

Porous polymer membranes used for wastewater treatment

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Abstract. This paper focuses on the study of the most recent ultra-filtration techniques, based on porous polymer membranes, used for the treatment of wastewater from oil, mine and hydrometallurgical industries. The performance of porous membranes used in separation and recovery of oil and heavy metals from wastewater, was evaluated by the polymer composition and by the membrane characteristics, as it follows: hydrophobicity or hydrophilicity, porosity, carrier (composition and concentration), selectivity, fouling, durability, separation efficiency and operating conditions. The oil/water efficient separation was observed on ultra-filtration (UF) techniques, with porous membranes, whereas heavy metals recovery from wastewater was observed using porous membranes with carrier. It can be concluded, that in the ultra-filtration wastewater treatments, a hybrid system, with porous polymer membranes with or without carrier, can be used for these two applications: oil/water separation and heavy metals recovery.

Keywords: ultra-filtration; membranes; polymers; separations; wastewater treatment

1. Introduction

In Canada, the process of producing bitumen from oil sands can use mining or in-situ methods. In mining, the surface layer of oil sand is excavated using a giant shovel and transported on a giant truck, then stirred with the addition of hot water (steam) to recover the bitumen. The wastewater, which includes sand, heavy metals, bitumen residue, and added water, is stored in tailing ponds. Hot water, in the form of steam, is produced by turbines. The water is drained from the river and undergoes general water treatment. It is then heated by the boiler and sent to the generator. The amount of water used is thought to be from two to four times higher than the amount of produced oil. More than 70% of the water is recycled and used for bitumen recovery. The quantity of wastewater requiring treatment reaches thousands of tones every hour. A wastewater treatment technology, able to purify the wastewater to a sufficient level for the water to return into the river, has not been reached yet.

There are three issues associated with water treatment such as: water supply, water quality and regulatory issues in Canada. Currently, available water sources for heavy oil/bitumen processing are *fresh water* (surface and ground water with low total dissolved solids (TDS) content), *produced water* (water produced with oil from steam injection) and *saline or brackish water* (deep

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groundwater with TDS content exceeding 4000 mg/L). Currently, Canadian heavy oil/bitumen thermal (in-situ) processes mainly use groundwater as the fresh water supply. After the start up, produced water has been used as a primary water source for generating steam for cyclic steam stimulation (CSS) and steam assisted gravity drainage (SAGD) operations by recycling and treating produced water. Treatment technologies for removal of high concentration of oil, silica, hardness, and total dissolved/suspended solids (TDS/TSS) for boiler feed water (BFW) are current challenges. Recent progress in technology has enabled the use of some saline or brackish groundwater in steam generation processes. This water is not widely used in heavy oil/bitumen processes due to its corrosiveness and high TDS. Current challenges using brackish water are: the water quantity and quality of water, assessment of these water zones and deliverability.

Table 1 show typical water qualities for each water source for the heavy oil operation at the CNRL's (Canadian Natural Resource Limited) Wolf Lake Plant (CNRL presentation 2006). There is a general deterioration in water quality (especially when considering BFW specifications) from fresh water to produced water to aquifer (brackish) water. Specifically, the highest concentrations of dissolved solids (as indicated by the specific conductance) as well as the Oil and Grease number in the produced water are also presented in Table 1.

Conventional 100% steam boilers have emerged and are used in SAGD applications since they generate 100% of the steam's quality and once-through steam generators systems (OTSGs) vaporize only 80% of the steam. BFW specifications for OTSGs and 100% conventional boilers are given in Table 2. The challenge in using steam for heavy oil processes is the high quality of water (relative to source) that is required for boilers.

Regulatory issues are specific to the region. In Alberta, regulations set as a target so that 95% of the injected water is recycled and 0% of the produced water is discharged. This has been a challenge for the process operation. Defining water recycle has been a challenge. For example,

Table 1 Typical water quality at CNRL Wolf Lake Plant (CNRL presentation 2006)

Water quality parameters	Fresh water	Produced water	Brackish water
pH	7.72	7.92	7.53
Specific conductance at 25°C (umhos)	1008.2	9268.75	12550
P alkalinity (CaCO ₃ ppm)	0.55	0.71	< 1
M alkalinity (CaCO ₃ ppm)	491.4	544.19	1125
Total sulphur (SO ₄ ppm)	77.9	129.9	0.5
Chloride (Cl ppm)	5.97	2920.2	4337.5
Total hardness (CaCO ₃ ppm)	344.3	99.56	191.3
Total iron (Fe ppm)	2.94	0.33	5.41
Sodium (Na ppm)	105.8	2041.2	2850
Lithium (Li ppm)	0.06	5.41	0.81
Total silica (SiO ₂ ppm)	26.61	274.0	9.4
Total organic carbon (C ppm)	8.6	137	1
Oil and grease (ppm)	0.43	6.75	1
Total suspended solids (TSS ppm)	7.11	28	4.67
Total dissolved solids (TDS ppm)	606	4905	8275

Table 2 Boiler feed water specifications for OTSGs and conventional boilers

Parameters	OTSG boiler specification	Conventional boiler with 100% steam specification
Total hardness	< 1 mg/L CaCO ₃ (0.5 mg/L recommended)	< 0.5 mg/L
Conductivity	not reported	< 0.3 μ s/L
Copper	not reported	< 0.005 mg/L
Barium	< 0.1 mg/L	not reported
Iron	< 0.25 mg/L	< 0.02 mg/L
Free chlorine	< 0.1 mg/L	not reported
Oxygen	< 0.02 mg/L	< 0.02 mg/L
pH	7.0-9.5	9.0-9.5
Silica	< 100 mg/L	< 20 μ g/L
TDS	< 12,000 mg/L (600 mg/L recommended)	not reported
Oil	< 0.5 mg/L	< 0.3 mg/L

during SAGD project life, retention of injected water (as steam) in the reservoir is typically about 5% but it can temporarily exceed 10%.

The water treatment technologies, currently utilized for BFW to generate steam in heavy oil processes, are commonly integrated processes with multi-step-technologies, due to the diversity of contaminants in the water sources available to heavy oil producers (CAPP 2008). Typically the treatment methodologies used are: the removal and the decrease of the content of TPH (total petroleum hydrocarbons), TDS, hardness, and silica compounds, so that the required specifications for BFW should be met. The main treatment objectives and newly emerging and already established treatment techniques for oilfield produced water are summarized by Hayes and Arthur (2004). These are *deoiling*, representing the removal of free and dispersed oil (ultra-filtration is one of the treatment techniques under this category) with *membrane processes*, lime softening process, ion exchange softening, evaporation technique, micro-bubble flotation, soluble organics and demineralization.

Since the focus area of this paper is a membrane process, the details of this technique will be given in the following paragraphs. This process is used as a post treatment process, for treating produced water, after the initial treatment. The common membranes are polymeric material, such as cellulose triacetate, polyamides, and/or polysulfones. The membrane processes emerged as a new process for treating both heavy oil produced water and brackish water. The selection factors for using membranes include the pH stability, working life, mechanical strength, pressurization capacity, selectivity for solution and fouling resistance.

A variety of processes exist to removal and recovers metal ions from wastewater. A lot of methods have been proposed in the literature and many patented processes exist. The most important chemical separation technologies are: chemical precipitation, electrolytic recovery, adsorption/ion exchange, and solvent extraction. Most metal rich wastewaters are treated by precipitation process, where the soluble metal ions are removed as insoluble metal hydroxide precipitates, but it has several disadvantages. An alternative to these technologies are the membrane separations due to the inherent simplicity of the equipment and operation involved, as

well as minimal energy requirements. Reverse osmosis (RO) and nano-filtration (NF) effectively removes dissolved inorganic (e.g., metals, metal-cyanide complexes, and other ionic species) and are the most used in the metal separation.

2. Chemical treatment methods used for removal and recovery of heavy metals from wastewaters

In the heavy metals group are included *toxic elements*, even the term “*heavy metal*” does not have a rigorous scientific basis or a chemical definition. Strictly from a chemical viewpoint, heavy metals constitute transition and post-transition elements along with metalloids, namely arsenic and selenium. These heavy metal elements often exist in different oxidation state in soil, water and air. The list of priority heavy metals pollutants include: Cr, Co, Ni, Cu, Zn, Ag, Cd, Hg, Ti, Pb, As, Se and Sb (SenGupta 2002).

Various chemical treatment methods have been developed for the removal and recovery of heavy metals from wastewaters. There are four major classes of chemical separation technologies: chemical precipitation, electrolytic recovery, adsorption /ion exchange and solvent extraction /liquid membrane separation. These major classes involves various methods such us: chemical treatment with lime, caustic oxidation, and reduction ion-exchange, adsorption, reverse osmosis, solvent extraction, membrane filtration, electrochemical treatment and evaporative recovery. But, most of these are often not economically viable especially when the effluents contain a large concentration of heavy metals. Most metal rich wastewaters are treated by precipitation process where the soluble metal ions are removed and insoluble metal hydroxide precipitates. This process has also several disadvantages. The presence of aqueous organic ligands in wastewater can hinder metal hydroxide precipitation, which may results in residual metal concentration that may no longer meet the increasingly stringent effluent discharge standards. With complex metals the results are not satisfactory. The major disadvantage of these treatment techniques is the production of sludge which represents a solid waste problem (Lewinsky 2007).

In this context the membrane technologies and techniques were developed, are faster more efficient, and more economical than conventional separation techniques.

3. Membrane technologies and techniques used for removal of oil and heavy metals from wastewater

Membrane processes such as micro-filtration (MF), ultra-filtration (UF), nano-filtration (NF) and reverse osmosis (RO) are applied for treating oily and heavy metals wastewater. The forward osmosis (FO) technique has been demonstrated successfully for the treatment of a wide range of oil-water emulsions from a low to a very high concentration up to 200,000 ppm (Duong and Chung 2014). These membrane technologies could be used together to produce water for irrigation, industrial and, maybe, even for potable water (Rawn-Schatzinger *et al.* 2004, 2003).

MF and UF are pressure-driven membrane processes that reject particles as small as 0.1 micrometer and 0.01 respectively (Allen 2008, Baker 2012). NF is a form of filtration that uses a semi-permeable membrane where the pores diameter is close to one nanometer and permits to pass a higher percentage, of monovalent salt ions than divalent and trivalent ions. RO, also known as hyper-filtration, uses a semi-permeable membrane that allows purified fluid to pass through, whereas the remaining contaminants allow the removal of the particles, as small as ions, from a

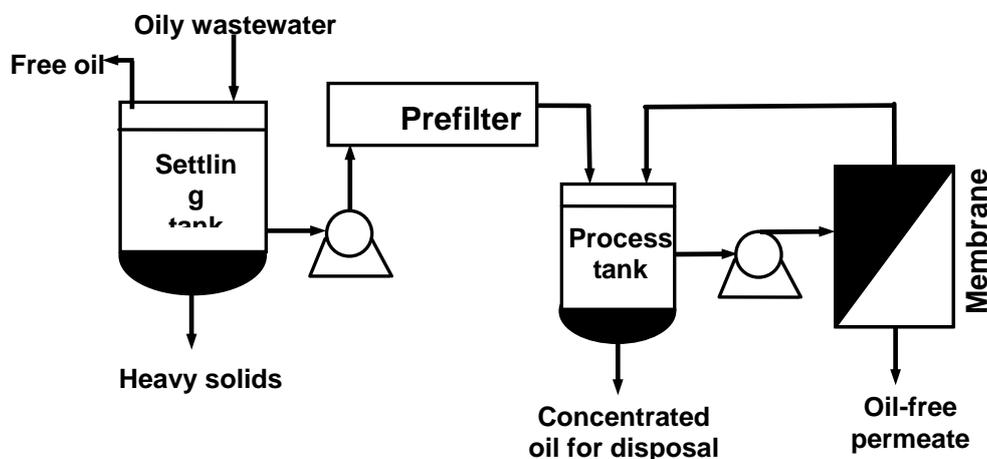


Fig. 1 General schematic of typical membrane system for treatment of oily wastewater

solution.

On worldwide, the application of a two-phase flow in membrane processes has received ample scientific deliberation of its potential to reduce concentration polarization and membrane fouling, and therefore enhance membrane flux. Gas /liquid flow are new used to promote turbulence and instabilities inside membrane modules in various membrane processes such as MF, UF, NF, RO, and membrane bio-reactors.

The most popular and extensively reported application is aeration in submerged membrane bioreactors (MBRs). However, a few recent publications report the application of a two-phase flow in industrial NF/RO, proving the potential of this technology (Wibisono *et al.* 2014).

Produced water (PW), water that is co-produced during oil and gas manufacturing, represents the largest source of oily wastewaters. Given high oil and gas prices, oil and gas production from non-conventional sources such as tar sands, oil shale and coal bed methane will continue to expand resulting in large quantities of impaired produced water. Treatment of this produced water could improve the economic viability of these oil and gas to a new source of water for beneficial use (Mondal and Wickramasinghe 2008).

In oil industry, the technologies described above are used for treating wastewater containing dispersed oil and suspended particles, after a pretreatment of streams, but the membrane fouling is a problem (Peng and Tremblay 2008). This can be reduced with the technological advances in membrane surface chemistry modifications, such as chemical additives, aeration and ultrasounds. Membranes are most useful with stable emulsions, particularly water-soluble oily wastes. Unstable oil/water emulsions can be mechanically or chemically broken and then separated through gravity. A general schematic of typical membrane system for treatment of oily wastewater is presented in Fig. 1 (Cheryan and Rajagopalan 1998).

The use of membrane filtration processes such as MF, UF, NF and RO offer a lot of advantages for the treatment of produced waters like:

- The technology is more widely applicable across a range of industries (e.g., off shore and shore oil exploration);
- Membranes can be used in process to allow recycling of selected waste streams;

- The membrane is a positive barrier to rejected components;
- No addition of chemicals is required;
- Membrane equipment has a smaller footprint, energy costs are often lower and the plant can be highly automated (Mondal and Wickramasinghe 2008).

In mine and hydrometallurgical industries, the most used technique for recovery of heavy metals is the active transport (carrier facilitated transport). This active transport through porous membranes, involves supported liquid membranes, containing a porous support, in which the carrier (liquid phase) is immobilized by the capillary forces (Baker 2004). In *carrier facilitated transport* through membranes the *active transport* occurs at the membrane interphase, and depends by the type of reaction between the carrier and permeates. The transport of a component by a carrier is mostly coupled and can be either *co-coupled* or *counter coupled*. In co-coupled transport processes, both components move in the same direction, whereas in counter-coupled transport processes the components move in opposite direction. A schematic presentation of the active transport by a cation across the membrane is presented in Fig. 2: by co-transport (Fig. 2(a)) and by counter-transport (Fig. 2(b)), $[M^+]$ – cation; $[C]$ – carrier; $[X^-]$, $[X^+]$ – aqueous soluble coupled-transport ions; $[HEM]$ –hemoglobin (Baker 2012, Fu and Wang 2011, Araki and Tsukube 1990).

The most important problem of membranes separation processes through carrier facilitated transport is the membrane stability expressed by the variation in coupled transport flux during long term-tests. The detailed mechanism for this flux instability is not very well known but is

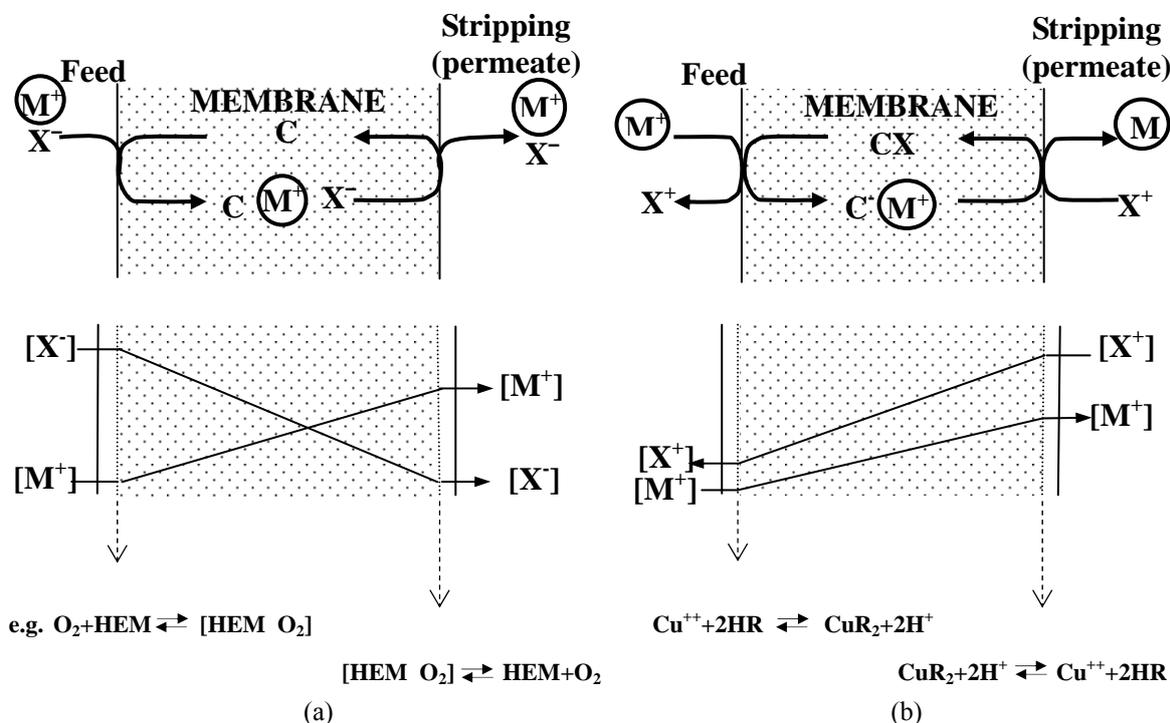


Fig. 2 Schematic presentation of carrier facilitated transport (active transport) by (a) facilitated transport and (b) coupled transport

appears to be related to loss of the organic complexing agent phase from the support membrane. Thus, it is possible to restore membrane fluxes to their original values by reloading the membrane with fresh complexing agent. Also, is possible the morphological deterioration of the membrane, which could be explained by the harsh acidic conditions used at the receiving solution (Porter 1990, Benavente *et al.* 1998, Oleinikova *et al.* 2000, Arkhangelsky *et al.* 2007, Hajdu *et al.* 2012, Zhu *et al.* 2014).

Other major technical problem on membranes separation processes is the organic fouling (Qu *et al.* 2014, Castrillón *et al.* 2014, Gao *et al.* 2012, Ang *et al.* 2011, Kim and Dempsey 2010), which may be attributed to the different deposition rates of the organics on/in membrane (Lin *et al.* 2013), due to adsorption of organic molecules prevalent in natural waters and wastewater effluents. A strong correlation was found between fouling resistance and the content of small molecules in dissolved organic matters (Miller *et al.* 2014, Alpatova *et al.* 2013) and a more serious fouling could be observed with a higher proportion of small molecules or a more negative charge density of solution. Protein foulants are known to have fouling effects on membranes by formation of a gel layer on the membrane surfaces, leading to increased hydraulic resistance. Likewise, surfactant can foul porous membranes by accumulation on the membrane surface at high concentrations. For this purpose, to decrease the transport of organic foulants from feed solution to membrane, the cross-linker content (CLC) in the mixture was changed to control the network structure of the membranes. Porous membranes with aliphatic anion exchange carriers decrease the mobility of aromatic foulants because the π - π interactions on transport process are smaller and the membrane fouling with aromatic compounds is very low (Xiao *et al.* 2013, Hashino *et al.* 2011, Tanaka *et al.* 2011, Contreras *et al.* 2009).

4. Applications

Daily, in hydrometallurgy, oil and mine industries, huge amount of wastewater, with main oily and heavy metals, is generated and then treated with traditional methods such as: mechanical (gravity) separation and skimming, air flotation, precipitation, physical and chemical adsorption, coagulation and flocculation and biological growth (Chu *et al.* 2005, El-Kayar *et al.* 1993, Kurniawan *et al.* 2006, Maine *et al.* 2006). All of them have high energy consumption, high costs and the resulted effluents are not totally unpolluted.

An alternative of these classical methods is green technology, a result of cooperation between interdisciplinary fields including physical sciences, technologies, engineering, resource management, economics and politics, in order to conserve and sustain the natural environment and resources, and to curb the negative impacts of human involvement. In this context the UF and NF processes, become advanced technologies for oil/water and heavy metals separation, precious metals recovery. Membranes are cheap and can be used in many applications (Peng and Tremblay 2008, Ho 1992, Association of Water Technologies 2012).

Nanofiltration removes molecules in the 0.001 micron range and is used in water softening, to remove organic compounds, desalting of organic reaction products. NF membranes have sufficiently high rejection of selected constituents such as hardness, metals and organic matter. Advantages to use NF, as green technology, for water softening are: no chemical regenerants necessary, occupies less spaces, better effluent quality, continuous process possible, possible NaCl rejection of 70-90%, reduced boiler blowdown, partial demineralization.

Reverse osmosis used membranes with pore size between 0.0001 to 0.001 μm . Applications are

in desalination (seawater and brackish water), metal plating effluent treatment, color removal from textile effluents production of high purity water (boiler feed, electronics, medical, pharmaceutical). Because all RO plants are susceptible to fouling, adequate pretreatment and operations are essential. Advantages of using RO for removal of natural organics, including oil, and for high purity water production are: no chemical regenerants necessary, no regeneration solutions disposal problems, occupies less space, better removal efficiency and effluent quality, partial demineralization (Mueller *et al.* 2012).

4.1 Applications of porous polymer membranes in oil industry

4.1.1 Polysulfone membranes

The major pollutant of wastewater (also known as produced water) generated from the oil field is the oil which may range between 100 to 1000 mg/L even higher, depending on the efficiency of demulsification and the nature of crude oil. Very small sizes of emulsion droplets, micron and submicron size, offer a long time stability of emulsions, on gravity separation, and the addition of chemicals cannot break the emulsions effectively. The use of porous polymer membranes could be a potential solution to this problem. Chakrabarty *et al.* (2008) reported an application of synthesized polysulfone (PSf) membranes for oily wastewater separation. The used membranes belong to PSf / NMP (N-methyl-2-pyrrolidone) / PVP (polyvinylpyrrolidone), PSf/NMP/PEG (polyethylene glycol), PSf / DMAc (N, N – dimethylacetamide) / PVP and PSf / DMAc / PEG systems. The PSf concentration is 12%, and the solvent and additive concentration is 88%. UF experiments with oily water were carried out using a membrane cell, a semi-batch operation mode (Fig. 3) at a concentration of oil about 100 mg/L and at four trans-membrane pressures: 68.9, 103.4, 137.9 and 172.4 kPa respectively. The experiments were also performed at pH 5-8 under the optimal operating conditions. The properties of the feed, in normal conditions, are presented in Table 3. It can be seen a big difference between the average droplet size in feed and retentate respectively, because the coalescence of smaller oil droplets on the membrane surface leading to the formation of bigger oil droplets (Darvishzadeh and Priezjev 2012). The results of application show that the increasing in permeation flux is correlated with increasing of pressure, irrespective of types of membrane, due to increasing of driving forces across the membrane.

The membrane total resistance is given by the resistance due to the pore blocking mechanisms and by the resistance due to concentration polarization (Wandera *et al.* 2012). If pores blocking is a very fast process, the flux declination will take place. More than 90% of oil rejection was

Table 3 Characteristics of oil in water emulsion (Chakrabarty *et al.* 2008)

Parameters	Values
Oil concentration (mg/L)	100
pH	6.0
Density (g/mL)	0.995
Viscosity (kg/m s)	$1,16 \times 10^{-3}$
Emulsion droplet size distribution, feed (μm)	0.003-5.0
Average droplet size in feed (μm)	0.34
Average droplet size in retentate (μm)	2.4

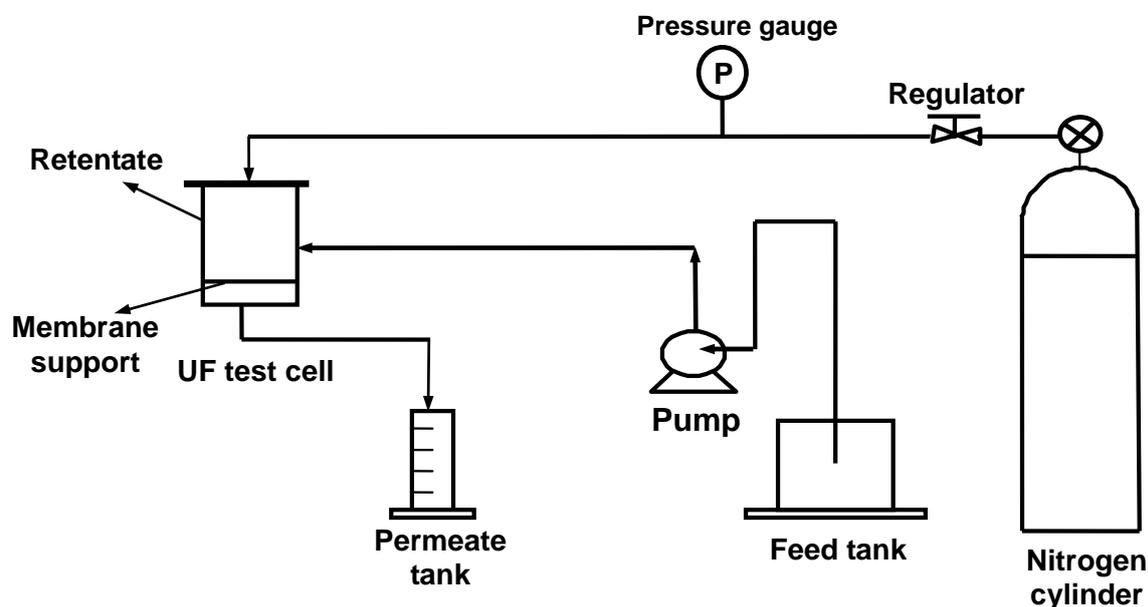


Fig. 3 Schematic of the experimental set-up (Ho 1992)

observed where the trans-membrane pressure ranged (103.4 - 172.4) kPa. The porosity of membranes (N_t), in range of $(0.48 - 10.5) \text{ cm}^2 \times 10^{-9}$, the average pore size (r_{av}) between 3.0 and 3.88 nm respectively, with cumulative pore size distribution cumulated with hydrophilicity (Zhang *et al.* 2011a), and difference in the thickness of the oil layer formed above the membrane surface influence the permeation flux through the membranes. The highest flux was $87.7 \text{ L m}^{-2} \text{ h}^{-1}$ and the lowest $3.7 \text{ L m}^{-2} \text{ h}^{-1}$ respectively. It is reported that surfactants may either decrease or enhance permeate flux of their adsorptive interactions with the membrane surface (Byhlin and Jönsson 2003). The fouling is mostly found to be higher with different pH values (Zhang *et al.* 2011c), for example with pH 6, usually find in oil wastewater. After the membranes cleaning, a fouling deposit was observed inside, indicating the existence of irreversible fouling. The research of Chakrabarty *et al.* (2008) presents an application of polysulfone membranes on oil-wastewater separation, with advantages and disadvantages, but not investigates the fouling mechanism of studied membranes.

Ju *et al.* (2008) tested PSf membranes coated with crosslinked poly (ethylene glycol) diacrylate PEGDA (XLPEGDA-hydrogels) on oil/water filtration. Water permeability increased strongly with increasing the water content in the prepolymerization mixture. The XLPEGDA is prepared with PEGDA ($n = 13$) (Hao 2010). The properties of uncoated PSf membrane and PSf membrane coated with XLPEGDA ($n = 13$) are presented in Table 4.

They reported that coated PSf membranes, compared to the uncoated PSf membranes, have higher resistance $(10 \pm 0.6) \times 10^{12} \text{ m}^{-1}$, contact angle to $(52 \pm 13)^\circ$ and effective thickness of XLPEGDA coating layers approximately $3 \mu\text{m}$. The experiments occurred in a commercial crossflow membrane filtration system (Separation Systems Technologies, San Diego, USA) using stable oil/water emulsions with 1500 ppm concentrations of organics in water. All tests take places at 25°C and pressures up to 20 bar, with a crossflow rate set to 68 L h^{-1} corresponding to 1300

Table 4 Properties of uncoated PSf membrane and PSf membrane coated with XLPEGDA ($n = 13$) prepared with 80wt. % water in the prepolymerization mixture (Ju *et al.* 2008)

Membrane	Water permeance (L/(m ² h bar))	Resistance ($\times 10^{12}$ m ⁻¹)	Contact angle (°)	MWCO* (Da)
Uncoated PSf	141 \pm 9	2.6 \pm 0.2	131 \pm 22	92,400
PSf composite	36 \pm 2	10 \pm 0.6	52 \pm 13	9,500

* MWCO - molecular weight cut-off

Reynolds number in the system, up to 3 days. The performances of coated and uncoated PSf membranes were evaluated through permeate flux and organic rejection. In case of uncoated PSf membrane the water flux dropped from 100 to around 15 L m⁻² h⁻¹ after 5 h of operation and the organic rejection gradually increases during the first 10 h of operation, possibly because of membrane fouling (Cho *et al.* 2011). In case of coated PSf membrane less fouling was reported and it has almost four times higher flux than the uncoated PSf membrane, after 24 hours. The higher organic rejection occurred and remained unchanged throughout the test. The experimental results showed that the coated PSf membranes had 400% higher water flux values than that of uncoated PSf membranes. A higher organic rejection, after 24 h of operation, was also observed. These could be more studied and optimized for a good separation of oil/water emulsion in oil industry. This study focused on the PSf membranes coated with crosslinked PEGDA (XLPEGDA), used in oil water separation, demonstrate a good removal of oil due to the higher water flux and higher organic rejection, for e.g., but not precise the time life of the membranes, knowing that the one of the most important issues facing membranes is the fouling.

4.1.2 Cellulose acetate membranes

Another possible application for separation of oil/water emulsion with new porous polymer membranes is reported by Chen *et al.* (2009). They synthesized cellulose acetate (CA)-graft-polyacrylonitrile (PAN) (CA-g-PAN) copolymer to obtain new UF membranes by phase inversion technique (Chen and Belfort 1999, Pieracci *et al.* 2000, Ulbricht and Belfort 1996). Because of CA-g-PAN copolymer these membranes possessed high water permeability and a good oil-fouling-resistance. After the membranes characterization with scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) (PHI-1600), using Mg K α (1254 eV) as the radiation source, were tested for separation of oil/water emulsions at different feed oil concentrations from 300 to 1800 mg/L. The ultra-filtration was carried out at 25°C with operation pressures of 0.03, 0.07, 0.1 and 0.15 MPa respectively and at 400 rpm stirring rate in a filtration cell (model 8200, Millipore Co). The oil droplets size in feed solution was measured using a Malvern Mastersizer Particle size analyzer and it was between 0.12 μ m and 22.8 μ m respectively with a volume average size of 1.7 μ m. An excellent antifouling property of CA-g-PAN membranes was reported because of the results of XPS and the water contact angle measurements (Wandera *et al.* 2012).

In Table 5 the static contact angle, pure water flux and BSA (bovine serum albumin) rejection of the CA, CA-g-PAN and PAN membrane are described. The PAN did not influence the hydrophilicity of the membranes and a good recovery flux was reported. In case of increasing the feed oil concentration, the oil/water emulsion flux decay ratio (DR) was increased, maybe due to

formation of thicker oil layer on the membrane surface at higher oil concentration and the flux recovery ratio (FRR) values of CA-g-PAN membranes were higher than 90%. Most of the membrane fouling (Semblante *et al.* 2013) could be eliminated by simple hydraulic washing. Also, authors report that the recycling potential of CA-g-PAN membranes for the treatment of oil/water emulsions, during three times ultra-filtration operation, was good. The pure water flux was almost totally recovered and the flux of the feed solution was also kept up to a high level (about 110 L m⁻²·h⁻¹) for all CA-g-PAN membranes. After each ultrafiltration of oil/water emulsion the authors present good results of the recycling properties of the used CA-g-PAN membranes but only at the 0.1 MPa operation pressure. Because the stream recycling is also a challenge on the membranes research, news' experiments, at different pressure, could be investigated to see if the pressure influences the irreversible fouling. These new porous membranes based on CA could be more studied, to demonstrate an appreciable separation performance and fouling resistance in the oil/water separation, very important to this purpose.

The same authors mentioned above, Chen *et al.* (2010), proposed another type of membranes based on in situ generation of silica (SiO₂) nanoparticles for preparing cellulose acetate (CA)

Table 5 Static water contact angle, pure water flux and BSA rejection ratio of the CA, CA-g-PAN and PAN membrane

Membrane	Static water contact angle (°)	Pure water flux (L/(m ² h))	BSA* rejection ratio (%)
CA	54.0 ± 1.3	3.4	49.0
CA-g-PAN(a)	55.4 ± 1.7	227.8	20.1
CA-g-PAN(b)	56.9 ± 0.9	334.5	27.3
PAN	68.5 ± 2.2	439.3	76.1

* BSA – bovine serum albumin

Table 6 The experimental values of the SiO₂ content in the membranes, the Si molar percentage on the membrane surfaces and the water contact angles (Chen *et al.*, 2010)

Membrane	SiO ₂ content in the membranes (wt. %)	Si molar percentage on the membrane surfaces (mol %)	Water contact angle (°)
Control CA	0	0	54.0 ± 1.0
CA(TEOS)-HCl 5%	3.6	3.3	53.7 ± 2.3
CA(TEOS)-HCl 10%	6.1	6.1	52.4 ± 1.3
CA(TEOS)-HCl 15%	7.1	6.5	51.7 ± 1.2
CA(TEOS)-HCl 20%	9.0	7.9	52.1 ± 1.6
CA(TEOS)-HCl 30%	14.0	8.1	51.3 ± 1.1
CA(TEOS)-NaOH 5%	3.5	3.3	52.4 ± 1.4
CA(TEOS)-NaOH 10%	6.0	6.0	53.8 ± 2.0
CA(TEOS)-NaOH 15%	7.0	6.4	51.2 ± 1.3
CA(TEOS)-NaOH 20%	10.6	7.5	50.3 ± 2.1
CA(TEOS)-NaOH 30%	14.3	8.4	52.1 ± 1.6

membranes with TEOS (tetraethyl orthosilicate) by the phase inversion method with enhanced permeation property. The experimental values of the SiO₂ content in the membranes, the Si molar percentage of the membrane surfaces and the water contact angle are presented in Table 6. The role of the silica nanoparticles is to increase the pore size and density in the skin layer of the membrane. The pore size was mostly in the range of (50 – 150) nm, the same with the size of SiO₂ nanoparticles. Furthermore, the SiO₂ nanoparticles showed high hydrophilicity due to the presence of great deal of hydroxyl groups (Wei *et al.* 2008a, b). These membranes were tested for oil/water emulsions separation. All the experiments were carried out in a cell filtration system (model 8200, Millipore Co, SUA) at 400 rpm stirring rate, at 25 ± 1°C, with 900 mg/L concentration of oil in feed solution and with sodium dodecylsulfate (SDS) emulsificator.

Before starting the experiments, each membrane was initially pressurized at 0.15 MPa, for 30 min. Then the used pressure for the ultra-filtration operation was 0.1 MPa. The size of the oil droplets in feed solution was reported in the range (0.12 - 23.4) μm with a volume average size of 1.7 μm (Chen *et al.* 2009). The membranes were characterized with FTIR spectrometer (Fourier transform infrared spectra) for molecular structure, with transmission electron microscopy (TEM) to observe the morphologies of SiO₂ nanoparticles embedded in the membranes, with SEM for membranes morphologies, with XPS analysis for surface compositions and with water contact angle to assess the membrane hydrophilicity. The oil water separation performances of these new membranes CA(TEOS)-HCl and CA(TEOS)-NaOH, obtained by inversion technique in hydrochloride acid/water bath (pH = 1) and sodium hydroxide/water bath (pH = 13) respectively, were evaluated on the antifouling property and oil rejection ratio, in comparison with most of the reported UF membranes (Chakrabarty *et al.* 2008, Ju *et al.* 2008, Cui *et al.* 2008, Kong and Li 1999, Li *et al.* 2006, Wu *et al.* 2008). In the initial operation stage, the membrane fouling was caused by the direct adsorption and deposition of the oil droplets on the membrane surface, and then an approximate stable flux was obtained. The authors suggested that occurs because of the rigorous stirring on the membrane surface and because the higher TEOS weight percentage in the membrane casting solutions. But, on the other hand, they not explain, for the studied membranes, which are the separation mechanisms that determine the high flux decline. In concordance with the reported values of the DR (decay ratio) (range of 33.3 - 67.3%) and with FRR (flux recovery ratio) higher than 90%, the rate of flux decline was greater. In addition these new membranes prove a good long-time recycling property. On three times oil/water emulsions ultra-filtration the pure water flux of CA(TEOS)-HCl membranes still maintained at high level, for example 398.7 Lm⁻²h⁻¹. The authors have also reported superior separation performance of the membranes, 110 L m⁻² h⁻¹ water permeate flux in the oil/water emulsions UF and 99.8% oil rejection ratio.

4.2 Applications of carrier facilitated transport (Active transport)

The most important applications of coupled transport are: the removal of metals from aqueous solutions, such as contaminated ground water or industrial (hydrometallurgical, mine, oil) streams, and removal of small organic solutes from different effluents. Thus, the first commercial applications of coupled transport are likely to be smaller plants installed in pollution control applications (Baker 2004, 2012). It has been predicted that practical industrial applications of polymer inclusion membranes (PIMs) and activated composite membranes (ACMs) will be achieved in the near future. Because RO is one of the techniques able to remove a wide range of dissolved species from water, is extensively studied in applications for removal of heavy metals from wastewater. In Table 7 are presented some examples of heavy metals removal by RO, NF

Table 7 A list with some heavy metals removed by RO, NF and NF + RO

Membrane	Heavy metal	Initial metal conc.	Removal efficiency (%)
RO	Cu ²⁺ , Ni ²⁺	500 mg/L	99.5
RO	Cu ²⁺	20-100 mg/L	70-95
RO	As	< 500 µg/L	As(V) 91-99 As(III) 20-55
RO	Ni ²⁺ , Zn ²⁺	Ni ²⁺ : 44-169 mg/L Zn ²⁺ : 64-170 mg/L	99.3 98.9
NF	Cu ²⁺	10 mM	47-66
NF	Cr(VI)	NA	99.5
NF	Cu ²⁺	0.47 M	96-98
RO + NF	Cu ²⁺	2 g/L	> 95
RO + NF	Cu ²⁺	15 mg/L	95-99

and NF + RO (Fu and Wang 2011). Below, some new laboratory research applications are presented.

4.2.1 Recovery of toxic metals

4.2.1.1 Recovery of Cr (VI)

Because Cr (VI) is one of the major toxic elements, present in the environment, a remarkable increase of the applications of composite liquid membranes in recovering of this metal from residual aqueous solutions, is observed, for example: generated by galvanic plants and mine waters. Chromium (VI) can be effectively removed from acidic chloride solutions using coupled transport across nanofiber membranes (Wang *et al.* 2013, Neghlani *et al.* 2011), PIMs and ACMs (Ines *et al.* 2012, Gherasim *et al.* 2011, Saf *et al.* 2011, Guo *et al.* 2012) with tertiary amines (R₃N, where R = n-C₆H₁₃-n-C₁₂H₂₅) and Aliquat 336 (methyltricaprylammonium chloride) as ions carrier. CTA (cellulose triacetate) or PVC (polyvinyl chloride) is used as a support. The stripping phase used, was 1 mol/L NaNO₃ (Scindia *et al.* 2005, Kozłowski and Walkowiak 2005). The highest fluxes of PIM transport were found for n-tributyl amines and Aliquat 336 (Matsumotto *et al.* 2011) as ion carrier. The variation of permeability coefficients of Cr (VI) was between 4.42 µm s⁻¹ and 1.46 µm s⁻¹, respectively, at pH 2 and 8, in the feed solution, because the ions transport across the membrane depends on their chemical form. The Cr (VI) permeation involves coupled-diffusion transport, whereby Cr (VI) permeates from feed to stripping compartment and NO₃⁻ permeates in the opposite direction. The diffusion mobility in the membrane phase is dependent by the nature of diffusing Cr (VI) species and membrane composition. The recovery of Cr (VI) from seawater samples was only 58% over a period of 10 h and, in the case of municipal water the recovery factor was ≈ 99% for the same period of time.

In case of recovery of Cr (VI) from metallurgical wastewater, ACMs were used (Melita and Popescu 2008), containing Aliquat 336 as carrier. The pH of feed and stripping solutions was maintained between 4.00 and 5.50 respectively, to decrease the conversion probability of Cr (VI) to Cr (III) (Galán *et al.* 2005, Chen *et al.* 2013). The good separation of chromium was observed at 25 and 50 mg L⁻¹ Cr (VI) respectively in feed solution. After 7 h treatment of the polluted water

with ACM, 0.2 mg L^{-1} was the maximum unpolluted low admissible concentration and it could be used by the purification plant. A good enrichment factor, E (12.5 and 14.5) in the separation process was obtained in concordance with the calculated membrane capacity accordingly. Studies have emphasized that the transport of Cr (VI) through porous polysulfone membranes (Shah and Murthy 2013, Cho *et al.* 2011) is still often diffusion-controlled, but the morphology of the membrane affects the coupled transport of (CrO_4^{2-}) and $(\text{Cr}_2\text{O}_7^{2-})$ through the membrane. In this case, the most sensitive problems are: the instability of Cr (VI) species, which pass easy to Cr (III) form, and the optimal conditions of operation that are required for removal of Cr (VI) with PIMs and ACMs.

4.2.1.2 Recovery of Cd (II)

Cadmium is known to be an environmental pollutant with toxic effects. In the human body it penetrates via inhalation of dust from industry, or orally by food. Cd accumulates in the kidneys and results in various diseases. But, despite its toxicity, Cd is widely used in metallurgy, electroplating, pigmenting and in the fabrication of Ni-Cd batteries. In the laboratory applications, the PIMs (Ines *et al.* 2012, Cherif *et al.* 2012, Adams *et al.* 2012, Han *et al.* 2012) for removal of Cd (II) were used. These membranes consisted of CTA (cellulose triacetate), as polymeric support, o-nitrophenyl octyl ether (NPOE) as plasticizer, and Aliquat 336 (methyltricaprylammonium chloride) and D2EHPA (di-(2-ethylhexyl) phosphoric acid) as carriers. Some of the aqueous samples used are collected from the Mediterranean Sea with the following characteristics: pH 8.2, conductivity 62 mS , 0.62 M Cl^{-1} , 0.68 M Na^{+} , $4325 \text{ mg L}^{-1} \text{ SO}_4^{2-}$, $1415 \text{ mg L}^{-1} \text{ Mg}^{2+}$ and Ca^{2+} , K^{+} , HCO_3^{-} concentration was $< 1000 \text{ mg L}^{-1}$. These were enriched with the appropriate amount of Cd stock solution (from 2 to 30 mg L^{-1}). Other real samples contained Cd, from a Ni-Cd battery leaking, were brought up to the desired volume with the same acid and are used as feed solution. The extraction of metallic anions (CdCl_3^{-} and CdCl_4^{2-}) by Aliquat 336 and metallic cations (Cd^{2+}) by D2EHPA is based on a coupled transport which involves the formation of an ion pair that can enter in the membrane. The transport of Cd (II) through membranes depends by the composition of the membrane, by the porosity (Shah and Murthy 2013), by the concentration of the carrier, by the type and amount of plasticizer as well as by the influence of aqueous phase. The presence of Cl^{-} in feed phase is necessary for the extraction of cadmium by Aliquat 336, but similar results are obtained when metal is contained in both NaCl and HCl media, showing the efficiency of the PIM system when dealing with either acidic or saline solutions. In case of D2EHPA, when the pH of the feed phase is increased, the transport flux tends to decrease. This result has been an outstanding one (Baker 2012, Pont *et al.* 2008, Vernet 1991, Bertin and Averbek 2006, Kebiche-Senhadji *et al.* 2008).

This phenomenon was attributed to the formation of hydroxide forms of the metal, less extractable with D2EHPA (Mellah and Benachour 2006), the formation of emulsion, which depends both by the pH, and by the concentration of the carrier (Alvarez-Salazar *et al.* 2005) or by the mechanism which involves the monomeric form (LH) or dimeric form (LH_2) of D2EHPA, to form the complex: ML_2 and $\text{ML}_2(\text{LH})_2$. The existence of LH_2 is more probable in a range of pH lower than the pK_a of D2EHPA, while the formation of ML_2 species predominates in the opposite range (Kebiche-Senhadji *et al.* 2008). The authors didn't explain why, in the studied pH low range, the presence of LH_2 form of D2EHPA is more probable, and in the opposite pH range are more predominant the ML_2 species. For a matrix with Cd (II) and a large amount of Ni (II), in feed solution, the PIM systems allowed the quantitative separation of Cd (II) after 400 min. of experimentation. In addition, the effect of the presence of Cu, Zn and Pb (Hajdu *et al.* 2012) in

feed solutions demonstrates that the membrane with D2EHPA carrier transports all the cations without any marked selectivity, while Aliquat 336 shows an improved selectivity for Cd (II) and Pb (II) as compared to Zn (II). The maximal Cd (II) recovery factors obtained in 8 h are 97.5% and 91.8% with D2EHPA and Aliquat 336, respectively.

4.2.1.3 Transport of Zn (II)

In order to extract metal ions from hydrometallurgical effluents, D2EHPA is a carrier that in membrane processes presents a great selectivity towards Zn^{2+} (Zhang *et al.* 2011a, Yilmaz *et al.* 2011, Kogelnig *et al.* 2011, Gajda *et al.* 2011), in relation to other metals such as Cu^{2+} , Ni^{2+} , Ca^{2+} , Mn^{2+} , Fe^{3+} , Al^{3+} and Cd^{2+} . That has been demonstrated in some membrane processes. On the other hand D2EHDTPA (di-(2-ethylhexyl) dithiophosphoric acid) is an analogous molecule to D2EHPA (di-(2-ethylhexyl) phosphoric acid) (Kebiche-Senhadji *et al.* 2011) where two sulphur atoms replace two oxygen atoms and its acidity is slightly stronger than that of D2EHPA. It has been shown that D2EHDTPA also shows a transport between protons and metallic ions in a counter-transport system. One of the most used applications in the clean-up effluent streams from the electroplating industry is, for example, the removal of Zn (II) with acidic carriers such as D2EHDTPA immobilized in ACMs (activated composite membranes) and D2EHPA immobilized in PIMs (polymeric inclusion membranes). In both situations, the separation was achieved by pH control of the feed phase with 1.0 M HCl as the stripping phase. Best selectivity for Zn (II) was achieved using the source phase at $pH < 2$ which was in accordance with the solvent extraction of D2EHPA for the metal ions. A new type of PIMs and HMs (hybrid membranes) system was prepared and used in applications. The metal ions used for selectivity experiments were Cd^{2+} , Cu^{2+} and Zn^{2+} that appear together in some industrial processes such as electroplating practices. Data were obtained by using ACMs and PIMs prepared with a concentration by 300 mM of D2EHPA, 230 mM of D2EHDTPA or, in other cases, including both carriers in the proportion 245:40 (mM) D2EHPA:D2EHDTPA. In case of binary mixtures Zn^{2+} - Cu^{2+} , D2EHPA transferred about 43% of Zn^{2+} from feed to stripping solution within 7 h of experiment, whereas almost all the Cu^{2+} remained on the feed. The scientific motivation why Cu^{2+} didn't pass through the membrane was not given. In case of Zn^{2+} recovery from a Zn^{2+} - Cd^{2+} binary mixture the same carrier transported 63% of Zn^{2+} in 7.5 h, while it was observed that there was no transport of Cd^{2+} . The tendency was reversed with D2EHDTPA, obtaining a major recovery for Cd^{2+} , 49% in 8 h while only 36% of Zn^{2+} was recovered in the same period of time. The obtained results, using a mixture of carriers, lead us to the conclusion that in the presence of D2EHPA most of the transport involves Zn^{2+} , and almost 60% of the metal was recovered, whereas Cd^{2+} was extracted in an insignificant amount of 3% (Resina *et al.* 2006, Macanas and Muñoz 2005, Ulevicz *et al.* 2003, Filippou 2005).

4.2.1.4 Transport of V (V)

Because the presence of vanadium, nickel and iron, in typical crude oil extraction out of bearing rocks, the water used on hot water extraction process (HWEP) contains the mentioned metals (Kasperski 1992). Also, in hydrometallurgical industry the vanadium recovery from resulted wash water, on various technological stages, used ion exchanges processes and then V_2O_5 precipitate (Wang *et al.* 2011). All nickel and vanadium compounds should be considered toxic. Tetravalent $VOSO_4$ has been reported to be about five times more toxic than trivalent V_2O_3 . Nickel salts are carcinogenic and nickel carbonyl $[Ni(CO)_4]$ is an extremely toxic gas (Occupational Safety and Healthy Guideline for Vanadium Pentoxide Dust 2009, Nickel Named 2008 Contact

Allergen of the Year 2009). ACMs with macro porous PSf support and carrier Aliquat 336 0.5M were used for V (V) and Ni (II) transportation. The aqueous feed acidity with pH between 5 and 6 respectively, with concentration range of V (V) and Ni (II) between 5 and 25 ppm respectively, different permeate solutions with NH_3 , HNO_3 and Na_2CO_3 and hydrodynamic conditions with stirring rate above 600 rpm were studied. These membranes were selective for V (V) transportation. This behavior might be attributed to selective interaction between Aliquat 336 and monocharged anion $\text{VO}_2(\text{OH})_2^-$ over other oxoanions (VO_2^+ , $\text{VO}(\text{OH})_3$, $\text{VO}_3(\text{OH})_2^-$) dependent by the pH. Vanadium diffuses from feed solution through ACMs into permeate solution due to the facilitated transport with Aliquat 336, acting as carrier, and the stability of aqueous species $\text{VO}_3\text{OH}^{2-}$ at pH used. Ni (II) was not extracted by ACMs because of its electronic configuration and the nickel kinetics is especially slow (Melita and Gumrah 2010, Palet *et al.* 1995).

4.2.1.5 Transport of Ni (II)

Nickel is one of many carcinogenic metals known to be an environmental and occupational pollutant. The New York University School of Medicine warns that chronic exposure has been connected with increased risk of lung cancer, cardiovascular disease, neurological deficits, developmental deficits in childhood, and high blood pressure (Chervona *et al.* 2012). Moreover, heavy metals cannot be degraded or destroyed. An application of a thin-film composite polyamide nanofiltration membrane for rejection of nickel ions from aqueous wastewater was presented by Murthy and Chaudhari (2008). They studied the influence of the operating variables as: feed concentration of nickel (5-250 ppm), applied pressure (4-20 atm.), feed flow rate (5-15 L/min) and the pH (2-8) on the separation process with membrane. The experimental data are analyzed using membrane transport models, combined-film theory-solution-diffusion (CFSD), combined-film theory-Spiegler-Kedem (CFSK) and combined-film theory-finely porous (CFFP) models to estimate membrane transport parameters and mass transfer coefficient, k . The maximum observed rejection of the metal was found to be 98% and 92% for an initial feed concentration of 5 and 250 ppm, respectively. Also the permeation of Ni(II) from aqueous solutions through a supported liquid membrane containing triethanolamine (TEA) dissolved as mobile carrier in cyclohexanone was studied by Bukhari *et al.* (2006). The optimum conditions for Ni(II) ions transport are 2M HCl, in feed solution, and 3M TEA in membrane. It has been observed that Ni(II) flux across the membrane tends to increase from 6.28×10^{-9} to 22.52×10^{-9} mol/m² s for Ni(II) ions concentration range $(8.43-29.47) \times 10^{-4}$ mol/dm³. Applying the studied conditions to nickel plating waste solutions indicated more than 99% removal of Ni ions. Other researchers (Katsou and Malamis 2010) investigated the removal of nickel ions from aqueous solutions and activated sludge by employing ultrafiltration (UF) membranes, together with natural aluminosilicate minerals (bentonite, zeolite and vermiculite). The experiments were conducted in a batch ultrafiltration unit with constant initial Ni(II) concentration of 320 mg/L and the performance of the system was examined with respect to different parameters such as: the membrane nominal pore size, the temperature and pH of aqueous solution and sludge, the mineral type and concentration, the Ni(II) initial concentration and the metal-mineral contact time. Good Ni(II) removal efficiencies by 65.3% and 80.0% respectively due to sorption, induced by minerals and sludge, were obtained with 15g/L addition of bentonite and 15g/L vermiculite at pH 6. The processes involved in the removal of nickel consisted of biosorption onto sludge flocs, adsorption onto the mineral, retention of insoluble metal ions by the UF membranes and chemical precipitation.

In case of Co(II) and Ni(II) separation through supported liquid membranes (SLM) and hybrid liquid membranes (HLM) with D2EHPA extractant and commercial extractants: Cyanex 272, 301

and 302 used as ion carriers Gega *et al.* (2001) investigated the competitive transport of both heavy metals in an equimolar mixture. They observed that the Co(II) cations are being transported much better than Ni(II) cations for both types of membranes and the selectivity coefficients, S of $\text{Co}^{2+}/\text{Ni}^{2+}$ are higher for HLM than for SLM because the acidity of the aqueous feed phase and because of nickel kinetics that are specially slow due to its electronic configuration. These causes demonstrate that the dehydration rate of solvent nickel ion is very time-consuming and this slow step affects the global extraction speed (Macanas and Muñoz 2005). The separation coefficients are also influenced by the receiving phase acidity for SLM processes, while HLM no influence was observed, and with increasing concentration of both metal ions in the feed phase and ionic carrier in the organic phase, the selectivity coefficients decrease.

4.2.1.6 Transport of Pb (II)

Lead can be emitted into the environment from industrial sources and contaminated sites, such as former lead smelters. While natural levels of lead in soil range between 50 and 400 ppm respectively, mining, smelting, and refining activities have resulted in substantial increases in lead levels in the environment, especially near mining and smelting sites (EPA 2013). Lead is a highly poisonous metal (regardless if inhaled or swallowed), affecting almost every organ and system in the body. The main target for lead toxicity is the nervous system, both in adults and children. To remove lead from water samples Mbareck *et al.* (2009) used an ultrafiltration-ion exchange membrane made of a semi-interpenetrating polysulfone (PSf) and polyacrylic acid (PAA), with high concentration: 1.37 mequiv/g, immobilized in the PSf matrix, forming a network. The SEM images of the membrane surfaces reveal that membranes contain small outer-surface pores, sub-structure open pores and fine pores inner with size by 68 nm, 136 nm and 25 nm respectively, depending by the PAA content. This membrane exhibited the best heavy metal retention (lead, chromium and cadmium) because of its high content in PAA and their small pore size. The calculated Reynolds number $R_e = 14,440$ shows that experiments were done under turbulent conditions and the mass transfer coefficient, k of 5×10^{-6} m/s is rather high due to the turbulent regime and the high salt diffusivity. The high metal rejection was due at $\text{pH} \geq 5.7$ that suggest the complexation between metal ion and carboxylate groups ($-\text{COO}^-$) on the inner surface of pores, and membrane matrix act as an electrostatic repulsion barrier against the non-complexed metal ions. Thus the permeation path through the membrane is highly tortuous and the ions transport has a high probability to be caught by the carboxylate groups on the pore walls. The large range of electrostatic interaction between ions and membrane charges was also reported by Nordmeier (1995) and Tsuchida and Nishide (1977). These membranes may offer several advantages due to the repartition of their charges over the whole membrane matrix and may be used for the deposition of polyelectrolyte layers and for the ultrafiltration assisted by complexation.

The facilitated transport of Pb(II) through PIMs consisting of cellulose acetate as polymeric support, bis-(2-ethylhexyl)-phosphoric acid (D2EHPA) as carrier and tris-(2-butoxyethyl) phosphate as plasticizer (TBEP) was investigated by Salazar-Alvarez *et al.* (2005). Thus Pb(II) transport is explained considering that D2EHPA/TBEP is the mixture which constitutes the extraction medium in the PIM. In order to have a quantitative description of the transport across the membranes a model was developed based on a simplified method described elsewhere (Danesi *et al.* 1981). The analyzed water samples contain lead concentration between 5×10^{-5} M and 5×10^{-4} M respectively (10-100 ppm). It is observed that as plasticizer content increases the permeability increases until a limiting value is reached (0.03 g in the PIMs) and the maximum of Pb(II) transport was obtained at 4.8 mol/dm^{-3} carrier content in the membrane such that TBEP can

solubilize. The maximum flux obtained for the membranes studied herein was calculated to be $3.5 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$, which is comparable to those reported earlier for SLMs (Nazarenko and Lamb 1997, Paugam and Buffle 1998, Aguilar *et al.* 2001). The D2EHPA carrier showed good extraction efficiency for Pb(II), 91% in a copper lead mixture (Belkhouche *et al.* 2006). The diffusion process is enhanced at a higher temperature, 322.6 K where the calculated apparent activation energy, E_a is of 11 kJ/mol, which increases the thermal motion of polymer chains thus resulting in higher diffusion coefficients. The aqueous diffusion layer thickness was calculated assuming the values of $9.45 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for the aqueous diffusion coefficient (Lide 2000). The diffusion coefficient found for the transport of Pb^{2+} across PIMs was $1.5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and is quite similar to those reported by Aguilar *et al.* (2001) who used Kelex as carrier and Nazarenko and Lamb (1997) who used trioctyl phosphine oxide as carrier. It was observed that the transport of protons increased with the number of runs and the Pb(II) flux decreased by approx. 30% after 5 cycles of 3 hours each. That could be explained by the morphological deterioration of the membrane because of the harsh acidic conditions used at the receiving solution. Other disadvantage of this membrane is the loss of membrane phase. It was found that the organic loss is about 10% which agreed with the loss registered from the EDS analysis. The same EDS analysis also revealed that no accumulation of lead in the membrane occurred. In conclusion the experiments to remove Pb(II) with PIMs using a commercial reagent is possible through a carrier-facilitated transport mechanism in which the diffusion of metal species across the membrane phase is the rate-controlling step in the experimental conditions employed. Also it was possible to re-use the same membrane for repeat transport experiment although the permeability rapidly deteriorated after a short number of runs.

5. Conclusions

The water treatment technologies, currently used for boiling feed water to generate steam in heavy oil processes, are commonly integrated processes with multi-step-technologies, due to the diversity of the contaminants in the water sources.

As it can be seen from the literature, the membrane separations are most frequently studied for the heavy metals wastewater treatment because of their high efficiency.

The effectiveness of most of the water treatment technologies has not been proved yet, at a bench or pilot scale. The understanding of how these technologies would perform, given the unique physical and chemical nature of produced water from oil-sands in the larger scale, is still needed.

The advanced and high-speed wastewater treatment technology, able to purify the wastewater, to a sufficient level prior to its disposal, is still needed.

The use of membrane technologies to treat wastewater is certainly going to increase in the future. The environmental friendly cleaning and simple operation offer unique advantages, in areas such as in-process recycling of aqueous cleaners.

The membranes fouling problem can be minimized with technological advances in membrane surface chemistry modifications, and permeate flux decline or chemical additives, aeration and ultrasound.

The most advantageous technology for wastewater final treatment, for oil removal, is nanofiltration (NF) to decrease the membranes fouling, and for removal and recovery of heavy metals the best option is reverse osmosis (RO).

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