺</td>
<td>Textile antistatic agent, antistatic in plastics, corrosion inhibitors</td>
</tr>
<tr>
<td>Non-ionic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyoxyethylenated alklyphenol</td>
<td>R₉C₆H₄(OC₂H₄)ₓOH</td>
<td>Foam control agent, agricultural and cosmetic emulsions, liquid detergents</td>
</tr>
<tr>
<td>Polyoxyethylenated alcohol</td>
<td>R(OC₂H₄)ₓOH</td>
<td>Laundry detergents</td>
</tr>
<tr>
<td>Long chain carboxylic acid esters</td>
<td>R-CO₂R</td>
<td>Cosmetic emulsifier, food emulsifier in bread, ice-cream and margarine, pharmaceutical emulsifier</td>
</tr>
<tr>
<td>Tertiary acetylenic glycols</td>
<td>R₁R₂C(OH)C≡CC(OH)R₂/R₃</td>
<td>Wetting agents in paints, foam reduction</td>
</tr>
<tr>
<td>Type of surfactant</td>
<td>Hydrophilic head group</td>
<td>Industrial uses</td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>Zwitterionics</td>
<td>pH sensitive: ( \text{RN}^+\text{H}_2\text{CHCH}_2\text{COO}^- ) ( \text{RN}^+\text{H(\text{CH}_2\text{COOH)}\text{CH}_3\text{COO}^-} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH insensitive: ( \text{RN}^+\text{(CH}_3\text{)}_2\text{(CH}_2\text{)}\text{SO}_3^- )</td>
<td>Bactericides, corrosion inhibitors, cosmetics, fabric softener, lime soap dispersant</td>
</tr>
</tbody>
</table>

**Micelle formation**

When adding a surfactant to an aqueous solution, the presence of the hydrophobic group causes a distortion of the water structure and the free energy of the system increases. In order to minimize the system free energy, the surfactants concentrate in the surface, orientating the hydrophobic tail away from the solvent. Since less work is required to bring a surfactant to an interface than the solvent molecule, the presence of the surfactant decreases the work needed to create unit area of the surface i.e. surface tension is decreased. (Myers 1999).

Another way of reducing the free energy of the system is by aggregation of surfactant monomers, where the hydrophobic tails are also orientated away from the water molecules i.e. micelle formation. On the other hand, the increase in work required to transfer surfactant monomers to the micelles as well as the electrostatic repulsion between similarly charged surfactant monomers opposes the micelle formation. Critical micelle concentration is the concentration of surfactants, where the factors promoting the micelle formation predominate over the factors opposing micelle formation. In other words, critical micelle concentration (CMC) is the concentration where surfactant monomers aggregate to form micelles. (Rosen 1978). The aggregation number (number of surfactant monomers forming the micelles) of surfactants is in the range of 50–200 (Myers 1999). The surfactant concentration and the micelle formation affect the physical properties such as surface tension, turbidity and conductivity of the bulk solution. Such changes in the physical properties can be used for determining the CMC of surfactants. Figure 6 shows how physical properties of surfactant solutions vary with the surfactant concentration. In the case of the conductivity measurement, when the surfactant concentration is below CMC, the surfactant monomers behave as a strong electrolyte. In addition, when the surfactant concentration is above its CMC the micelles are partially ionized and consequently there is a change in the electrical conductance.
The critical micelle concentration is dependent on the structure of the surfactant such as the type of the hydrophobic tail (amount of carbons, linear or branched, presence of polar atoms), hydrophilic head and solution characteristics (presence of electrolyte and organic materials, temperature, pH) (Myers 1999). Table 6 summarizes different CMC values of the anionic surfactant sodium dodecyl sulphate (SDS) measured at different conditions and found in the literature. As it can be observed in Table 6, in the presence of electrolytes the counter ion concentration around the micelles increases, decreasing the mutual repulsion of the ionic heads of the micelles. Therefore, the work required for micelle formation is smaller and the CMC is reduced.

**Table 6. CMC of SDS at different solution conditions found in the literature.**

<table>
<thead>
<tr>
<th>Method</th>
<th>CMC (mM)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductimetry</td>
<td>8.3</td>
<td>(Juang et al. 2003, Landaburu-Aguirre et al. 2009)</td>
</tr>
<tr>
<td>Conductimetry</td>
<td>7.49</td>
<td>(Zeng et al. 2011)</td>
</tr>
<tr>
<td>Conductimetry</td>
<td>7.49</td>
<td>(Huang et al. 2009)</td>
</tr>
<tr>
<td>Conductimetry Buffer, pH = 7.8</td>
<td>5.31</td>
<td>(Samper et al. 2009)</td>
</tr>
<tr>
<td>Conductimetry 25 ºC</td>
<td>8.10</td>
<td>(Umlong &amp; Ismail 2007)</td>
</tr>
<tr>
<td>Conductimetry [NaH$_2$PO$_4$] = 42.0 mM</td>
<td>3.5</td>
<td>(Landaburu-Aguirre et al. 2011)</td>
</tr>
<tr>
<td>Conductimetry 25 ºC,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[LiClO$_4$] = 0</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>[LiClO$_4$] = 15 mM</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>[NaClO$_4$] = 15 mM</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>[KClO$_4$] = 15 mM</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Method</td>
<td>CMC (mM)</td>
<td>Reference</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>Conductimetry</td>
<td>25 °C,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[NaCl] = 0 7.8</td>
<td>(Dutkiewicz &amp; Jakubowska 2002)</td>
</tr>
<tr>
<td></td>
<td>[NaCl] = 15 mM 4.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[NaCl] = 40 mM 2.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[NH₄ClO₄] = 15 mM 3.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[NH₄ClO₄] = 40 mM 2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[KCl] = 15 mM 1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[(MgClO₄)₂] = 15 mM 2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[(MgClO₄)₂] = 40 mM 1.6</td>
<td></td>
</tr>
<tr>
<td>Surface tension</td>
<td>20 °C,</td>
<td>(Umlong &amp; Ismail 2007)</td>
</tr>
<tr>
<td></td>
<td>[NaCl] = 0 7.76 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[NaCl] = 15.2 mM 3.98 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[NaCl] = 79.7 mM 1.49 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25 °C,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[NaCl] = 0 8.10 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[NaCl] = 15.2 mM 4.10 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[NaCl] = 79.7 mM 1.58 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 °C,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[NaCl] = 0 7.59 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[NaCl] = 15.2 mM 4.07 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[NaCl] = 79.7 mM 1.48 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>Surface tension</td>
<td>[CuCl₂] = 0 8.0</td>
<td>(Tung et al. 2002)</td>
</tr>
<tr>
<td></td>
<td>[CuCl₂] = 2 mM 2.0</td>
<td></td>
</tr>
<tr>
<td>Titrimetric method</td>
<td>[NaCl] = 0 6.02</td>
<td>(Corrin &amp; Harkins 1947)</td>
</tr>
<tr>
<td></td>
<td>[NaCl] = 18.52 mM 3.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[NaSO₄] = 18.06 mM 2.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[(Na₄P₂O₇)] = 18.66 mM 1.86</td>
<td></td>
</tr>
<tr>
<td>UF membranes</td>
<td>7.7</td>
<td>(Carswell et al. 2003)</td>
</tr>
<tr>
<td>Not reported</td>
<td>8.5</td>
<td>(Liu &amp; Li 2004)</td>
</tr>
<tr>
<td></td>
<td>8.2</td>
<td>(Rosen 1978)</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>(Juang et al. 2010)</td>
</tr>
<tr>
<td></td>
<td>8.11</td>
<td>(Yurlova et al. 2002)</td>
</tr>
<tr>
<td></td>
<td>8.2</td>
<td>(Scamehorn et al. 1994)</td>
</tr>
</tbody>
</table>

**Solubilization of solutes in the micelles**

Another important characteristic of micelle formation is that it enhances the solubilization of solutes into the solution which would not be soluble in the absence of micelles. Organic compounds can be solubilized in different sites in the micelles such as,
- between the hydrophilic head groups
- between the hydrophilic head group and the first few carbon atoms of the hydrocarbon chain (palisade layer)
- more deeply in the palisade layer and in the inner core of the micelle
- inner core of the micelles.

The solubilization of organic compounds is dependent on the nature of the surfactant and solute such as polarity and the length of the hydrocarbon chain, temperature and ionic strength (Gadelle et al. 1995, Paria 2008). In this way, organic compounds tend to be solubilized in sites of the micelle that have similar polarity (Baek & Yang 2004, Dunn et al. 1985).

With regard to ionic compounds, as it has been previously mentioned they are trapped on the surface of the micelles due to electrostatic interaction with the oppositely charged hydrophilic head of the micelles. The charge cloud around the micelles is called the electrical double layer (EDL) (Myers 1999). Figure 7 shows the ion distribution based on the Gouy-Chapman-Stern model. As it can be observed from Figure 7, next to the micelle surface there is a layer (Stern layer, Helmholtz layer) composed by counter ions that are associated with the negatively charged surface. In addition, there is a second layer called the diffuse layer where the concentration of counter ions and the electrical potential decreases exponentially with distance from the surface towards the bulk. The dividing line between the Stern and the diffuse layers is called the Shear plane and the electrical potential at the plane is called the zeta potential. The length of the diffuse layer is called the Debye length and it is dependent on the ionic strength of the solution. Therefore, at higher ionic strength, where the concentration of counter ions is higher, the diffuse layer becomes thinner (shorter Debye length) and the electrical potential drops faster (Rosen 1978).
Due to the surfactant properties and their ability to dissolve solutes, surfactants are widely used in industries as adhesives, wetting and foaming agents, emulsifiers, etc. (Table 5). In addition, the surfactant capability of trapping toxic organic compounds and metals opens new possibilities for environmental applications such as the remediation of soil and water contamination (Mosler & Hatton 1996, Mulligan et al. 2001). Surfactant based separation technologies such as micellar-enhanced ultrafiltration, are widely studied in environmental research.

MEUF was first introduced by Scamehorn et al. in the 1980s as a potential surfactant based separation process for wastewater pollution control. Initial applications of MEUF were based on the removal of dissolved organic compounds such as 4-tert-butyl-phenol and multivalent metal ions such as calcium and zinc from aqueous streams (Dunn et al. 1985, Dunn et al. 1987, Scamehorn et al. 1989). Following, MEUF studies during the past 30 years have been applied for the removal of phenols (El-Abbassi et al. 2011, Purkait et al. 2005), aniline (Jadhav et al. 2001), amino acids such as α-phenylglycine (Escudero et al. 2006), dyes such as methylene blue, reactive black and reactive orange (Ahmad et al. 2006, Zaghbani et al. 2007), nutrients such as phosphates and nitrates (Baek et al. 2003a, Baek et al. 2003b), rhodium based catalyst (Schwarze et al. 2009) and heavy metals such as copper, cadmium, nickel (Xu et al. 2007, Yurlova et al. 2002), from aqueous streams.
3.3.2 Removal of heavy metals by MEUF

Table 7 collects some of the papers published in the area of heavy metal removal using MEUF, including the papers composing this thesis. In MEUF, the membranes used are anisotropic ultrafiltration membranes ranging in nominal pore size from about 1 to 10 nm (1000 to 50,000 molecular weight cut-off (MWCO)) (Fillipi et al. 1999). The decision of choosing which MWCO is the most appropriate one is based on the aggregation number of the surfactant, and thus, on the molecular size of the micelles formed. In the case of sodium deoxycholate (NaDC) micelles, the aggregation number of the micelles is in the range of 3–12. NaDC micelles are relatively small (1700–4200 g/mol) and the membrane MWCO used is between 1–3 kDa (Huang et al. 1994). Some studies reported that the aggregation number of the anionic surfactant sodium dodecyl sulphate (SDS) without any additives is around 50–64 and the molecular weight of its micelles is around 14,000–18,000 g/mol (Gadelle et al. 1995, Kowalska et al. 2004). Therefore, as it can be observed from Table 4, in most of the studies where SDS is used as the anionic surfactant, the membrane MWCO range is 1–10 kDa. In this thesis, regenerated cellulose membranes of 3, 5 and 10 kDa were used in Papers I and II.

In addition to the membrane MWCO, the membrane material also plays an important role in the MEUF performance (Juang et al. 2003). Consequently, research has also been focused on studying different membrane materials. Following this issue, in Papers III-IV and V, 10 kDa regenerated cellulose membrane and 10 kDa polyethersulphone membranes were used, respectively.

As it can be observed in Table 4 sodium dodecyl sulfate (SDS) is widely used as the anionic surfactant. In general, an ideal surfactant requires very low critical micelle concentration (CMC), high molecular weight to form larger micelles so that they can be rejected by a large pore-size membrane, and biodegradability (Ahmad et al. 2006, Huang et al. 1994). When a surfactant has a high critical micelle concentration, relatively large concentration of surfactant must be used for forming the micelles and to have an efficient removal of heavy metals. In addition, since the monomers in the retentate are not rejected by the ultrafiltration membrane, the total surfactant concentration in the permeate is equal or slightly less than the CMC of the surfactant. The use of large amount of surfactants and the surfactants loss into the permeate during the MEUF process can be reduced by lowering the critical micelle concentration. One way of reducing the CMC is by incorporating non-ionic surfactants into the ionic micelles. This topic has been
addressed by the scientific community and several research papers can be found using anionic-nonionic surfactant mixture in the removal of heavy metals (Table 7).

Surfactants leakage to the permeate remains a challenge in MEUF since it can create secondary pollution. Therefore, research has been conducted using biosurfactants such as rhamnolipids and sodium deoxycholate (DCA). Biosurfactants are potentially useful for the removal of heavy metals due to their anionic nature, low toxicity, biodegradability and low critical micelle concentration. (El-Abbassi et al. 2011, Huang et al. 1994).

As can be observed from Table 7, extended research has been conducted for the removal of heavy metals from synthetic wastewater samples. However, the removal of heavy metals from real wastewaters has been very scarce. Table 7 summarizes all the publications found in the literature related to the removal of heavy metals from real wastewaters by MEUF. In order to fully evaluate the feasibility of MEUF for industrial application there is a substantial need for research to be conducted on the MEUF process with real wastewaters. This issue has been addressed in this thesis (Papers IV and V) where the simultaneous removal of heavy metals from real wastewaters has been studied.
Table 7. Publications related to the removal of heavy metals by MEUF.

<table>
<thead>
<tr>
<th>Source</th>
<th>Heavy metal</th>
<th>Used membrane</th>
<th>Used surfactant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>wastewater</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single metal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>Regenerated cellulose, 20 kDa, Spiral wound</td>
<td>Anionic SDS; Anionic-non ionic micelles (SDS–Brij35)</td>
<td>(Rahmanian et al. 2010)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cellulose acetate, 5 kDa, flat sheet membrane</td>
<td>Anionic SDS; Anionic-non ionic micelles (SDS–NMP)</td>
<td>(Fillipi et al. 1999)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Regenerated cellulose, 3, 5 and 10 kDa, flat sheet membrane</td>
<td>Anionic SDS</td>
<td>(Landaburu-Aguirre et al. 2009)</td>
<td></td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>Polyethersulfone, 6 kDa, hollow fiber</td>
<td>Anionic-non ionic micelles (SDS–Brij35; SDS–TritonX-100)</td>
<td>(Huang et al. 2009)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polyethersulfone, 6 kDa, hollow fiber</td>
<td>Anionic-non ionic micelles (SDS–NMP)</td>
<td>(Fang et al. 2008)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Regenerated cellulose, 3, 5 and 10 kDa, flat sheet membrane</td>
<td>Anionic SDS</td>
<td>(Landaburu-Aguirre et al. 2010)</td>
<td></td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>Polycarbonate, pore size of 0.1 μm</td>
<td>Anionic Sodium lauryl ether sulfate (SLES)</td>
<td>(Danis &amp; Aydiner 2009)</td>
<td></td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>Regenerated cellulose, 5 and 10 kDa, flat sheet membrane</td>
<td>Anionic-polymer mixture (SDS-PEG)</td>
<td>(Xiarchos et al. 2008)</td>
<td></td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>Regenerated cellulose, 10 kDa, spiral wound</td>
<td>Anionic SDS</td>
<td>(Rahmanian et al. 2011)</td>
<td></td>
</tr>
<tr>
<td>Cd$^{2+}$; Cu$^{2+}$; Ni$^{2+}$; Pb$^{2+}$; Zn$^{2+}$</td>
<td>Polyethersulfone, 10 kDa, flat sheet membrane</td>
<td>Anionic SDS; Anionic LAS</td>
<td>(Samper et al. 2009)</td>
<td></td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>Zirconium oxide–titanium oxide, 15 kDa, tubular membrane</td>
<td>Anionic SDS; Anionic-non ionic micelles (SDS-NPE)</td>
<td>(Aoudia et al. 2003)</td>
<td></td>
</tr>
<tr>
<td>Source</td>
<td>Heavy metal</td>
<td>Used membrane</td>
<td>Used surfactant</td>
<td>Reference</td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------------------</td>
<td>----------------------------------------</td>
<td>---------------------------------------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>Multicomponent</td>
<td>Ni(^{2+}), Co(^{2+})</td>
<td>Polysulfone, 20 kDa</td>
<td>Anionic SDS</td>
<td>(Karate &amp; Marathe 2008)</td>
</tr>
<tr>
<td></td>
<td>Cd(^{2+}), Cu(^{2+}), Zn(^{2+})</td>
<td>Cellulose acetate, 1 and 5 kDa</td>
<td>Anionic SDS;</td>
<td>(Scamehorn et al. 1994)</td>
</tr>
<tr>
<td></td>
<td>Ni, Zn(^{2+})</td>
<td>Regenerated cellulose, 10 kDa, flat sheet membrane</td>
<td>Anionic SDS</td>
<td>(Landaburu-Aguirre et al. 2011)</td>
</tr>
<tr>
<td></td>
<td>Cd(^{2+}), Pb(^{2+}), Cu(^{2+}), Ni(^{2+}), Zn(^{2+})</td>
<td>Acrylanitrile, 2 kDa</td>
<td>Anionic biosurfactants (DCA, lecithin)</td>
<td>(Huang et al. 1994)</td>
</tr>
<tr>
<td>Cd(^{2+}), phenol</td>
<td>Polysulfone, 10 kDa, hollow-fibre</td>
<td>Anionic SDS, Mixed anionic-non ionic micelles (SDS-TritonX-100)</td>
<td>(Li et al. 2011)</td>
<td></td>
</tr>
<tr>
<td>Cu(^{2+}), phenol</td>
<td>Regenerated cellulose, 5 kDa, flat sheet membrane</td>
<td>Anionic SDS, Mixed anionic-nonionic micelles (SDS-TritonX-100)</td>
<td>(Tung et al. 2002)</td>
<td></td>
</tr>
<tr>
<td>Cd(^{2+}), methylene blue</td>
<td>Polysulfone, 10 kDa, hollow-fibre</td>
<td>Anionic SDS</td>
<td>(Zeng et al. 2011)</td>
<td></td>
</tr>
<tr>
<td>Real wastewater</td>
<td>Pb(^{2+})</td>
<td>Polyethersulfone, 10 kDa, flat sheet membrane</td>
<td>Anionic SDS; Anionic-non ionic micelles (SDS-TX-100; SDS-NP12)</td>
<td>(Yenphan et al. 2010)</td>
</tr>
<tr>
<td>Single metal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Multicomponent</td>
<td>Cd(^{2+}), Pb(^{2+}), Zn(^{2+}), Ni(^{2+}), Cu(^{2+})</td>
<td>Polysulfone 10 kDa and 30 kDa, hollow-fibre</td>
<td>Anionic biosurfactant (Rhamnolipid)</td>
<td>(El Zeftawy &amp; Mulligan 2011)</td>
</tr>
<tr>
<td></td>
<td>Cd(^{2+}), Cu(^{2+}), Ni, Zn(^{2+})</td>
<td>Regenerated cellulose, 10 kDa, flat sheet membrane</td>
<td>Anionic SDS</td>
<td>(Landaburu-Aguirre et al. 2012)</td>
</tr>
<tr>
<td></td>
<td>Cd(^{2+}), Cu(^{2+})</td>
<td>Polyethersulfone, 10 kDa, spiral wound membrane</td>
<td>Anionic SDS</td>
<td>(Häyrynen et al. 2012)</td>
</tr>
</tbody>
</table>
4 Statistical design of experiments

Traditionally, research and experimental work is conducted using the one variable at a time approach, where the effect of each factor is investigated separately. The factor to be studied is varied while the rest of the factors are maintained constant. However, in the case of studying the effect of multiple factors, this approach implies a large amount of experiments and, therefore, an inefficient use of resources such as time and raw materials. In addition, the effect of one factor might be dependent on the level of other factors, i.e. factor interaction effect. The use of the one variable at a time approach may often miss important conclusions about the effect of (one) experimental variable when the level of another variable is changed. Further, the process optimization is inefficient due to the difficulty of finding the true optimum with a reasonable amount of experiments. (Morgan 1991).

The use of statistical design of experiments is an alternative methodology in experimental work, which overcomes the limitations explained above. In contrast to the one variable at a time approach, in statistical experimental designs the values (levels) of the factors are varied in each experiment following a systematic experimental plan. Further, an empirical model is fitted to the multivariate experimental data, which is used to get a better understanding of the system studied. Compared to the traditional approach, statistical design of experiments has the advantages of evaluating relatively large number of factors in a smaller amount of experiments, detection and more precise evaluation of factor interactions and process optimization (Goupy 1993).

There is a wide variety of experimental designs that can be used in a study. The type of experimental design to be used can be selected based on the objective of the study (screening designs or response surface designs).

4.1 Screening designs

Screening designs are used at the beginning of a study and the main objective is to identify which are the main factors affecting the response. In this way, screening designs allow screening relatively large amount of factors in a relatively small amount of experiments (Dejaegher & Vander Heyden 2011). Results obtained in the screening part can also be used to redesign the range of the factors studied. In screening designs the factors are varied usually within two
levels and, therefore, the empirical models developed are linear empirical models (or linear with interaction models) as described in Equation 5.

\[ Y = b_0 + \sum_{i=1}^{f} b_i X_i + \sum_{i=1}^{f-1} \sum_{j=i+1}^{f} b_{ij} X_i X_j, \]

where \( Y \) is the predicted response, \( b_0 \) the constant coefficient, \( b_i \) the linear coefficients, \( b_{ij} \) the interaction coefficients, and \( X_i \) and \( X_j \) are the coded levels of process factors studied.

Among the different types of screening experimental designs, factorial designs such as full factorial design and fractional factorial designs are commonly used in this stage of design of experiments (Dejaegher & Vander Heyden 2011).

### 4.1.1 Two level full factorial designs

In two level full factorial designs the experimental matrix is formed by combining all the factors and levels with each other. In this way, there are \( 2^f \) combinations of \( f \) number of factors. Figure 8 shows the design matrix and design region of a two level full factorial design when three factors are studied. As it can be observed in Figure 8 the factors are varied from their low coded level (-1) to their high coded level (+1). Replicated experiments in the centre point (0,0,0) are often included in screening designs in order to detect curvature (need of quadratic term in the model) and also in order to estimate the pure error of the experiments.

The set of experiments to be conducted contains all possible factor combinations and consequently, full factorial designs provide the maximum amount of information about the effects of factors and their interactions.

One of the main disadvantages of full factorial design is that the amount of experiments to be conducted increases rapidly as the number of factors increases (Table 8). In addition, as can be observed in Table 8 the amount of two and three factor interactions also increases rapidly.

Besides the complete information that can be obtained using full factorial designs, three factor interaction effects are small compared to the main and two factor interaction. Further, main effects tend to be larger than two factor interactions. In addition, when a study contains a large number of factors, often only few of the main factors are important. (Morgan 1991). Consequently, when the number of factors to be studied is relatively high, it is often more appropriate to reduce the number of experiments at the expense of having less complete information about the effects (Georgiou 2007). For this kind of experiments
fractional factorial designs are very useful because they assume that the effects of higher order interactions are negligible and consequently experimental design can contain a fraction of the experiments required in the full factorial designs (Morgan 1991).

\[
\begin{array}{ccc}
X_1 & X_2 & X_3 \\
-1 & -1 & -1 \\
+1 & -1 & -1 \\
-1 & +1 & -1 \\
+1 & +1 & -1 \\
-1 & -1 & +1 \\
+1 & -1 & +1 \\
-1 & +1 & +1 \\
+1 & +1 & +1 \\
\end{array}
\]

Fig. 8. a) Design matrix and b) design region of a two level full factorial design with 3 factors (X₁, X₂, and X₃).

Table 8. Number of experiments to be conducted with two level full factorial design.

<table>
<thead>
<tr>
<th>Number of factors (f)</th>
<th>Number of experiments (n)</th>
<th>Effect that can be estimated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Main factor</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>32</td>
<td>5</td>
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<tr>
<td>6</td>
<td>64</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>128</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>256</td>
<td>8</td>
</tr>
</tbody>
</table>

4.1.2 Two level fractional factorial designs

As has been mentioned above, fractional factorial design contains a fraction of the full factorial design. Using fractional factorial designs the effect of large amount of factors can be determined in few experimental runs. Therefore, they are usually
used in the very beginning of an investigation when little is known about a system and the main objective is to screen the actual significant factors.

The number of experiments to be conducted can be expressed as $2^{f-v}$, where $f$ is amount of factors to be studied and $(1/2)^v$ represents the fraction of the full factorial design (Dejaegher & Vander Heyden 2011). For example, when $v = 1$ and $v = 2$, the fractional factorial design contains one half and a quarter of experiments of the full factorial design, respectively. As an example, in this thesis, a half fractional factorial design was applied in Paper III, where 5 factors were evaluated in 16 experiments (using full factorial design 32 experiments would be needed).

As the amount of experimental data is reduced, some of the information is lost and the estimation of the effects is not as complete as in full factorial design. As a consequence, all the effects cannot be estimated independently i.e. effect confounding. The design resolution describes the degree to which extent the main effects are confounded with two factor interaction, three factor interactions, etc. (Georgiou 2007). Higher resolution designs have less severe confounding but the amount of experiments to be conducted is higher. The design resolutions can be:

- **Resolution III**: The main effects are confounded with two factor interactions. The main effect cannot be estimated independently.
- **Resolution IV**: The main effects are not confounded with two factor interactions. However, two factor interactions are confounded with each other.
- **Resolution V**: No main effects or two factor interactions are confounded with each other. However, two factor interactions are confounded with three factor interactions. In addition, the main effects can be confounded with four factor interactions. Since three and four factor interactions are most likely to be insignificant, the main effects and two factor interactions can be estimated independently.

### 4.2 Response surface designs

After determining which are the main factors affecting the response, response surface designs are used to evaluate the important factors of a study in more detail (Dejaegher & Vander Heyden 2011, Lundstedt et al. 1998). Developed response surface plots give a better and more visual understanding of the relationship between the responses and factors. In addition, response surface designs are used for finding optimal conditions. Finding the optimal conditions can be achieved by
maximising or minimising a response or by approximating the response to a targeted value (Dean et al. 1998).

When there is no evidence of curvature, a linear model involving only the main effects and interactions is valid to describe the response surface. However, in case of strong curvature, higher order polynomial functions should be fitted to the experimental data. Therefore, response surface designs containing at least three levels of factors are necessary. Quadratic empirical models (Equation 6) are commonly used to fit the experimental data.

\[
Y = b_0 + \sum_{i=1}^{f} b_i X_i + \sum_{i=1}^{f} b_{ij} X_i^2 + \sum_{i=1}^{f-1} \sum_{j=i+1}^{f} b_{ij} X_i X_j ,
\]

where \( Y \) is the predicted response, \( b_0 \) is the constant coefficient, \( b_i \) are the linear coefficients, \( b_{ij} \) are the two factor interaction coefficients, \( b_{ii} \) are the quadratic coefficients, \( X_i \) is the coded level of process factors studied and \( X_i X_j \) represents the two factor interactive variables.

Response surface designs were first introduced by Box and Wilson in 1951 to improve manufacturing processes in the chemical industry. The purpose was to optimize chemical reactions to obtain high yields and purity at low cost. In their study, Box and Wilson described central composite designs, which are one of the most commonly used response surface designs. (Dean et al. 1998).

Central composite designs are factorial designs (full or fractional) augmented with star points. Star points are points located at a specified distance (\( \alpha \)) from the design centre in each direction on each axis of the coded factor. The total number of experiments of central composite designs (\( n \)) can be calculated as follows,

\[
n = n_a + n_o + n_c ,
\]

where, \( n_a \) is the number of experiments of the factorial design, \( n_o \) is the number of replicates in the centre point and \( n_c \) is the number of star points. Further,

\[
n_c = 2 \times f ,
\]

where \( f \) is the amount of factors to be studied.

As Figure 9 shows, there are three types of central composite designs that can be classified depending on the location of the star points.
4.2.1 Face Centred Composite designs (CCF)

In face centered composite designs (CCF) the star points are located at the centre of each face of the factorial space (Figure 9 a). Consequently, CCF requires only three levels of each factor studied. Advantages of face centered composite designs are that they do not require using points outside the original factor range and they provide relatively high quality predictions over the entire design space. However, they give poor precision for estimating pure quadratic coefficients.

4.2.2 Central Composite Design Circumscribed (CCC)

In central composite designs circumscribed (CCC) the star points are located outside the original factor range (Figure 9 b). Therefore, it is very important to ensure that the star points are experimentally feasible levels. CCC designs require five levels of each factor studied and provide high quality predictions over the entire design. CCC are rotatable designs, which means that responses can be predicted equally well in all equidistant directions from the centre point and allows a more accurate calculation of all the model terms. To maintain rotatability, the location of the star points will vary depending on the number of experiments (n) conducted in the factorial design as follows,

\[ \alpha = \left\lfloor \left[ \frac{n}{4} \right] \right\rfloor \]

(9)

If the factorial design is full factorial design the distance of the star points would be dependent on the amount of factors (f) studied as follows,

\[ \alpha = \left\lfloor \left[ \frac{2^f}{4} \right] \right\rfloor \]

(10)

4.2.3 Inscribed central composite designs (CCI)

CCI designs use the star points as factor settings (low and high level of the factors) and create a factorial or fractional factorial design within those limits (Figure 9 c). CCI designs can be described as scaled down CCC designs useful for those situations in which the factor levels of the factorial design are truly limits. As in CCC designs, CCC requires 5 levels of each factor and are also rotatable designs.
Fig. 9. Design region of composite designs for two factors ($X_1$, $X_2$) a) face centred (CCF) b) circumscribed (CCC) c) inscribed (CCI).
5 Material and methods

5.1 Feed solutions

5.1.1 Synthetic wastewaters

Synthetic wastewaters were used to study the single or/and simultaneous removal of heavy metals by MEUF (Papers I-III). The single metal solutions studied in Papers I and II were zinc and cadmium solutions. In Paper III the synthetic wastewaters contained a mixture of cadmium, zinc, copper, nickel and phosphate electrolytes. All the synthetic samples were prepared using ultrapure deionized water (MilliQ water). The chemicals used for preparing the synthetic waters are summarized in Table 9. All the chemicals were used as such without further purification. In Paper III, the pH of the synthetic waters was adjusted by 0.1 M NaOH and 6 wt-% HNO₃.

Table 9. Characteristics of the chemicals used to prepare the synthetic wastewaters.

<table>
<thead>
<tr>
<th>Chemical compounds</th>
<th>Molecular weight (g/mol)</th>
<th>Purity (%)</th>
<th>Supplier</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCl₂</td>
<td>136.29</td>
<td>99.99</td>
<td>Fisher Scientific, UK</td>
<td>I, II, III</td>
</tr>
<tr>
<td>CdCl₂</td>
<td>183.31</td>
<td>99.99</td>
<td>Fisher Scientific, UK</td>
<td>II, III</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>134.45</td>
<td>&gt; 99</td>
<td>Across Organics</td>
<td>III</td>
</tr>
<tr>
<td>Ni(NO₃)₂ x 6H₂O</td>
<td>290.80</td>
<td>&gt; 99</td>
<td>Across Organics</td>
<td>III</td>
</tr>
<tr>
<td>NaH₂PO₄ x H₂O</td>
<td>137.99</td>
<td>&gt; 99</td>
<td>Sigma Aldrich</td>
<td>III</td>
</tr>
</tbody>
</table>

5.1.2 Real wastewaters

The real wastewaters used were phosphorous-rich drainage waters of the fertilizer company Yara Suomi Oy, located in Uusikaupunki, Finland (Papers IV and V). The phosphorous-rich drainage waters are mainly formed when rainwater infiltrates and washes a heterogeneous gypsum landfill of the company, gypsum that contains traces of heavy metals such as cadmium, copper, zinc and nickel. The composition of the real wastewaters studied is summarized in Table 10.

The real wastewater was treated in order to reduce the calcium concentration of the drainage waters. When adding the anionic surfactant to the wastewater precipitation of SDS was observed due to the high content of calcium in the wastewater. Therefore, the removal of calcium prior to the MEUF process was
needed and it was conducted by precipitation. Calcium was precipitated by adding SDS (20 mM). The precipitate Ca(DS)$_2$ was then separated by centrifugation using the laboratory centrifuge Z61 from Cepa. As it can be observed from Table 10, calcium was largely removed with no effect on the heavy metal and phosphorous concentrations. The remaining SDS concentration in the supernatant was insignificant (1.5 mM). Further, the supernatant was filtered using 0.5 μm poresize Opticap XL5 capsule filters (Millipore) in order to remove the remaining suspended solids. The pH of the real samples was adjusted by 0.1 M NaOH and 6 wt-% HNO$_3$ (Paper IV). In Paper V the pH of the real wastewaters was not adjusted.

Table 10. Main compounds in the real wastewater before and after pre-treatment. The not unadjusted pH of the real wastewater was 2.8 before and after the pre-treatment (Paper V © Elsevier).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration before pretreatment (ppm)</th>
<th>Concentration after pretreatment (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$^{2+}$</td>
<td>0.37</td>
<td>0.35</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>0.41</td>
<td>0.40</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>1.96</td>
<td>1.97</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>1.00</td>
<td>0.95</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>380.3</td>
<td>56.40</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>79.50</td>
<td>70.77</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>7.93</td>
<td>6.36</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>33.96</td>
<td>9.84</td>
</tr>
<tr>
<td>PO$_4^{3-}$</td>
<td>2453.0</td>
<td>2453.0</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>NA</td>
<td>1700.0</td>
</tr>
<tr>
<td>F$^-$</td>
<td>NA</td>
<td>505.0</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>NA</td>
<td>181.0</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>NA</td>
<td>67.50</td>
</tr>
</tbody>
</table>

5.2 Surfactant

Sodium dodecyl sulfate (NaC$_{12}$H$_{25}$SO$_4$, SDS) was the anionic surfactant used (Figure 10). SDS was purchased from Fisher Scientific, UK. SDS was added to the waters as such without further purification. The critical micelle concentration (CMC) of SDS was determined by measuring the conductivity of the SDS systems (conductimeter model 20, Denver Instruments) (Table 11).
Fig. 10. Molecular structure of SDS.

Table 11. Characteristics of used SDS.

<table>
<thead>
<tr>
<th>Supplier</th>
<th>purity (%)</th>
<th>molecular weight (g/mol)</th>
<th>CMC (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fisher Scientific</td>
<td>&gt; 99</td>
<td>288.38</td>
<td>8.3&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.5&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> CMC of SDS using deionized water as the solvent (Paper I, II)

<sup>b</sup> CMC of SDS using deionized water as the solvent and in presence of 1.3 g/l of P (in form of NaH<sub>2</sub>PO<sub>4</sub>) (Paper III)

5.3 Experimental procedure

5.3.1 Experiments conducted at dead-end laboratory scale (Papers I-IV)

The laboratory scale experiments of MEUF were conducted in an Amicon stirred cell (Figure 11, model 8400, Millipore). The stirred cell was placed on top of a stirrer table. The stirring speed was maintained constant at 375 rpm to obtain effective agitation and vortex approximately one-third of the depth of the liquid as recommended by the equipment supplier. Experiments were conducted at room temperature. The tube fitting assembly was connected to a nitrogen gas bottle, which was used to achieve the required overpressure. The stirred cell volume capacity is 0.4 dm<sup>3</sup>. In this thesis, the initial feed volume was 200 cm<sup>3</sup> and the ultrafiltration experiments were carried out until 100 cm<sup>3</sup> of the total sample was filtered.
The membranes used were ultrafiltration flat sheet membranes of 3, 5 and 10 kDa (Amicon, PL series, Millipore). Table 12 shows the main characteristics of the membranes used. All membrane discs are pretreated with glycerine to prevent drying and sodium azide is added as preservative. To remove these materials before use, the membranes were placed in the ultrafiltration cell and it was rinsed by filtering deionized water for at least five minutes at 3.5 bar. The diameter of the membranes was 76 mm and the membrane effective area was 0.00418 m$^2$ (41.8 cm$^2$).

After each experiment the membrane was cleaned by flushing it with ultra-pure deionized water at a pressure of 2.5 bar for 45 min. The water flux was re-calculated to evaluate the degree of membrane damage. The membrane was changed if the water flux measured after cleaning the membrane differed more than 10% from the initial water flux.
Table 12. Characteristics of the regenerated cellulose membranes used in the laboratory scale equipment.

<table>
<thead>
<tr>
<th>Membrane name</th>
<th>Ultracel Amicon PL series</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMWL (kDa)</td>
<td>3, 5, 10</td>
</tr>
<tr>
<td>Top layer material</td>
<td>Regenerated cellulose acetate</td>
</tr>
<tr>
<td>Support material</td>
<td>Non-woven polypropylene</td>
</tr>
<tr>
<td>Thickness (μm)</td>
<td>230</td>
</tr>
<tr>
<td>pH range</td>
<td>3–13</td>
</tr>
<tr>
<td>Maximum operating temperature (°C)</td>
<td>50</td>
</tr>
</tbody>
</table>

5.3.2 Experiments conducted at cross-flow semi pilot scale (Paper V)

Figure 12 illustrates the schematic diagram of the semi-pilot cross-flow ultrafiltration equipment. The experiments were conducted in a continuous mode with total recycle of the retentate and permeate in order to maintain constant feed concentration. The feed volume was 15 L. The feed temperature was maintained constant at 21 ± 1 °C. The transmembrane pressure and the feed flow velocity were controlled by the pump speed (Grundfos centrifugal pump model CRNE 1) and the valve installed on the retentate side.

The membrane used was a 10 kDa spiral wound polyethersulfone membrane (PW-series, GE Process & Water technologies) with an active filtration area of 1.6 m². The membrane diameter and the length were 0.61 m and 1.016 m, respectively. The thickness of the feed channel spacer is 0.0012 m. The membrane persisted pH-range between 2.0–10.0 and in short term 1.0–11.5 in cleaning.

After each experiment the membrane was cleaned with the following three steps. First, the membrane was rinsed with deionized water for 30 minutes. The membrane was further cleaned for 40 minutes with a solution containing 0.3 v% of Divos 116 VM19 (Diversey) and 8.0 mM of SDS. The water permeate flux was measured after each step. The membrane permeability was recovered after cleaning the membrane with pure water. Chemical cleaning was done in order to remove heavy metals and other contaminants from the membrane surface and in this way, preventing heavy metal contamination in the samples. Finally, the membrane was again rinsed with deionised water for 30 min.
Fig. 12. Cross-flow equipment diagram. F: feed, P: permeate, R: retentate (Paper V © Elsevier).

5.4 Analytical methods

Different analytical methods have been used in order to determine the composition of the feed, permeate and retentate solutions studied in this thesis. Heavy metals concentration was determined using Atomic Adsorption Spectroscopy (AAS). Phosphorous concentrations were determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (Papers III, IV and V). Sodium dodecyl sulphate concentrations were determined using total organic carbon (TOC) analyzer.

5.5 Statistical design of experiments

MODDE 8.0 software (Umetrics AB) was use for the design of experiments and data analysis. The experimental design was selected according to the research objective (screening or response surface) and the factors to be studied. Table 13 summarizes the experimental designs with the factors and responses studied in the original papers composing this thesis. In all the experimental designs three replicates were introduced to calculate the pure error. The experiments were performed randomly in order to reduce time dependent systematic errors.
After conducting the set of experiments the empirical models were fitted using Multiple Linear Regression (MLR). The validity of the empirical model was tested with analysis of variance (ANOVA). The confidence level used was 95%. The model was also evaluated in terms of the coefficient of determination (R²), the adjusted coefficient of determination (R²_adj) and the response variation percentage predicted by the model according to cross validation (Q²). In addition, various residual plots (normal probability plot of residuals and variable vs. residuals plot) as well as predicted vs. observed response plots were used to evaluate the model and to check if further improvement of the model was needed.

The responses studied were selected to evaluate the membrane process performance (Table 13). The membrane performance was characterized by the permeate flux and/or the selectivity of the membrane.

Table 13. The design of experiments, factors with levels and responses studied in the papers composing this thesis.

<table>
<thead>
<tr>
<th>Paper</th>
<th>Model</th>
<th>Design</th>
<th>Number of experiments modeled</th>
<th>Response</th>
<th>Factors</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Linear</td>
<td>FF</td>
<td>19</td>
<td>R&lt;sub&gt;z&lt;/sub&gt;</td>
<td>C&lt;sub&gt;SDS&lt;/sub&gt; (mM)</td>
<td>- 8.3 12.45 16.6 -</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>J&lt;sub&gt;v&lt;/sub&gt;</td>
<td>C&lt;sub&gt;z&lt;/sub&gt; (mM)</td>
<td>- 0.5 1.75 3.0 -</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NMWL (kDa)</td>
<td>- 3 5 10 -</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TMP (bar)</td>
<td>- 1 2 3 -</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>Quadratic</td>
<td>CCF</td>
<td>27</td>
<td>R&lt;sub&gt;z&lt;/sub&gt;/R&lt;sub&gt;CD&lt;/sub&gt;</td>
<td>C&lt;sub&gt;SDS&lt;/sub&gt; (mM)</td>
<td>- 8.3 12.45 16.6 -</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>J&lt;sub&gt;v&lt;/sub&gt;</td>
<td>C&lt;sub&gt;z&lt;/sub&gt;/C&lt;sub&gt;CD&lt;/sub&gt; (mM)</td>
<td>- 0.5 1.75 3.0 -</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NMWL (kDa)</td>
<td>- 3 5 10 -</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TMP (bar)</td>
<td>- 1 2 3 -</td>
<td></td>
</tr>
<tr>
<td>III&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Quadratic Complemented</td>
<td>FrF</td>
<td>25</td>
<td>R&lt;sub&gt;CD&lt;/sub&gt;</td>
<td>C&lt;sub&gt;SDS&lt;/sub&gt; (mM)</td>
<td>- 3.5 11.75 20 -</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C&lt;sub&gt;Cd&lt;/sub&gt;</td>
<td>C&lt;sub&gt;z&lt;/sub&gt; (mg/dm³)</td>
<td>- 2.0 3.0 4.0 -</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C&lt;sub&gt;Cd&lt;/sub&gt;</td>
<td>pH</td>
<td>- 3.5 4.25 5.0 -</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C&lt;sub&gt;Phosph.&lt;/sub&gt; (g/dm³)</td>
<td>- 0 0.65 1.3 -</td>
<td></td>
</tr>
<tr>
<td>IV&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Quadratic</td>
<td>CCC</td>
<td>11</td>
<td>R&lt;sub&gt;CD&lt;/sub&gt;</td>
<td>C&lt;sub&gt;SDS&lt;/sub&gt; (mM)</td>
<td>31.7 40.0 60.0 80.0 88.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C&lt;sub&gt;Cd&lt;/sub&gt;</td>
<td>pH</td>
<td>3.2 3.5 4.25 5.0 5.31</td>
</tr>
<tr>
<td>V&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Quadratic</td>
<td>CCC</td>
<td>17</td>
<td>J&lt;sub&gt;v&lt;/sub&gt;</td>
<td>C&lt;sub&gt;SDS&lt;/sub&gt; (mM)</td>
<td>36 40 60 80 84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TMP (bar)</td>
<td>1.8 2.0 3.0 4.0 4.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>feed velocity (m/s)</td>
<td>0.11 0.13 0.24 0.35 0.37</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>C<sub>CD</sub> = C<sub>Cd</sub> = 0.5 mg/dm³, TMP = 3 bar, 10 kDa regenerated cellulose; <sup>b</sup> TMP = 3 bar, 10 kDa regenerated cellulose; <sup>c</sup> 10 kDa polyethersulphone
5.5.1 Design of experiments and model fitting

As was previously explained in Section 4.1, screening designs are very useful at the very beginning of a study because they help to gain a better understanding of the system and to determine the main factors affecting the process performance. In this way, in the screening stage simple models are developed such as linear models with interactions.

In Paper I a linear model with interaction was developed using a two level full factorial (FF) design as the experimental design. The objective was to determine the main factors affecting the process performance on the removal of zinc from synthetic samples. The addition of centre points (replicates) in the screening design is recommendable to evaluate the reproducibility of the results. Further, the relationship between the responses and the factors studied is not often linear. Therefore, as shown in Paper III, adding centre points to the screening design enables evaluating the curvature degree of the developed model by using statistical tools such as the plot of residuals vs. variable.

In Paper III, the objective was to determine the main factors affecting the simultaneous removal of heavy metals from P-rich synthetic water on the rejection coefficients of cadmium and copper. The fertilizer company involved in this study was mainly interested in these two heavy metals and therefore, the experimental design was performed in order to model the rejection coefficients of copper and cadmium. However, rejection coefficients of zinc and nickel were also calculated and reported due to the scientific interest.

The first stage of the experimental design was conducted with a fractional factorial (FrF) design of resolution V, which means that all the main effects and two-factor interactions can be estimated without confounding. Figure 13 shows the residual vs. variable plot obtained in Paper III after fitting the linear model to the experimental data. The residuals should be random, with no pattern. A curved pattern, as displayed in Figure 13, indicates that a quadratic term is missing from the model. When adding a quadratic term to the model the residuals became random, showing that the model was improved (Figure 14). Therefore, the fractional factorial design was further complemented by adding extra experiments to estimate the effect of the quadratic terms and to improve the model.

After the screening designs are completed and the main important factors identified, response surface designs are used to develop more complete models such as quadratic models. The developed models can be further used to make predictions, find optimal conditions or find regions of operability. In addition,
with the fitted quadratic empirical models response surface plots can also be created, which give a better and a visual understanding of the relationship between the responses and factors studied.

In Papers II, IV and V central composite designs were used as the response surface designs. The central composite designs were based on two level full factorial designs, which were augmented with centre and star points.

The experimental design used in Paper II was a direct continuation of Paper I, where the main factors affecting the membrane performance of the removal of zinc were determined. In this way, the objective of Paper II was to optimize the removal of heavy metals such as zinc and cadmium from their respective synthetic samples and to gain a better understanding of the systems using response surface methodology (RSM) approach. The experimental design presented in Paper II was a face central composite design (CCF), where the star points are at the center of each face of the factorial space (See Section 4.2.1). Optimal conditions according to the models were determined running the optimizer of the Modde software for each system. The optimizer uses a Nelder Mead simplex method with the fitted response functions to maximize the retention of the heavy metals.

In Papers IV and V the experimental design was central composite design circumscribed (CCC), where the star points are at a distance from the centre (See Section 4.2.2). In this way, the star points establish new levels for the low and high settings for all factors. In Papers IV and V the simultaneous removal of heavy metals from phosphorous-rich real wastewater was studied. The response surface design used in Paper V aimed to understand the effect of factors on the permeate flux in semi-pilot scale by MEUF process. In Paper IV a sweet spot plot was developed to highlight the area where cadmium and copper rejection coefficients are within targeted values. In addition, optimal conditions for maximum rejection coefficients of cadmium and copper were determined within the sweet spot.
5.5.2 Evaluation of model validity

ANOVA tables presented in the papers composing this thesis show that all the regression models developed in this thesis were statistically significant with the 95% confidence interval ($F_{\text{value}} > F_{\text{tabulated}}$ and $p < 0.05$). In addition, the lack of fit
was not significant in either of the developed models with the 95% confidence level ($F_{\text{value}} < F_{\text{tabulated}}$ and $p > 0.05$).

Table 14 summarizes the values of $R^2$, $R^2_{\text{adj}}$, and $Q^2$ for the empirical models fitted in this thesis. These results were very satisfactory and also show the good validity of the models developed.

The fitted models were also evaluated by analyzing different plots available in the MODDE 8.0 software such as the Predicted vs. observed response plot. As an example, Figure 15 displays the observed vs. predicted plot obtained in Paper III for the rejection coefficients of cadmium and copper. With a good model all the points are located close to the straight line and as is shown in Figure 15, the predicted responses are very close to the experimental data thus showing the good validity of the models.

After validating the empirical models the effects of factors on the membrane performance of each study were evaluated.

### Table 14. $R^2$, $R^2_{\text{adj}}$, and $Q^2$ values obtained for the empirical models fitted in the papers composing this thesis.

<table>
<thead>
<tr>
<th>Paper</th>
<th>Modelled response</th>
<th>$R^2$</th>
<th>$R^2_{\text{adj}}$</th>
<th>$Q^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Zn removal</td>
<td>$J_v$</td>
<td>0.981</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R$</td>
<td>0.978</td>
<td>–</td>
</tr>
<tr>
<td>II</td>
<td>Zn removal</td>
<td>$J_v$</td>
<td>0.977</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R$</td>
<td>0.964</td>
<td>0.944</td>
</tr>
<tr>
<td></td>
<td>Cd removal</td>
<td>$J_v$</td>
<td>0.988</td>
<td>0.981</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R$</td>
<td>0.966</td>
<td>0.993</td>
</tr>
<tr>
<td>III</td>
<td>Cd removal</td>
<td>$R$</td>
<td>0.988</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>Cu removal</td>
<td>$R$</td>
<td>0.985</td>
<td>0.979</td>
</tr>
<tr>
<td>IV</td>
<td>Cd removal</td>
<td>$R$</td>
<td>0.979</td>
<td>0.969</td>
</tr>
<tr>
<td></td>
<td>Cu removal</td>
<td>$R$</td>
<td>0.970</td>
<td>0.955</td>
</tr>
<tr>
<td>V</td>
<td></td>
<td>$J_v$</td>
<td>0.955</td>
<td>0.940</td>
</tr>
</tbody>
</table>
Fig. 15. Observed vs. predicted values of the rejection coefficients of a) cadmium and b) copper (Paper III © Elsevier).
6 Results and discussion

6.1 Effect of process factors on the rejection coefficients of heavy metals

The analyses of phosphorous obtained by the ICP-OES method showed that concentrations of phosphorous in the feed, permeate and retentate were the same (Papers III, IV and V). The separation of phosphorous from heavy metals is thus dependent on how successfully the heavy metals are trapped by the SDS surfactants and consequently retained by the ultrafiltration membrane. This section summarises the results obtained during this thesis regarding the removal efficiency of heavy metals from synthetic and real wastewaters by MEUF.

6.1.1 Heavy metal feed concentration

In Paper I and II it was established that micellar-enhanced ultrafiltration is more efficient to remove heavy metals from diluted systems. Figure 16 shows the response surface plots developed in Paper II, where the single removal of zinc and cadmium from their respective synthetic samples was studied. As it can be observed in Figure 16, heavy metal concentration has a statistically significant negative effect on the retention coefficients of zinc and cadmium in the concentration range studied. Consequently, at higher heavy metal feed concentration, lower retention coefficients are achieved.

It has been previously reported that the decrease in retention at higher heavy metal feed concentration is due to the lack of available binding sites since the surfactant micelles achieve a saturated state, where no more heavy metals are trapped (Fang et al. 2008, Huang et al. 2010). Fang et al. (2008) explained the lack of available binding sites in terms of the increase in zeta potential of the SDS micelles. They observed a substantial increase in SDS zeta potential from −91.1 mV (pure SDS micelle) to −17.2 mV with a Cd concentration of 2.67 mM, indicating that the surface charge density of micelles is reduced. On the other hand, Huang et al. (2010) explained the saturated state of the SDS micelles using the Langmuir adsorption isotherms. They reported that the adsorption capacity of Cd\textsuperscript{2+} and Zn\textsuperscript{2+} on SDS micelles increased first linearly and then achieved a steady state value corresponding to the maximum adsorption capacity of the SDS micelles (Huang et al. 2010).
6.1.2 SDS feed concentration and its interaction

It is well established that SDS feed concentration has a positive effect on the heavy metal removal efficiency. Therefore, complementing previous studies, the effect of SDS feed concentration on the removal efficiency of heavy metals has been shown to be positive in all the papers composing this thesis (Papers I, II, III, IV and V). Increasing the SDS feed concentration has increased the values of retention/rejection coefficients of heavy metals. This is understandable since at higher SDS feed concentrations more surfactant monomers are in micellar form (Huang et al. 1994, Purkait et al. 2004, Purkait et al. 2005). This will increase the micellar surface charge and therefore, more heavy metals will be trapped on the micellar surface, achieving higher retention coefficients (Chhatre & Marathe 2006).
**Single removal of zinc and cadmium from synthetic samples**

In the single synthetic wastewaters studied (Papers I, II) a relatively low SDS feed concentration was needed in order to achieve a successful removal of heavy metals. Retention coefficients up to 99% for zinc (Papers I and II) and cadmium (Paper II) were obtained from their respective single solutions with SDS feed concentration of 16.6 mM. However, as it was concluded in Papers I and II, the effect of SDS feed concentration on the removal efficiency was dependent on the heavy metal concentration, and vice versa.

This dependence between surfactant and heavy metal feed concentrations has been widely described in the literature as the surfactant to metal concentration ratio (S/M) (Liu & Li 2004). Results in Paper I show that when working with single metal solutions, the surfactant to metal ratios (S/M) should be above 5 to have enough available binding sites for an efficient removal of zinc using SDS as the surfactant. This was in concordance with other reports (Huang et al. 1994, Liu & Li 2004). However, the SDS concentration does not need to be too high either, since the positive effect of increasing SDS feed concentration shows certain limits (Paper II). As it can be observed from Figure 17, at low heavy metal concentration, the SDS feed concentration increases less than 5%. At diluted heavy metal feed concentration, when SDS concentration is further increased to concentration up to 16.6 mM, the sodium counter ion concentration might increase to an extent competing with the heavy metals. Consequently, the heavy metal adsorption is no longer enhanced, achieving a plateau in retention coefficients. The same explanation has been before reported by other authors (Chhatre & Marathe 2006, Fang et al. 2008, Ghosh & Bhattacharya 2006, Kamble & Marathe 2005). Consequently, in order to find the maximum retention in the process optimisation, it is essential to find the optimum S/M. The optimal S/M ratios obtained in the concentration range studied for the removal of zinc and cadmium are 27.8 and 28.4, respectively (Paper II). The optimal S/M ratios obtained are very similar and are comparable to the results reported by Yurlova et al. (2002), who observed a maximum retention of nickel when the S/M ratio was 21.
Simultaneous removal of heavy metals from phosphorous-rich synthetic waters

In Paper III, the applicability of MEUF to simultaneously remove heavy metals from phosphorous-rich synthetic waters was studied using regenerated cellulose membrane of 10 kDa and maintaining the pressure at 3 bar. In the absence of phosphate electrolytes, cadmium, copper, zinc and nickel were successfully removed. The achieved rejection coefficients were around 98% for all four heavy metals studied using SDS feed concentration of 20 mM. However, results in Paper III showed that in the presence of phosphate the removal efficiency of MEUF decreases achieving lower rejection coefficients of heavy metals.
Figure 18 shows the significant interaction effect between SDS feed concentration and phosphorous feed concentration on the rejection coefficients of cadmium and copper. As it can be observed from Figure 18, the effect of the SDS feed concentration is smaller in the presence of phosphorous electrolyte (added as NaH$_2$PO$_4$) than in the case where no electrolyte is present. This is in agreement with previous studies, where the effect of sodium chloride concentration (NaCl) was shown to decrease rejection coefficients of heavy metals (Chhatre & Marathe 2006, Danis & Aydiner 2009, Scamehorn et al. 1994, Xu et al. 2007). In the presence of electrolytes, the counter ion surrounding the anionic micelles increases and the electrical double layer and the surface charge density of the micelles decreases. As a consequence, the electrostatic interaction of the free heavy metals and the micelles decreases and less heavy metals will be trapped by the micelles achieving lower rejection coefficients (Xiarchos et al. 2008).

The presence of electrolytes decreases the CMC of ionic surfactants and consequently less surfactant concentration is required to create micelles. However, as it was concluded in Paper III, the competition that the counter ions create towards the heavy metals overcomes the positive effect of decreasing the CMC value. This also explains the very low rejection coefficients reported in Paper III at the 3.5 mM of SDS in the presence of phosphorous, even though there is micelle formation (Figure 18).
Fig. 18. Interaction plot displaying the predicted change in the rejection coefficients of a) cadmium and b) copper when the SDS feed concentration is varied and the phosphorous feed concentration is set at its low ($C_{\text{Phosph.}} = 0 \text{ g/dm}^3$) and high levels ($C_{\text{Phosph.}} = 1.3 \text{ g/dm}^3$), all other factors are set at their centre points (Paper III © Elsevier).

Simultaneous removal of heavy metals from phosphorous-rich real wastewaters

In Papers IV and V the simultaneous removal of heavy metals from P-rich real wastewaters was studied. As reported in Papers IV and V, the process efficiency of MEUF decreased substantially in real wastewaters and relatively high concentration of SDS (> 60 mM) was needed in order to achieve rejection coefficients up to 80% for cadmium, zinc and nickel and 70% for copper. The real wastewaters contained relatively high concentrations of metals such as calcium and magnesium among others that compete with the heavy metal cations to balance the charge of the micelles, and consequently, decreasing the retention of
heavy metals. Similar behavior has been previously reported (Danis & Aydiner 2009, Xiarchos et al. 2008). Further, taking into account the wide range of SDS feed concentration studied, the increase in the rejection coefficients for the heavy metals was relatively small (around 10%) (Fig. 19). As was concluded in Paper IV the small increase in the rejection coefficients with the SDS feed concentration might be due to a change of micellar shape. Previous studies reported that the number of efficient binding sites of a micelle does not increase with the increase in SDS feed concentration due to the changes in shape and the aggregation number of the micelles (Samper et al. 2009, Xu et al. 2007).

![Fig. 19. Predicted rejection coefficients for the removal of a) cadmium and b) copper, spanned by the SDS feed concentration and pH. The membrane used was 10 kDa regenerated cellulose and the pressure was 3 bar (Paper IV © Elsevier).](image)

### 6.1.3 Effect of pH

The effect of pH from phosphorous-rich synthetic and real waters was studied in Papers III and IV. As was concluded in these studies pH has statistically significant effect on the rejection coefficients of cadmium and copper. Several studies have previously shown a positive effect of pH on the removal efficiency of heavy metals by MEUF (Juang et al. 2003, Xiarchos et al. 2008, Xu et al. 2007). At low pH values the H⁺ concentration increases and the competition between the H⁺ ions and the heavy metal cations to be trapped by the micelles also increases, decreasing the rejection coefficients of heavy metal. The positive effect of pH has been mainly reported in studies conducted with synthetic samples where no substantial complex formation is observed. As has been shown in Papers III and IV, the effect of pH is related to the complex formation and speciation of the heavy metals studied. The complex formation of a metal
depends on different factors such as concentration, ionic strength, and pH. Thus, equilibrium in solution has to be taken into account in order to predict and understand MEUF results (Reiller et al. 1996).

**Phosphorous-rich synthetic wastewater**

In Paper III the effect of pH on the rejection coefficients of cadmium and copper was studied. The results showed that pH had a small but statistically significant effect on the rejection coefficients of copper. Further, results in Paper III showed that there is a significant interaction effect between the phosphorous feed concentration and the pH on the rejection coefficient of copper (Figure 20). As can be observed from Fig. 20, the effect of pH is dependent on the concentration of phosphate electrolyte. As was concluded in Paper III, copper starts forming $\text{Cu}_3(\text{PO}_4)_2$ strongly at very low pH values and the complex formation becomes more substantial above the pH = 4. As the complex formation is enhanced when increasing the pH, the concentration of divalent copper will decrease in solution and, therefore, less copper cations will be retained by the micelles obtaining lower rejection coefficients than cadmium, zinc and nickel.

On the contrary to copper, results in Paper III showed that pH had a small but statistically significant positive effect on the rejection coefficient of cadmium. Cadmium does not create complexes with phosphates and it is found in its divalent cation form over the whole pH range studied. Therefore, the positive effect of pH might be explained by the enhanced adsorption of $\text{H}^+$ ions on the micellar surface at low pH values (Juang et al. 2003, Xiarchos et al. 2008, Xu et al. 2007).
Fig. 20. Interaction plot displaying the predicted change in the rejection coefficients of copper when pH is varied and the phosphorous feed concentration is set at its low ($C_{\text{Phosph.}} = 0$ g/dm$^3$) and high level ($C_{\text{Phosph.}} = 1.3$ g/dm$^3$), other factors were set at their centre points (Paper III © Elsevier).

**Phosphorous-rich real wastewater**

Figure 19 shows the statistically significant negative effect of pH on the removal of cadmium and copper from phosphorous-rich real wastewaters (Paper IV). In the case of copper removal a substantial decrease (20%) in copper rejection coefficients was observed, when increasing the pH from 3.5 to 5. As it can be observed from Figure 21, when increasing the pH, divalent copper cation decreases mainly due to CuF$^+$ and soluble CuSO$_4$ formation. It was concluded that the negative effect of pH on the copper rejection coefficients was due to the decrease in divalent cation concentration and the competition among Cu$^{2+}$ and copper complexes to be trapped by the micelles. In the case of cadmium removal, pH had a statistically significant negative effect on the cadmium rejection coefficients but the effect was substantially smaller than for copper. Cadmium species and their concentrations do not vary significantly within the pH range studied and, consequently, the negative effect of pH on the cadmium rejection coefficient was not very significant (Figure 19).

Besides the copper complex formation, the removal of heavy metals from P-rich real wastewaters by MEUF was concluded to be feasible since the main species in the real wastewaters are the divalent metal cations. Consequently,
rejection coefficients around 80% were achieved for cadmium, zinc and nickel and around 70% for copper. Figure 22 shows the sweet spot plots developed in Paper IV in order to find the area where the rejection coefficients of cadmium and copper were predicted to be higher than 80% and 70%, respectively. As it was concluded in Paper IV, the area where both criteria are met is at very low pH values (maximum pH = 3.5) and starting from SDS feed concentration of 60.0 mM. At higher pH values only the criteria for cadmium is met. This is due to the higher negative effect of pH on the rejection coefficients of copper.

Table 15 summarizes the optimal conditions within the sweet spot area with the predicted rejection coefficients. The observed rejection coefficients were consistent with the predicted values showing the good validity of the empirical models. As the original pH of the real wastewater is around 3.0, it was concluded that no further pH adjustment is needed to achieve an efficient separation of phosphorous from the heavy metals by MEUF. Consequently and in line with Paper IV, experimental work in Paper V was conducted in a semi-pilot scale and without any pH adjustment. The similar rejection coefficients obtained in Paper V ascertains the good performance of MEUF to the successful removal of heavy metals from low pH phosphorous-rich real wastewaters.

Table 15. Predicted and experimentally achieved rejection coefficients of cadmium and copper at the optimal conditions (Paper IV).

<table>
<thead>
<tr>
<th>Factors</th>
<th>( R_{Cd} (%) )</th>
<th>( R_{Cu} (%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS (mM)</td>
<td>Predicted</td>
<td>Achieved</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75.6</td>
<td>3.20</td>
<td>84.8 ± 2.0</td>
</tr>
</tbody>
</table>
Fig. 21. Distribution diagram of a) copper and b) cadmium species as a function of pH at pre-treated real phosphorous-rich wastewater conditions (Paper IV © Elsevier).
6.1.4 Study of heavy metal competition

As has been previously stated increasing the heavy metal feed concentration decreases the removal efficiency of MEUF in terms of achieving lower rejection coefficients. Therefore, as was concluded in Papers I and II, MEUF is more efficient for diluted heavy metal solutions. However, as has been shown in Section 6.1.2 the presence of other metals such as calcium and magnesium compete with the heavy metal cations to balance the charge of the micelles, and consequently, decreases the retention of heavy metals. In addition, it is very important to evaluate the heavy metal competition among each other. Table 7 summarizes the publications found in the literature regarding the use of MEUF in multicomponent systems and heavy metal competition.

Huang et al. (1994) studied the metal competition of Pb, Cu, Ni, Zn and Cd in heavy metal mixture solutions and at total heavy metals concentration of 6.0 mM using SDS as the anionic surfactant. They observed different rejection coefficients until S/M ratio of 2 and concluded that the affinity for heavy metal ions is Pb > Cu > Ni > Zn > Cd. However, at higher S/M ratio all five metals were removed similarly.
This section summarizes the results regarding the competition between cadmium, copper, zinc and nickel studied in synthetic and real wastewaters.

**Phosphorous-rich synthetic samples**

The simultaneous removal of heavy metals from phosphorous containing synthetic samples was studied in Paper III. The heavy metal competition was evaluated first, by studying the effect of zinc and nickel feed concentration on the rejection coefficients of cadmium and copper (the concentrations of these two last metals were maintained constant at 0.5 ppm).

As was established in Paper III the concentration of zinc and nickel did not have a statistically significant effect on the rejection coefficient of cadmium and copper. Increasing the zinc and nickel feed concentrations from their low levels to the high levels did not affect the rejection coefficients of cadmium and copper. As was concluded in Paper III, the total heavy metal concentration studied was low and the concentrations of zinc and nickel were not high enough to decrease the surface charge density of the micelles significantly. Consequently, the competition between heavy metals was concluded to be negligible in Paper III.

In order to ascertain the negligible heavy metal competition two extra experiments were conducted at SDS and phosphorous feed concentrations of 11.75 mM and 0.65 g/dm$^3$, respectively, without adding zinc and nickel and at the pH value of 4.25. The purpose was to observe if the rejection coefficients of copper and cadmium varied significantly due to the absence of zinc and nickel. The rejection coefficients achieved were $90.0 \pm 0.26\%$ for cadmium and $85.0 \pm 1.6\%$ for copper. These results are very similar to the rejection coefficients obtained at identical conditions in the presence of zinc and nickel ($R_{\text{Cd}} = 89.94 \pm 1.70\%, \ R_{\text{Cu}} = 85.81 \pm 1.38\%$), showing the negligible effect of zinc and nickel presence in the system.

**Phosphorous-rich real samples**

As was concluded in Paper IV, heavy metal competition was significant in the real wastewaters studied. The phosphorous real wastewaters contained relatively high concentrations of other metals such as magnesium, calcium, aluminium, and iron among others that compete with the heavy metal cations to balance the charge of the micelles. As has been explained in Section 3.3.1, in the presence of electrolytes the electrical double layer becomes thinner (Rosen 1978).
Consequently, there will be less available sites for the metals to be trapped by the micelles and the competition between divalent metals to be trapped on the micelles is enhanced in the real wastewaters. Table 16 shows the rejection coefficients of all four heavy metals obtained in Paper IV at low pH values. The comparison of the rejection coefficients at low pH value ensures that complex formation is negligible and that the difference in rejection coefficients is due to the metal competition. Results obtained in Paper IV show that among all four heavy metals studied, copper was the least rejected heavy metal. Zinc, nickel and cadmium showed more affinity than copper towards the SDS micelles. In Paper V the same behavior was observed where rejection coefficients of copper were smaller than that of cadmium Figure 23.

<table>
<thead>
<tr>
<th>Factor</th>
<th>pH</th>
<th>Responses</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSDS</td>
<td></td>
<td>RCd (%)</td>
</tr>
<tr>
<td>40</td>
<td>3.5</td>
<td>71.5</td>
</tr>
<tr>
<td>60</td>
<td>3.2</td>
<td>79.8</td>
</tr>
<tr>
<td>80</td>
<td>3.5</td>
<td>84.8</td>
</tr>
</tbody>
</table>

Table 16. Rejection coefficients of all heavy metals studied in the real wastewaters (Paper IV).

Fig. 23. Effect of SDS concentration on the rejection coefficients of cadmium and copper at the centre point conditions (v = 0.24 m/s and TMP = 3 bar) (Paper V © Elsevier).
6.2 Effect of factors on the permeate flux

In membrane processes such as ultrafiltration, the permeate flux is often significantly reduced due to the concentration polarization and/or fouling. In this way, monitoring the permeate flux and understanding the fouling phenomena is crucial for conducting a realistic evaluation of the process. In this thesis the response surface plots helped to gain a better understanding of the effect of various factors on permeate flux and the concentration polarization/fouling phenomena.

It is important to mention that after each experiment the membrane permeability was recovered by cleaning the membrane with pure water without the need for chemical cleaning. Therefore, in this study the irreversible fouling has been concluded to be negligible and the permeate flux was limited by the concentration polarization phenomena.

6.2.1 Effect of pressure

In pressure driven membrane processes such as ultrafiltration the driving force for the mass transfer to occur is the pressure applied to the membrane. Therefore, as can be expected, at higher applied pressure the permeate flux will increase. Results reported in Papers I, II and V show that pressure had a statistically significant effect on the permeate flux. However, as it has been shown in this thesis pressure often is not an independent factors and indeed, the effect of pressure on the permeate flux is dependent also on the levels of other factors.

In Paper II, the effect of pressure on the permeate flux was studied in a dead-end UF stirred cell, using three different nominal molecular weight limits (NMWL) regenerated cellulose membranes. As can be observed in Figure 24, with the regenerated cellulose membranes of 5 and 10 kDa a linear increase in permeate flux is observed with the pressure. However, in the case of the 3kDa membrane a slight curvature is observed achieving a plateau when the pressure is around 3 bar due to a more significant concentration polarization phenomenon. Concentration polarization is caused by the accumulation of retained solutes, i.e. micelles, on the membrane surface where their concentration will gradually increase. The micelles retained on the membrane surface generate a deposited layer on the membrane surface increasing the resistance against the solvent transmembrane flux. When concentration polarization is more severe, increasing
the pressure the deposited micelles layer is compressed and the flux-pressure relationship becomes non-linear (Xu et al. 2007).

Previous studies have shown a more severe concentration polarization phenomenon when using bigger pore size membranes (Barredo-Damas et al. 2010, Benítez et al. 2006). At higher NMWL the permeate flux through the membrane is higher and consequently the concentration of the retained solutes will accumulate faster on the membrane surface, enhancing the concentration polarization phenomena (Laorko et al. 2010). On the other hand and in line with the results obtained in Paper II, Hong et al. (1998) reported that the ultrafiltration membrane with 1 kDa pore size exhibited more rapid decrease in relative flux than the 3 kDa pore size membrane. They stated that the comparable size of the micelles to the pore size could enhance its pore blocking and consequently a smaller relative flux (Hong et al. 1998).

Results in Paper I show that with the 10 kDa regenerated cellulose membrane the relative flux value were close to unity, indicating that absolute flux does not significantly differ from the pure water flux. However, it is important to note that besides the lower relative flux values obtained with the 3 kDa membrane, they were close to 0.8. Therefore, the flux decline was only about 20%. In Paper II the flux decline observed was concluded not to be very significant and all membranes show good operational stability.
Fig. 24. Predicted permeate flux values for the removal of cadmium, spanned by the pressure \((P)\) and SDS feed concentration \((C_{SDS})\) for three different levels of NMWL a) 3 kDa, b) 5 kDa and c) 10 kDa. The cadmium feed concentration is 1.75 mM (Paper II © Elsevier).

6.2.2 Effect of SDS feed concentration

It has been previously reported that at higher SDS feed concentration, concentration polarization is enhanced, achieving lower permeate flux (Ghosh & Bhattacharya 2006, Purkait et al. 2004, Xu et al. 2007). This issue was also studied within this thesis using regenerated cellulose membranes (Papers I–IV) and a polyethersulphone membrane (Paper V).

Experiments conducted with regenerated cellulose membranes

Results obtained in Papers I, II and III show that SDS feed concentration did not have a statistically significant effect on the permeate flux in the synthetic samples studied in this thesis. As was shown in Papers I and II, increasing the SDS feed concentration from 8.3 mM to 16 mM did not affect the permeate flux significantly. Further, the same negligible effect on the permeate flux was also observed in Paper III when increasing the SDS feed concentration from 3.5 to 20
mM (Figure 25). It was concluded that the SDS feed concentration studied in synthetic wastewaters was too low to create a significant concentration polarization phenomenon. Scamehorn et al. (1994) reported that as long as the retentate SDS concentration does not exceed the concentration of 200 to 300 mM, the concentration polarization effect is not severe.

The effect of SDS feed concentration with the regenerated cellulose 10 kDa membrane was further studied in Paper IV with real wastewater. In this case, the SDS concentrations studied were higher (31.7–88.3 mM) and as it can be observed from Figure 26, permeate flux decreased when increasing the SDS feed concentration. As was shown in Paper IV, when SDS feed concentration is around 30 mM the membrane resistance is the main resistance and the concentration polarization resistance is very small. However, when SDS feed concentration was increased above 60 mM the concentration polarization resistance started to become more substantial and competitive towards the membrane resistance, obtaining a 50% decrease in permeate flux from the pure water flux.

![Fig. 25. Relative flux obtained at different SDS feed concentrations using 10 kDa regenerated cellulose membrane, pressure of 3 bar, pH = 4.25 and C_{Phosph.} = 0.65 g/dm³ (Paper III © Elsevier).](image)
Membrane material and its interaction with SDS surfactants also play an important role in the flux decline. It has been previously reported that surfactant adsorption on the membrane surface is less enhanced in hydrophilic membranes, such as regenerated cellulose membranes than in more hydrophobic membranes such as polyethersulphone membranes (Majewska-Nowak et al. 2005).

The effect of SDS feed concentration on the permeate flux using the polyethersulphone membrane was evaluated in Paper V in semi-pilot scale.

**Experiments conducted with polyethersulphone membrane**

In Paper V the effect of SDS feed concentration on the permeate flux was studied with the real wastewaters and using a 10 kDa spiral-wound polyethersulfone membrane. On the contrary to the results obtained in Paper IV, results of Paper V show that increasing the SDS feed concentration from 40 to 80 mM did not have a statistically significant effect on the permeate flux. This was due to the very significant concentration polarization phenomena observed even at the lowest SDS feed concentration (relative flux value of 0.5). The concentration range studied (40–80 mM) was insufficient to increase significantly the already significant resistance of the concentration polarization layer. As a consequence, at the SDS range studied, the permeate flux did not vary significantly and, the relative flux achieved a stable value of 50%. Other authors have also reported that the permeate flux achieved a stable value after certain SDS feed concentration.
Xu et al. (2007) observed that the permeate flux stabilizes after 33 mM of SDS feed concentration.

The low relative flux obtained in the cross-flow semi-pilot scale was surprisingly worse than the relative flux obtained in the dead-end concentration mode (Paper IV). This might be partially due to the membrane material as explained by Majewska-Nowak et al. (2005). Polyethersulfone membranes are more hydrophobic than regenerated cellulose membranes and the micelle-membrane interaction might be stronger with the polyethersulfone membrane.

6.2.3 Effect of cross-flow velocity

In Paper V it was shown that cross-flow velocity has a statistically significant positive effect on the permeate flux. As can be observed in Figure 27, the permeate flux was enhanced at the cross-flow velocity range of 0.13 m/s–0.24 m/s. At higher cross-flow velocities the fluid turbulence is higher and the mixing of the solution is improved. Consequently, the concentration polarization phenomenon is decreased (Barredo-Damas et al. 2010, Llanos et al. 2009, Lobo et al. 2006, Macedo et al. 2011, Sarkar et al. 2009). As the concentration polarization phenomenon decreases the total resistance towards the solvent flow will be smaller and, consequently, a higher permeate flux will be achieved. Further, in agreement with other reports, a plateau in the permeate flux was achieved at cross-flow velocities higher than 0.24 m/s (He et al. 2007, Lobo et al. 2006) showing that the concentration polarization phenomena is not further improved.

Further, it was shown that the effect of cross-flow velocity is dependent on the level of transmembrane pressure. As can be observed in Figure 27 cross-flow velocity significantly affects the permeate flux at high transmembrane pressure. However, the effect of cross-flow velocity is much more moderated at low transmembrane pressures. At high transmembrane pressure the concentration polarization layer is compressed and the total resistance towards the permeate flow increases. Therefore, increasing the cross-flow velocity enhances the fluid turbulence promoting less concentration polarization and consequently achieving a more significant increase in permeate flux. However, the influence of cross-flow velocity is less significant at low transmembrane pressures because in these conditions concentration polarization layer is less severe. Llanos et al. (2009) observed the same behavior. It is important to mention that the concentration polarization phenomenon was significant in all the experiments conducted with
the polyethersulphone membrane in the cross-flow semi-pilot scale. At low cross-flow velocities and high pressures the relative flux was noticeable low (0.3). However, increasing the cross-flow velocity did not significantly improve the flux behavior, obtaining relative flux values around 0.5.

Fig. 27. Predicted permeate flux spanned by the cross flow velocity and transmembrane pressures in the semipilot scale study with real wastewaters.

6.3 Critical evaluation of micellar-enhanced ultrafiltration

As has been shown in this thesis, micellar-enhanced ultrafiltration can be successfully applied for the simultaneous removal of heavy metals from wastewaters. The advantages of this method are the low-energy requirements involved in the UF processes and the high removal efficiency owing to the effective trapping of metals by the micelles, even at diluted heavy metal concentration. The removal efficiency of MEUF towards the heavy metals can achieve values up to 99%. Furthermore, as has been shown in this thesis, due to the high selectivity of the anionic surfactants towards the metals, MEUF has been proven to be a viable technique for separating phosphorous compounds from heavy metals since they were not retained by the micelles and passed through the ultrafiltration membrane. Therefore, MEUF can be used for novel applications.
such as the purification of nutrients from wastewater streams prior to their recovery. However, certain challenges of the process and possible solutions to overcome the existing problems remain and will be further discussed in this section.

6.3.1 SDS leakage to the permeate

In MEUF, the surfactant monomers that do not aggregate and do not form micelles will go through the ultrafiltration membrane to the permeate side. Therefore, one of the main disadvantages of micellar-enhanced ultrafiltration well known and formulated by the research community is the surfactant leakage to the permeate site. The surfactant constitutes a large portion of the operating cost and surfactant leakage increases the process cost. Further, surfactant leakage to the permeate side can also create secondary pollution due to its toxicity towards living organisms. The amphoteric character of ionic surfactants enables their accumulation in living organisms. In the case of anionic surfactants, the negatively charged head groups (for example sulphates) can bind to the positively charged molecular structures by electrostatic forces. Further, the hydrophobic tail may interact with apolar parts of the target organisms by hydrophobic forces. Due to these interactions bacteria, aquatic plants, invertebrates and vertebrates can show toxic symptoms. In human beings anionic surfactants mainly cause eye and skin irritation (Cserháti et al. 2002).

In order to address this issue and as was mentioned in Section 3.3.2, different papers have been published to encourage the use of surfactants produced by microorganisms (biosurfactants), which are more biodegradable and less toxic than the synthetic surfactants (Banat 1995, El Zeftawy & Mulligan 2011). Biosurfactants such as rhamnolipids and sodium deoxycholate have been successfully applied in the removal of heavy metals from wastewaters (El Zeftawy & Mulligan 2011, Huang et al. 1994). However, biosurfactants still remain more expensive than synthetic surfactants and much more work has to be carried out in various aspects of biosurfactant production to make them economically competitive with synthetic surfactants (Dubey & Juwarkar 2001).

It is well known that the surfactant concentration in the permeate achieves a maximum value around the CMC value (Gecol et al. 2004). Therefore, reducing the CMC value of the surfactant can also be used as a tool for reducing secondary pollution. For this purpose, previous studies have evaluated the possibility of using ionic-nonionic surfactant mixtures (Huang et al. 2009, Lee et al. 2005).
When a nonionic surfactant is inserted into the ionic surfactant solution, the hydrophilic parts of nonionic surfactants counterbalance the charge of ionic hydrophilic groups. The decrease in charge density at the surface of the micelle leads to diminish the electrical potential. As a result, the lowered electrical potential will stimulate the formation of micelles with lower CMC due to the reduction of electrical repulsion (Lee et al. 2005). However, it has been previously reported that, as the nonionic surfactant mole fraction in the micelle increases, the surface charge density of the mixed micelle is also reduced decreasing the separation efficiency of the MEUF process per ionic molecule in micellar form that is used (Fang et al. 2008, Fillipi et al. 1999).

In this thesis, the degree of SDS leakage from phosphorus rich wastewaters was evaluated by determining the SDS concentration in the permeate side using a TOC analyzer. Results obtained in Paper III showed that the permeate SDS concentration was reduced when phosphorous electrolytes were added into the system studied. This is understandable since in the presence of electrolytes the counter ion concentration around the micelles increases, decreasing the mutual repulsion of the ionic heads of the micelles (Rosen 1978, Tung et al. 2002, Umlong & Ismail 2007). The work required for the micelle formation is smaller (CMC decreases) and the free monomer surfactant concentration will decrease, reducing the SDS leakage to the permeate side.

To ascertain this issue the SDS leakage was further studied in Papers IV and V, where the simultaneous removal of heavy metals from phosphorus rich real wastewater was studied. As concluded in Papers IV and V, SDS rejection coefficients obtained were above 99%, obtaining negligible concentration of SDS in the permeate (<1 mM). Consequently the SDS leakage seems not to be a limiting factor for the novel use of MEUF to purify nutrient rich wastewater streams.

### 6.3.2 SDS precipitation

An important disadvantage of using ionic surfactants, which can inhibit their use in many applications, is their tendency to precipitate from aqueous solutions. As an example, surfactants such as SDS that are used in detergents tend to precipitate in hard water and they are no longer available in the cleaning process (Rodriguez et al. 2001). The tendency of an anionic surfactant to precipitate can be quantified as a hardness or salinity tolerance i.e. the minimum concentration of cation,
which is required to form precipitate with the surfactant (Stellner & Scamehorn 1989).

As is shown in Papers IV and V, when adding the anionic surfactant to the phosphorous-rich real wastewater, precipitation of SDS was observed. This was due to the relatively high concentrations of cations such as calcium and magnesium present in the real wastewater that exceed the salinity tolerance of the SDS. Consequently, pretreatment of the real wastewater to reduce the cation content was needed prior to the micellar-enhanced ultrafiltration process as explained in Section 5.1.2. The main objective was to alter as little as possible the wastewater composition. Consequently, SDS which shows high selectivity towards calcium, was chosen as the precipitant compound. However, at the moment the use of the surfactant as the precipitant will not be feasible in large scale due to the prohibitive cost of SDS. Therefore, before MEUF can be applied for separating heavy metals from phosphorous a more economic way of pre-treatment is needed to be found.

6.3.3 SDS cost reduction

Anionic surfactants have relatively high CMC value when compared to cationic or non-ionic surfactants. Therefore, relatively high concentration of surfactant is needed in order to achieve an efficient removal of heavy metals by MEUF. Consequently, surfactants constitute a large portion of the operating cost of the process. In order to make the process more economic and to improve resource efficiency surfactants should be recovered for their further reuse. The retentate, which contains concentrated amount of SDS and heavy metals could be the source for surfactant recovery. In addition, recovery of compounds from the retentate also deals with the challenge of what to do with the concentrate, which is a common disadvantage of membrane processes.

The surfactant recovery was studied in Paper II from the retentate sample solution containing 23 mM of SDS. The recovery of the surfactant was performed in two different steps. First, 98% of the dodecyl sulphate was precipitated as calcium dodecyl sulfate by adding 115mM CaCl$_2$ (ten times the stoichiometric amount) to the retentate sample according to the following reaction,

\[
2C_{12}H_{25}SO_4(aq) + Zn^{2+}(aq) + Ca^{2+}(aq) + 2Cl^-(aq) \rightarrow Ca(C_{12}H_{25}SO_4)_2(s) + Zn^{2+}(aq) + 2Cl^-(aq).
\]  

(1)
However, calcium dodecyl sulfate is not soluble in water, and it cannot be directly recycled into the MEUF system. Therefore, the precipitated calcium dodecyl sulfate was further treated by adding 22.5 mM Na$_2$CO$_3$ solution (stoichiometric amount). 86% of the dodecyl sulphate was redissolved as SDS with the following reaction,

\[ \text{Ca(C}_{12}\text{H}_{25}\text{SO}_4)_2 \ (s) + 2\text{Na}^+ (aq) + \text{CO}_3^{2-} (aq) \leftrightarrow 2\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}^+ (aq) + \text{CaCO}_3 \ (s) \ (2) \]

Brant et al. (1989) also reported achieving high recovery rates of the surfactant with the same method used in this thesis.

Juang et al. (2003) studied the recovery of SDS by adding 7 N of NaOH to the retentate. The main purpose of the study was to precipitate the heavy metals trapped on the micelles and reuse the SDS remaining in the solution. However, the SDS recovery rate was not very high (45–55%) and the removal efficiency of the SDS recovered dropped substantially, achieving maximum rejection coefficient of 57% for zinc. Li et al. (2009) studied the recovery of SDS by adding a chelating agent or sulphuric acid to the retentate, followed by the UF process. They reported a SDS recovery of 73% using EDTA as the chelating agent. Further, the recovered SDS was shown to maintain its removal efficiency obtaining rejection coefficients up to 90.0% for cadmium and zinc. In the case of acidification followed by ultrafiltration, they reported SDS recovery rates up to 58% using sulphuric acid (1 M) and at pH = 1. Recovered SDS also showed good removal efficiency achieving rejection coefficients of 88.0% for zinc and cadmium, respectively (Li et al. 2009). In addition, Liu et al. (2004) proposed a hybrid process based on MEUF and electrolysis to simultaneously recover SDS and copper from the retentate. While MEUF is used to retain the metal, the electrolysis liberates the metal ions from the micelles by electroplating them onto a cathode electrode. Liu et al. (2004) reported recovery rates of 93% and 96% for copper and SDS, respectively.
7 Summary and Conclusions

Wastewater can be a potential resource of phosphorous, which is a valuable compound for the fertilizer industry. However, these wastewaters often contain heavy metals that constrain, even at diluted concentrations, the recovery and further utilization of the nutrient. Consequently, heavy metals must be separated from the phosphorous-rich wastewaters. In this study micellar-enhanced ultrafiltration (MEUF) was applied and evaluated as a potential technique for the simultaneous removal of heavy metals from phosphorous-rich wastewaters. The purification of wastewaters follows the principles of clean technologies since it enables the segregation of valuable compounds and allows their recovery and further utilization improving resource efficiency. Consequently, the purpose of this study was moving beyond the end-of-pipe approach and viewing wastewaters as a resource of valuable compounds instead of a source of pollutants.

The applicability and evaluation of MEUF for the removal of diluted heavy metals from wastewaters has been conducted following a systematic methodology, starting from single heavy metals solutions (Papers I and II) to phosphorous containing complex synthetic solutions (Paper III) and, ultimately, real wastewater solutions (Papers IV and V). Further, statistical design of experiments has been applied as the research methodology in all the papers composing this thesis to gain a better understanding of the systems (effect of factors) and process optimization. With statistical design of experiments, the use of time, raw materials and natural resources is decreased.

This study established MEUF as a viable technique for separating heavy metals from phosphorous compounds. Whilst heavy metals were successfully removed, phosphorous was not retained by the micelles and passed through the ultrafiltration membrane. Further, it was concluded that MEUF is more efficient for diluted heavy metal solutions, overcoming the limitations of other techniques commonly used in industry and recognized by authorities as Best Available Techniques (precipitation and crystallization).

This study also provides new and valuable scientific information regarding the use of MEUF with complex synthetic and real wastewaters. It was shown that understanding the heavy metal complex formation in solution is very important in order to predict the MEUF results. The heavy metal removal efficiency of MEUF decreased in the presence of phosphorous electrolytes. It was concluded that the presence of phosphates affected the rejection coefficients of copper more negatively due to complex formation, which was also enhanced at higher pH.
levels. At low pH values and in the presence of phosphorous the heavy metals were present as divalent cations and no complex formation was observed. Consequently, maximum rejection coefficients of heavy metals were achieved at low pH values. Considering that the pH of the real wastewater studied in this thesis is around 3.0, it was concluded that no further pH adjustment is needed to achieve an efficient separation of phosphorous from the heavy metals by MEUF.

It was concluded that, in the studied synthetic waters heavy metal competition is not significant because the total metal concentration is not high enough to decrease the surface charge density of the micelles significantly. However, in real wastewaters, the competition among the heavy metals increased due to the presence of other electrolytes such as calcium and magnesium. Zinc, nickel and cadmium showed more affinity than copper towards the SDS micelles.

Further, it was demonstrated that a relatively high concentration of SDS was needed ($C_{SDS} > 60 \text{ mM}$) in order to achieve satisfactory rejection coefficients with real wastewaters. As surfactants constitute a large portion of the operating cost of the process, in order to make the process more economical and to improve resource efficiency, surfactants should be recovered for their further utilization. This thesis showed that the recovery of SDS from the retentate is feasible, leading the process towards a more sustainable and cleaner process that enables the recovery of compounds as raw materials.

Apart from the removal efficiency of MEUF towards the heavy metals, the process performance has also been evaluated in terms of permeate flux. In the studied synthetic waters, the regenerated cellulose membranes show good performance and the concentration polarization phenomenon was concluded to be insignificant. On the contrary to results obtained in synthetic waters, concentration polarization phenomenon was more severe when applying MEUF to real wastewater in laboratory scale stirred cell equipment. In this way, it was observed that the flux declined when increasing the SDS feed concentration using the 10 kDa regenerated cellulose membrane and at pressure of 3 bar.

The evaluation of the permeate flux was further extended using a polyethersulphone 10 kDa membrane in a cross-flow semi-pilot scale. The concentration polarization phenomenon was shown to be more severe in this study even though it was conducted in a cross-flow equipment. At a low cross-flow velocity and high pressure the relative flux was noticeable low (0.3). Further, increasing the cross-flow velocity did not significantly improve the flux behavior obtaining relative flux values around 0.5. It was concluded that the more
hydrophobic character of polyethersulphone might have partially affected the more severe flux decline.

Further to the concentration polarization phenomenon it is important to mention that irreversible fouling was concluded to be insignificant within the whole study. Consequently, membrane permeability was recovered by cleaning the membrane with pure water without the need for chemical cleaning.

One of the main concerns formulated by the research community regarding the use of MEUF is the SDS leakage to the permeate that can create secondary pollution and increase the total process cost. The effort from the research community has been to give alternatives for reducing the impacts of SDS leakage to the permeate. However, research has focused mainly on synthetic wastewaters, which limits a more realistic evaluation of the MEUF performance. In this study, the evaluation of MEUF for the purification of real wastewater has contributed new knowledge regarding this issue. It was concluded that the SDS leakage is relatively insignificant when MEUF is performed on real wastewaters. Consequently, the environmental and economic aspects and the potential applicability of MEUF are significantly improved.

One of the key challenges observed when applying MEUF to real wastewaters has been the precipitation of the surfactant due to the calcium content of the wastewaters. Therefore, precipitation of calcium with the SDS anionic surfactant was used as the pre-treatment method. This method will not be feasible on a larger scale, due to the current prohibitive cost of the SDS pre-treatment. Therefore, before this technology is feasible on an industrial scale, further research is required to find a proper pre-treatment process.

Overall, this study has shown that MEUF is a feasible technology for the simultaneous removal of heavy metals, allowing its potential application for the purification of wastewaters containing valuable compounds. However, MEUF is not yet a completely mature technology for industrial implementation, and further research is needed prior to its application in industry. Furthermore, while research conducted with synthetic wastewater samples is extensive, research with real wastewater applications is very scarce. Therefore, in order to fully evaluate MEUF process feasibility, considerably more weight should be put on research efforts on real wastewater applications. In addition, surfactant cost is one of the main limitations for industrial application. Therefore, research should also focus on finding more ecological and cost-effective surfactant alternatives. For example, the evaluation of large-scale by-products streams as surfactants should
be encouraged, in order to improve the feasibility of MEUF and resource efficiency in industry.
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Original papers


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FROM END-OF-PIPE TO CLEAN TECHNOLOGY