UNIVERSITÉ DU QUÉBEC À MONTRÉAL

UTILISATION DES TECHNOLOGIES MEMBRANAIRES DANS LE CADRE DE LA DÉCONTAMINATION DES SOLS POLLUÉS PAR LES MÉTAUX TOXIQUES

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APPLICATION OF MEMBRANE TECHNOLOGIES IN THE DECONTAMINATION OF SOILS POLUTED BY TOXIC METALS

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LIST OF ABBREVIATIONS AND SYMBOLS

AAS	Atomic absorption spectrometry
ADA	β-alaninediacetic acid
$A_{\iota d}$	Dynamic solution permeability of membrane (m)
$A_{\iota pw}$	Pure water permeability of membrane (m)
C	Residual metal concentration (dimensionless)
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
Co	Initial metal concentration (dimensionless)
DTPA	diethylene-triamine-pentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
f, f'	Overall and intrinsic separation factor separation, (dimensionless)
FQRNT	Fonds de recherche sur la nature et les technologies
IARC	International Agency for Research on Cancer
ICP-AAS	Inductively coupled plasma, atomic absorption spectrometry
I_p	Isoelectric point
J_p	Solution permeate flux (m/s)
M	Molar concentration (mol/l)
MEFQ	Ministère de l'Environnement et de la Faune
MF	Microfiltration
MINEQL^{+}	Environmental research software
$\mathrm{M}_{\mathrm{dep}}$	Amount of metals deposited on cathode electrodes (mg)

M_{int}	Amount of metals in solution before electrolytic treatment (mg)
M_{pre}	Amount of metals in the metallic sludge residues (mg)
M_{res}	Amount of residual metals in solution after electrolytic treatment (mg)
NF	Nanofiltration
NSERC	Natural science and engineering research council of Canada
NPL	National Priorities List
NPRI	National Pollutant Release Inventory
NRC	National research council
NTA	Nitrilotriacetic acid
ORP	Oxydoreduction potential (mV)
P	Pressure (Pa)
P_a	Apparent gradient pressure (Pa)
PAHs	Polyaromatic hydrocarbons
PCBs	Polychlorinated biphenyls
$\Delta P_{e_{ff}}$	Effective pressure gradient (Pa)
PVC	Polyvinyl chloride
Q_c	Feed flow rate (m^3/s)
Q_p	Permeate flow rate (m^3/s)
RCRA	Resource Conservation and Recovery Act
RO	Reverse Osmosis
rpm	Rotations per minute
SARA	Superfund Amendments and Reauthorization Act

S_m	Membrane area (m^2)
T	Temperature (°C)
TCE	Trichloroethylene (TCE)
TOC	Total organic carbon ($mg.O_2/l$)
UF	Ultrafiltration
USD	United States Dollars
US EPA	United States Environmental Protection Agency
STEPPE-ETS	Station expérimentale des procédés pilotes en environnement - École de technologie supérieure
WHO	World Health Organization
X	Molar fraction
X_{A1}	Molar fraction of the feed
X_{A2}	Molar fraction of the concentrated boundary layer
X_{A3}	Molar fraction of the permeate

Greek letters

Δ	Gradient
μ	Fluid viscosity (Pa.s)
Π	Osmotic pressure (Pa)
$\sum_i$	Number of ions per molecule of solute

ABSTRACT

This research was carried out in order to develop new theoretical and applied knowledge, to contribute to the development of new technologies with the scope of solving the growing problem of soils contaminated with metals.

This thesis focused on the treatment of soils contaminated with toxic metals, principally Pb, from the Pointe-aux-Lièvres site located in Quebec City, Canada, through the application of different decontamination processes. More specifically, this investigation was divided into three phases. The first phase consisted of treating contaminated soil with inorganic acids, HCl, H_2SO_4 and a mixture of H_2SO_4-NaCl as soil-washing agents to produce the acidic leachate solutions. The experiment results showed the effectiveness of the application of these reagents as soil-washing agents for extracting metal ions from the soil. Principally, the leachate prepared with the combined H_2SO_4-NaCl presented a slight increase in metal ion solubilization for some ions, such as Cr, Mn and Pb, compared to the other washing agents.

In the second phase, the performance of two commercial nanofiltration (NF) membranes, namely Desal 5 and NF-270, were studied to investigate their ability to recover metals using the three different leachates prepared in the first phase. The results showed that the nanofiltration membranes demonstrated different behaviors according to their chemical nature. Membrane performance was evaluated in terms of permeability, metal-ion retention of the feed solution and the effect of various operating conditions, such as different pH, pressure, recirculation flow rate and solution concentration on the permeate. The results showed that the application of NF membranes on leachate solutions is a promising alternative for the removal of metal ions stemming from leachate solutions. For example, it was observed that overall the membranes presented good retention capacity of multivalent and divalent ions in comparison with monovalent ions, which are harmless to the environment.

The third part of this research consisted of looking for an advanced method for treating the concentrate fraction produced by the NF membrane process. In this case the performance of the electrochemical process was investigated. The laboratory study demonstrated a high reduction of toxic ions, such as Cu, Mn and Pb, from the leachate solutions particularly resulting from the H_2SO_4-NaCl process ($\geq$ 97%). In addition, the cost of the electrochemical treatment of the leachates in terms of energy consumption and metallic sludge disposal was presented, as well as the feasibility of the application of this process for economical and effective metal removal.

The results obtained in this study not only provide a process for treating contaminated soil, thereby directly reducing the volume of contaminated water produced, but also offer a new approach in treating complex waste residues generated during different industrial processes.

Keywords

Soil decontamination; Toxic metals; Soil washing; Sulphuric acid; Hydrochloric acid; Sodium chloride; Acidic leachate; NF membranes; Membrane characterization; Water permeability; Dynamic permeability; Metal-ion retention; Electrochemical process; Metal-ion removal

RESUME

Cette recherche a été réalisée dans le but de développer de nouvelles connaissances théoriques et appliquées pouvant contribuer à la mise au point de nouvelles technologies visant à résoudre le problème croissant de la contamination des sols pollués par les métaux.

Cette thèse a porté sur le traitement du sol du site de Pointe-aux-Lièvres (PAL) localisé à Québec, Canada, lequel est pollué par des métaux toxiques, principalement le Pb, en utilisant différents processus de décontamination. Plus spécifiquement, cette recherche a été divisée en trois phases.

La première phase consistait à traiter le sol contaminé avec des acides inorganiques, HCl, H_2SO_4 et un mélange H_2SO_4-NaCl comme agents de lavage de sol pour produire des solutions acides. Les résultats expérimentaux ont montré l'efficacité de l'application de ces réactifs comme agents de nettoyage de sols pour extraire les ions métalliques des sols. Principalement, le lixiviat préparé avec la combinaison H_2SO_4-NaCl a montré une légère augmentation de solubilisation des ions métalliques pour quelques ions tel que le Cr, Mn, et le Pb, comparé aux autres agents de lavages.

Dans la seconde phase, la performance de deux membranes commerciales de nanofiltration (NF), nommé Desal 5 et NF-270, a été étudiée pour connaître leur habilité à récupérer les métaux en utilisant les trois différents lixiviats préparés dans la première phase. Les résultats ont montré que les membranes de nanofiltration ont des comportements différents selon leur nature chimique. La performance des membranes a été évaluée en fonction de leur perméabilité, de leur capacité de rétention d'ions métalliques de la solution d'alimentation et de l'effet des conditions d'opérations différentes, tel que le pH, la pression, le débit de recirculation, et la concentration de la solution sur le perméat. Les résultats ont montré que l'application de membranes NF sur les lixiviats de décontamination de sol est une alternative prometteuse pour la récupération des ions métalliques. Par exemple, il a été observé que, dans l'ensemble, les membranes ont une bonne capacité de rétention des ions multivalents et divalents en comparaison avec les ions monovalents, lesquels sont inoffensifs pour l'environnement.

La troisième partie de cette recherche a consisté à étudier une méthode avancée pour traiter la fraction concentrée obtenue par le procédé de NF. Dans ce cas, la performance d'un procédé électrochimique a été évaluée. L'étude en laboratoire a démontré une élimination importante des ions toxiques tels que Cu, Mn et Pb, provenant de lixiviats résultant particulièrement du procédé H_2SO_4-NaCl ($\geq 97\%$). De plus, le coût du traitement électrochimique des lixiviats en terme de consommation d'énergie et de disposition de boues métalliques a été estimé, tout comme la faisabilité de l'application de ce procédé pour enlever les métaux de façon effective et économique.

Les résultats obtenus dans cette étude ne donnent pas seulement un procédé pour traiter les sols contaminés, de ce fait, réduisant directement le volume de l'eau contaminée produite, mais offrent également une nouvelle approche pour traiter les résidus de déchets complexes produits pendant différents procédés industriels.

Mots-clés

Décontamination de sol; Lavage de sol; Acides inorganiques; Lixiviat acide; Membranes de NF; Caractérisation de membrane; Perméabilité de l'eau; Perméabilité dynamique; Rétention métal-ion; Procédé électrochimique; Enlèvement d'ion métallique

CHAPTER I

INTRODUCTION

1.1 Problem statement

Soils are multi-component systems, which contain a mixture of organic and inorganic pollutants from different sources and interact with different environmental medias (Manouchehri *et al.,* 2006). These interactions have provoked the accumulation of more pollutants due to their transport from source to source and their accumulation and retention (Bridges and Van Baren, 1997). Among the pollutants, metals in particular are considered harmful to the environment, since they do not biodegrade and remain in the soil for many years, until they are transported by different chemical and/or physical mechanisms to a different environmental compartment (Hong *et al.*, 2002; Molinari *et al.*, 2007). Consequently, a number of processes have been developed to remove metals from soil, including physical, chemical and biological treatments. However, soil decontamination has remained a challenge, because many technologies are expensive, disruptive and efficient for only certain contaminants and concentrations. As a result, attention has been diverted towards the development and application of reliable, affordable and environmentally friendly technologies.

Technologies such a soil washing have been used in order to remove metals from the solid phase to a liquid matrix. They have brought many advantages not only for their successful implementation in the removal of toxic metals contaminated soils, but also for the fact that the clean soil can be returned to the affected site, and the contaminants can be reduced to regulatory limits or perhaps below those limits (Masscheleyn *et al.*, 1999; Peters, 1999). On the other hand, the washing process itself produces large volumes of contaminated wastewaters that must be treated by another remediation technique (Molinari *et al.*, 2007; Sikdar *et al.*, 1998).

Consequently, separation processes for the removal of metal ions from aqueous solutions, such as membranes filtration (reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF)), can represent a good alternative. These technologies have been effectively implemented for the removal of metals coming from various industrial applications (pharmaceutical, biotechnology, chemical and so on), complying with the increasingly stringent standards enforced in some countries. Additionally, these techniques can offer benefits such as low operational costs, conceptual simplicity, modularity and optimal quality of treated water (Molinari *et al.*, 2004).

Hence, the conjunction of both technologies can be a significant advance in soil decontamination, because of the possibility of removing different types of pollutants. While the NF concentrate remains a challenge, because most of the cases resulted in unusable waste, a new approach, an electrochemical treatment, can be applied to decontaminate the concentrated waste solution. This new treatment not only is able to remove toxic metals in high percentage without production of metallic sludge residue from different effluents but also reduce the operating cost when is applied in large scale application.

Therefore, the aim of this work is to update theoretical and practical knowledge with the scope of developing and optimizing an economic process for soil decontamination by combining chemical leaching, nanofiltration membranes and an electrochemical treatment.

1.2 Context of the thesis

The objective of this research was to reduce environmental risks arising from metal pollution in soils that consisted of the removal of metal ions from contaminated soil using a combination of techniques, namely soil washing followed by the application of nanofiltration membranes and electrochemical treatments.

The research was divided into three phases. The first phase deals with selecting and treating a contaminated soil with inorganic acids (HCl, H_2SO_4 and a combination of H_2SO_4-NaCl) to produce the leachate solutions. The second phase evaluates two NF membranes according to their ability to recover metals using the three acidic leachates, previously mentioned. The third phase involves the application of electrochemical process in order to decontaminate the concentrate produced by the NF treatment.

More specifically, the selected soil for this study comes from the Pointe-aux-Lièvres site, located in Quebec City. This site is mainly contaminated by metals, due to industrial activities. According to the methodology proposed for this research, the soil will be treated with HCl, H_2SO_4 and a combination of H_2SO_4-NaCl (pH approximately of 2), which will be used to extract the metals from the soil. These washing agents were selected due to their effectiveness in the removal of metals from the soil, their low cost for soil remediation and their rapid remediation process (Djedidi *et al.*, 2005). Consequently, these solutions will be treated by two commercial NF membranes (Desal 5 and NF-270). The selection of these membranes was based on the fact that they presented different surface charges. Desal 5 was a negatively-charged membrane, and NF-270 was positively charged when the pH > Ip. Also, both membranes presented a wide pH resistance, ranging between 3 and 11 (Platt *et al.*, 2004; Tanninen *et al.*, 2004). In this part, membrane performance will be evaluated and will be expressed by water permeability, dynamic permeability, ionic separation, membrane interaction with pollutants and membrane fouling. Finally, in order to treat the concentrate produced by the nanofiltration treatment, an electrochemical process will be applied. This treatment will be applied for this research due to its effectiveness in the removal of metals from solutions and its low cost compared to other technologies. During this phase, the performance of this process using solutions with high concentration of toxic metals will be investigated. For the experimental part, it is important to take into account that the concentrate is coming only from the membrane Desal 5. This membrane was selected for this experiment due to its better performance in terms of permeability and ionic retention, compared with NF-270 membrane.

1.3 General objective

The general objective of this research was to apply a membrane process for the removal of metal ions resulting from an acidic leachate produced during soil decontamination. In order to achieve this general objective, the following specific objectives were pursued:

1. To chemically characterize the leachate produced during soil decontamination using different analysis such as ICP-AES, ionic chromatography, oxydoreduction potential, conductivity, AAS, etc. Additionally, to predict the forms of the metals present in the effluents by the software MINEQL$^+$ that will contribute to the analysis of the chemical characterization.
2. To select and to study the performance and behaviour of each membrane under several conditions using a specific leachate produced during soil decontamination. The membranes will be selected based on structure and acidic separation considerations.
3. To evaluate the potential of membrane technologies for the recovery of different metals after chemical leaching.
4. To evaluate the effectiveness of electrochemical deposition in the treatment of the NF concentrate.
5. To reach low levels of toxic metals in the wastewater based on government and local (community) standards.

6. To recover metals for beneficial further use and to reuse water from membrane processes.

These objectives were met by conducting a number of successive studies, for which each finding was reapplied to the subsequent experiments.

1.4 Thesis structure

This thesis is composed of six chapters, including an introduction, literature review, three scientific articles, conclusions and suggestion for future works.

The organization of the thesis is as follows:

CHAPTER 2 gives a general literature review concerning this research study, followed by the general objective and a listing of the specific objectives.

CHAPTER 3 deals with the treatment of an acidic leachate containing metal ions with nanofiltration membranes. This paper has been published in *Separation and Purification Technology*.

This chapter presents the experiment results for the preparation of the acidic leachate (pH = 1.97), coming from a contaminated soil using HCl as a washing agent to extract metal from the soil, as well as the results from the treatment of the leachate by NF membranes using two different types of membranes, Desal 5 and NF-270. Furthermore, the membrane performance is investigated for its use with a NaCl-HCl solution at different pH and with the main solution of this research, the HCl-leachate solution.

CHAPTER 4 describes the removal of metal ions from an acidic leachate solution by nanofiltration membranes. This paper was accepted for publication in *Desalination*.

The main objective of this paper was to study the performance of two nanofiltration membranes (previously mentioned in Chapter 1) when used with the acidic leachate (pH = 3.15) prepared with H_2SO_4 as a soil-washing agent. To study membrane performance, different criteria were evaluated, such as membrane permeability and ionic retention in the tank and permeate, and different operating conditions were taken into account, such as pressure, flow rate and pH.

CHAPTER 5 deals with the effectiveness of soil washing, nanofiltration and electrochemical treatment for the recovery of ions from a contaminated soil. This paper was submitted to *Water Research* journal.

For this investigation, laboratory experiments were conducted in order to study the performance of three technologies applied to decontaminate the soil: first of all, soil washing to evaluate the extraction efficiency of metal ions using HCl and H_2SO_4-HCl as washing agents. Second the influence of the leachate solution on the nanofiltration membranes performance, in terms of ionic retention and membrane permeability. During this filtration treatment, only the Desal 5 membrane was studied, due to its better performance with inorganic pollutants, compared with the NF-270 membrane. Finally, the application of electrochemical process to evaluate the effectiveness of this technology applied to decontaminate the concentrate produced by the NF treatment. In this case, it was introduced an economic study of this treatment in terms of energy consumption and sludge disposal.

CHAPTER 6 gives the main conclusions and offers comments based on the findings of the investigation. It concludes by suggesting future research work.

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CHAPTER 2

LITERATURE REVIEW

Over the past five decades, the world has released 22 000 tons of cadmium, 939 000 tons of copper, 783 000 tons of lead and 1 350 000 tons of zinc into the environment. According to the National Pollutant Release Inventory (NPRI), about 33 tons of cadmium, 13 300 tons of copper, 1 300 tons of lead and 9 500 tons of zinc have been released to the air, water and soil (NPRI, 1995) in Canada. Once released, these elements circulate in the environmental media (soil, water and air) and become bioavailable to plants, animals and humans. Principally, metals affect human health, because humans are exposed to metals in soil through the food chain and by direct ingestion of soil particles, inhalation or skin contact (Bertin and Averbeck, 2006; Satarug and Moore, 2004).

Many of these metals at numerous government and private sites have been found to be toxic, mutagenic and carcinogenic (Harvey *et al.,* 1990). For example, cadmium is known to cause renal and bone injuries (Bertin and Averbeck, 2006; Satarug and Moore, 2004) and osteoporosis (Järup and Alfvén, 2004; Staessen *et al.,* 1999). Also, according to the International Agency for Research on Cancer (IARC), cadmium has been classified as a carcinogen (Bertin and Averbeck, 2006; Waalkes *et al.,* 1991). Lead can cause neurological and behavioural disturbances in children (WHO, 1995) as well as intellectual impairment in children (Canfield *et al.,* 2003). Arsenic is a strong carcinogen that produces skin cancer and cancer of various internal organs (NRC, 2001). Table 2.1 summarizes the toxicity of some metals following chronic exposure.

Sources of soil contamination include rapid industrialization, increased anthropogenic activities, modern agricultural practices and faulty waste disposal methods that cause serious environmental and health issues (Hani, 1990). Table 2.2 gives an example of the main metals found in some industries (Dean *et al.,* 1972). According to the US Environmental Protection Agency's (US EPA) through the list of priority pollutants cadmium, copper, lead, mercury, nickel and zinc are considered the most hazardous pollutants. Consequently, soils have suffered from degradation produced by the deposition of toxic metals in the soil system, which leads to their accumulation and creates a long-term impact on the soil (Bridges and Van Baren, 1997).

For that reason, this contamination has resulted in restricted utilization of some sites and, in some cases, a complete prohibition on cultivation or other potential use of the area. Therefore, a necessity to remove the contaminants from the soil through different approaches has come about in order to remove the potential sources of contamination and to create strict regulations. Table 2.3 presents the inventory of contaminated terrestrial sites in some industrialized countries.

Table 2.1 Target organs of some metals and their compounds after chronic exposure (adapted from Wardenbach, 2006)

Target organ	Metal and metalloid													
	As	**Be**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Hg**	**Mn**	**Mo**	**Ni**	**Se**	**Ti**	**Pb**
Liver	■						■			■			■	
Respiratory Tract	■	■	■	■	■		■				■		■	■
Blood	■					■						■	■	■
Nerves								■	■				■	■
Kidney	■		■					■		■			■	
Skin	■	■			■						■			■
Reproductive Organs												■		
Heart				■			■						■	

Table 2.2 Metals found in major industries (adapted from Dean *et al.*, 1972)

Industry	Inorganic contaminant														
	Al	Ag	As	Cd	Cr	Cu	F	Fe	Hg	Mn	Pb	Ni	Sb	Sn	Zn
Pulp, paper, paperboard, building paper, board					■	■			■		■	■			■
Organic chemicals, petrochemicals	■		■	■	■		■	■	■		■				■
Alkalis, chlorine, inorganic chemicals	■		■	■	■		■	■	■		■				■
Fertilizers	■		■	■	■	■	■	■	■	■	■	■			■
Petroleum refining	■		■	■	■	■	■	■			■	■			■
Basic steel works, foundries			■	■	■	■	■	■	■		■	■	■	■	■
Basic non-ferrous metal-works foundries	■	■	■	■	■	■	■		■		■		■		■
Motor vehicles, aircraft-plating, finishing	■	■		■	■				■			■			
Plate glass, cement, asbestos products, etc.					■										
Textile mill products					■										
Leather tanning, finishing processes					■										
Steam generation power plants					■										■

Table 2.3 Inventory of contaminated terrestrial sites in some industrialized countries (adapted from White and Claxton, 2004)

Country	Total area (km^2)	Population (millions)	Number of contaminated sites	Sites per 1000 km^2	Sites per 10^6 people
Canada	9 976 140	31.6	15 000-40 000	1.5-4.0	475-1266
United States	9 656 345	288.4	45 516	4.7	157.8
Current NPL sites			1 238	0.1	4.3
Germany	356 910	82.8	202 880	568.4	2450.2
Denmark	43 090	5.3	37 000	858.7	6981.1
Switzerland	41 290	7.3	35 000	847.7	4794.5
Austria	83 850	8.1	28,000	333.9	3456.8
Finland	338 130	5.2	10 396	30.7	1999.2
Belgium	30 518	10.2	7 728	253.2	757.6
Sweden	449 960	8.9	7 000	15.6	786.5
Spain	504 780	40.0	4,902	9.7	122.6
Norway	323 900	4.5	2 121	6.5	471.3
Lithuania	65 300	3.6	4 430	67.8	1230.6
Romania	238 381	22.4	1 634	6.9	72.9
Estonia	45 227	1.4	1 565	34.6	1117.9

2.1 Soil protection and contaminated site rehabilitation policy

Soil cleanup has become a major concern in industrialized countries, and the application of reliable techniques is necessary in order to remove the contaminants. However, some techniques have brought disappointing results due to high cost, long decontamination process, large volumes of liquid wastes and harmful effects on soil structure and fertility. In addition, some techniques have been effective for certain concentrations only (Ho *et al.*, 1995; Krämer, 2005), and have resulted in the transferring of pollution to other environmental media. For this reason, many companies have tended to postpone cleanup operations as long as possible, either by delaying expenditures or by waiting for new developments (Boopathy, 2000). These considerations have led the government to develop different approaches for soil cleanup, such as the imposition of stricter regulations to address the effectiveness and efficiency of soil remediation.

For example, in the United States management of the environment is a collective responsibility of federal and state governments (De Sousa, 2001). Sites are cleaned up under the supervision of government agencies such as the United States Environmental Protection Agency. US EPA satisfies the requirements of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) known as Superfund. Sites not on the Superfund list need to satisfy federal and state requirements for cleanup operations. In addition, through regulations such as the Clean Water Act (control of water discharges from soil-washing activities), the Resource Conservation and Recovery Act (RCRA) (control of hazardous wastes), and the Superfund Amendments and Reauthorization Act (SARA) (importance of permanent remedies and innovative treatment technologies in cleaning up hazardous waste sites), pollution is regulated and controlled to improve soil quality (De Sousa, 2001). US EPA has estimated that approximately more than 20 million cubic yards of soil at current NPL (National Priorities List) are contaminated with metals (Griffiths, 1995).

In Canada, the provinces and territories are responsible for developing site-specific cleanup approaches. For example, in Quebec, the provincial government, through the Ministère de l'Environnement et de la Faune du Québec (MEFQ) has provided guidelines for soil rehabilitation. According to MEFQ and the document "Soil Protection and Rehabilitation of Contaminated Sites" approximately 150 sites are contaminated with metals, representing an average volume of 17,500 m^3 and a total volume of 2,625,000 m^3 of soil to be restored (MEFQ, 1999). Therefore, the MEFQ has established controls to preserve the health of future users and protect the environment (MEFQ, 1999). Table 2.4 presents the grid of generic criteria (A, B, C) for soils given by the MEFQ. These letters represents the maximum concentration for each type of land used. The levels (A, B, C) may be defined as follows:

- **Level A**: Natural concentration or normal levels of inorganics in the soil.

Range A: At this level, the soil is slightly contaminated. It is not necessary to decontaminate the soil; however, it is convenient to know the sources of contamination and verify if new sources of contaminants exist. Soil with this type of contamination can be used for residential purposes. On the other hand, it will be necessary to take protective measures (excavation of a surface layer, addition of a layer of clean ground, etc).

- **Level B**: Maximum tolerable levels for residential, recreational and institutional sites (hospitals, schools and daycare centers), including commercial sites located in residential districts.

Range B-C: At this level, the soil is considered contaminated. However, the soil will not automatically be subjected to decontamination, unless the impact of the contaminants on the groundwater does not require such type of work. This level of contamination restricts its use on certain levels. Consequently, restoration could be necessary before this soil is used for agricultural, residential or recreational purposes. Other uses, such as industrial and commercial activities, could however be considered without necessarily undertaking restoration techniques.

In all cases, it is necessary to take into account that the decontamination to be carried out depends on the nature of the contaminants, the intended soil use and the impact on both the groundwater and the surrounding environment.

- **Level C:** Maximum acceptable limit for industrial sites and for commercial sites not located in a residential area. At this level, it is necessary to take action to decontaminate the soil.

Range > C: At this level, the soil is entirely contaminated and it will be necessary to carry out a detailed study and restoration process before allowing any use of the soil. This soil cannot be used for any purpose.

According to the MEFQ, the levels presented in Table 2.4 indicate that soils having a higher level of contamination than these must be treated, excavated and managed carefully, until the concentration of metals diminishes or remains equal to the generic criteria values.

Table 2.4 Grid of generic criteria for soils (adapted from MEFQ, 1999)

Metal and metalloid	Soil criteria (mg/kg) of dry material		
	A	B	C
Silver (Ag)	2	20	40
Arsenic (As)	6	30	50
Barium (Ba)	200	500	2000
Cadmium (Cd)	1.5	5	20
Cobalt (Co)	15	50	300
Total chromium (Cr)	85	250	800
Copper (Cu)	40	100	500
Tin (Sn)	5	50	300
Manganese (Mn)	770	1000	2200
Mercury (Hg)	0,2	2	10
Molybdenum (Mo)	2	10	40
Nickel (Ni)	50	100	500
Lead (Pb)	50	500	1000
Selenium (Se)	1	3	10
Zinc (Zn)	110	500	1500
Available bromide (Br^-)	6	50	300
Available cyanide (CN^-)	2	10	100
Total cyanide (CN^-)	2	50	500
Available fluoride (F^-)	200	400	2000
Total sulphur (S)	400	1000	2000

2.2 Soil, metals and restoration techniques

Soils are natural mixtures of mineral and organic particles and their derivatives, which contain different types of weekly- and strongly-bonded pollutants (Masscheleyn *et al.,* 1999). The typical particle size of soil distributions are: oversize fraction, sand fraction (74 µm) and fine particle, which consists of materials smaller than the size of silt (Mann, 1999).

Pollutants frequently remain in the upper horizons and in trapped phases as a residual (Wang and Mulligan, 2004) where they cause adverse effects on microbial activities in soil and crop productivity, thereby resulting in the added risk of contamination of the food chain. More specifically, several contaminants are concentrated in the fine particle fraction, while lower concentrations of the main contaminants are usually found in the sand and oversize fractions (Ko *et al.,* 2005). Generally, metals are bound to the soil because cationic metals associate with the anionic components of the soils (Wang and Mulligan, 2004), such as colloidal clays and humus. These are present in the soil in several chemical forms and bindings, which can influence their reactivity with the soil and therefore affect not only the mobility and bioavailability of metals, but also the pH and organic matter content of the soil (Abollino *et al., 2006*). For example, copper is mainly organically bound and exchangeable, cadmium and zinc are principally organically bound and are exchangeable and water soluble, while lead is slightly mobile and strongly bound to the residual fraction (Mulligan *et al.,* 2001). In soils, metal ions can be present in different forms, such as soluble compounds like ions and metal complexes or as exchangeable forms. Also, they can be immobile, because they are associated to different soil fractions and compartments, such as carbonate, oxide, hydroxide, organic matter and residual materials (Tan, 1998). The availability and mobility of metals are controlled by several factors such as:

- Soil chemical properties. For example: pH and redox potential, which in turn can affect the chemical speciation and solubility (Lindsay, 1979);

- Solute-solute interactions. For example, metal complexation with either organic or inorganic species (Vulkan *et al.*, 2002). Metal complexation reactions and metal–soil interactions are consecutively affected by pH and redox conditions, which affect metal solubility (McLean and Bledsoe, 1992);
- Surface characteristics of soil (pore fluid chemistry) and metal-soil interactions, which influence sorption reactions (Sparks, 2005);
- Physical properties of soil that have an effect on water movement (Camobreco *et al.*, 1996);
- Bond strength. For example some metals with weak bond strength can be mobilized more easily than metals with a stronger bond strength (Masscheleyn *et al.*, 1999).

Knowing the type and concentration of the metals and their distribution in the various particle size fractions could be a key factor in predicting soil contamination and treating the soil. It is also important to know the background information about the soil, which can provide important insight regarding possible treatments that can help decontaminate the soil. Nevertheless, the choice of a soil treatment depends on several factors, such as the chemical structure and concentration of the present pollutants, the characteristics of the soil (e.g., its granulometry, porosity and humic matter content), the geology of the site, and the presence of groundwater (Hamby, 1996). Principally, the extraction of metals from soil is a complex task, because metals are difficult to decompose either biologically, chemically, or by physical treatment (Bosecker, 2001). The options for soil decontamination can be divided into four categories: biological treatments, including bioremediation and phytoremediation; chemical treatments, including solidification/stabilization; physical treatments, including flotation, density or gravity separation, particle size separation, magnetism and gravimetric method; or a combination of these as a physicochemical treatment, namely soil washing. Nevertheless, the review of literature demonstrates that current technologies must be developed to achieve a low-cost remediation process and an ecological alternative which does not alter the physical and chemical properties of soils.

The goal of soil treatments should be to reduce the metal content in the soil medium, so that these metals no longer pose potential hazard to public health and the environment. In their investigations, US EPA (1997) and Mulligan *et al.* (2001), described several available and current remediation technologies for soils contaminated with metals. Table 2.5 gives the cost of some soil remediation techniques.

Table 2.5 Cost of some soil remediation technologies (adapted from Mulligan *et al.*, 2001)

Soil remediation technique	Description	Cost ($US/Ton)
In situ		
Bioremediation	Use of micro-organisms to remove different pollutants	15-200
Soil flushing	Use of water or chemicals to extract the metals	100-200
Solidification/Stabilization	Mobility reduction of metal by addition of an agent that solidifies and then immobilizes the metals	30-250
Phytoremediation	Use of plants to extract the metal from the soil	50 000 -200 000 (acre)
Vitrification	Application of electrical energy to vitrify the pollutant	400-870
Ex situ		
Physical separation	Includes: froth flotation, gravity separation, screening, etc.	60-245
Soil washing	Addition of water and additives to solubilize the pollutants	25-300
Pyrometallurgical separation	Use of elevated temperature to extract metals	200-1000
Electrokinetic	Application of electrical current	No information

2.3 Soil washing

Among the more popular remediation processes, soil washing has been widely used to remove toxic metals. According to US EPA (US EPA, 2001), this technique is applied to large contaminated areas, because of its rapid kinetics, ease of operation and economic efficiency (Tuin and Tels, 1990).

Soil washing is the transfer of contaminants to the liquid phase through desorption and solubilization (Peters, 1999) (Figure 2.1). This technique generates a large volume of toxic liquid waste that must be treated before it is discharged along with desorbed pollutants requiring disposal and/or subjection to further treatments for complete detoxification (Mann, 1999).

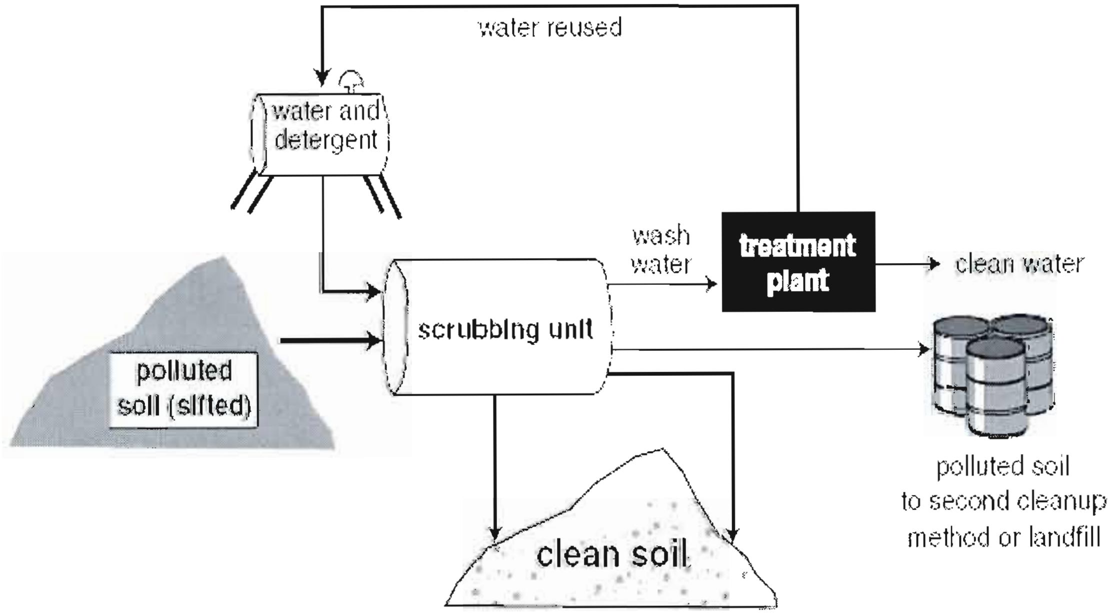

Figure 2.1 Schematic diagram of Soil Washing (US EPA, 2001)

The efficiency of this technique depends chiefly on the target contaminants, bond strength, characteristics of the soil and selection of a good extractant or washing agent that will increase metal solubility, which helps raise the concentration of cations in the leachates (Davis and Singh, 1995; Min *et al.*, 2007). The most commonly used washing agents are: inorganic salts (potassium phosphate, potassium chloride, potassium nitrate, potassium sulphate or sodium perchlorate), inorganic acids (sulphuric acid, nitric acid, phosphoric acid, hydrochloric acid or mixed acid) organic acids (citric or acetic acids) and alkaline agents (sodium hydroxide) (Cline and Reed, 1995; Neale *et al.*, 1997; Reed, 1996; Tuin and Tels, 1990).

During the removal of metals by dissolution with a soil washing agent, extraction is affected by:

- pH. The extraction of metals increases with increasing acid strength. Generally, the acid extraction occurs when the pH drops below 6;
- Valency of the element removed. For example, metals with a valence of two are generally more soluble at a low pH (Kuhlman and Greenfield, 1999). Therefore, metals such as mercury (Hg), lead (Pb) or cadmium (Cd) can be extracted using acids;
- Metal-soil particle bond. Metals with weak bond strength can be mobilized and solubilized by the washing agent and be available for uptake. On the contrary, metals bonded strongly to soil minerals are less exchangeable (Ko *et al.*, 2005). Also, it is important to understand the chemical forms of metals for the remediation process;
- Size of soil particles. Since fine particles have a high surface area, they absorb more contaminants; therefore, contamination levels in fine particles are high. On the other hand, extraction of toxic metals in fine particles is very poor, and toxic metals are available for uptake in the ecosystem (Ko *et al.*, 2005);

- Separation of particles. When fine particles are properly separated from the soil, the efficiency of soil washing can increase.

Even though strong acids are effective in the removal of toxic metals from the soil, these agents are not environmentally friendly since they are toxic and disturb the physical, chemical and biological properties of soils. Thus, it is necessary to apply a reliable wastewater technique in order to decontaminate the wastewaters produced by these treatments.

2.4 Pressure-driven membrane processes

The pressure-driven membrane process is a promising and growing technology that has been applied successfully in various industries (drinking water production, textile industry, food industry, mining industry, metallurgical industry, etc.). This technique offers a purified product, outstanding quality of permeate, moderate temperatures (varies according to the system), no added chemicals to the system and generally low energy requirements, according to its application (Van der Bruggen *et al.*, 2003). Membrane filtration can be classified according to different criteria, such as membrane permeability, applied pressure, chemical nature of the membrane, rejection and separation mechanism of particles and membrane application (Sikdar *et al.*, 1998). Its performance can be affected by different factors (Capar *et al.*, 2006):

- Characteristics of the membrane, such as molecular weight cut-off, porosity, charge of the membrane and hydrophobicity;
- Solute characteristics, such as pH, hardness, organic matter, etc.;
- Operating conditions, such as flow rate, pressure and separation rate.

Depending on the size of particle that can be retained, various types of membrane filtration can be employed for metal removal, such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). They are presented as follows:

2.4.1 Reverse osmosis (RO)

RO membranes are also known as ultra-low-pressure membranes. Their pore size is as small as 10^{-4} µm (Bohdziewicz *et al.*, 1999). They are dense membranes without predefined pores. Therefore the rejection and separation is due to the diffusion-solution mechanism. RO are the finest, and/or tightest, level of aqueous filtration available today.

RO have the lowest permeability compared to other membranes, and bear the highest pressure (between 1 400-6 800 kPa). Consequently, high energy consumption is required. RO works efficiently with a pH range of 3-11 (Madaeni and Mansourpanah, 2003).

2.4.2 Nanofiltration (NF)

Nanofiltration has a performance characteristic between that of ultrafiltration and reverse osmosis. NF membranes have a pore size measuring approximately 1 nm in diameter with fixed charges developed by dissociation of groups as sulphonated or carboxyl acids. They can vary according to morphology, material separation mechanisms and applications.

Typically, NF membranes are either positively or negatively charged and are therefore ion permselective. During NF, transport is influenced by different mechanisms, such as convection (applied pressure difference over the membrane), diffusion (concentration gradient across the membrane) and charge effects (electrostatic repulsion between ions or charged molecules and the membrane surface). The separation process involves a combination of charge (Donnan exclusion) and size exclusion (sieving mechanism) (Childress and Elimelech, 2000). The combination of these mechanisms allows a high rejection of multivalent ions and a relatively small amount of organic solutes combined with a low retention of monovalent ions.

The advantage of using an NF membrane is that it requires lower operating pressures (between 350 and 1 000 kPa), it has higher fluxes than RO membranes, it has better retention than a UF membrane and it can effectively remove metal ions at a wide pH range of 3-8 (Madaeni and Mansourpanah, 2003). Principally, the pH of the solution affects the membrane charge; that varies according to various pH values. Therefore, NF membranes are positively charged in acidic conditions and negatively charged in neutral and alkaline conditions (Rautenbach and Gröschl, 1990). Generally, acids can permeate the membrane easily. On the other hand, monovalent ions can be more or less retained, depending on the feed solution, Donnan effects and sieving mechanism. At a low pH, the selectivity of the membrane can be affected by the protonation and deprotonation of the functional groups of the thin film (Childress and Elimelech, 2000).

2.4.3 Ultrafiltration (UF)

Ultrafiltration membranes are porous membranes. The pore size is approximately 5-20 nm, the range of operating pressure is between 70 and 500 kPa, and the molecular weight of the separating compounds is between 1 000 and 100 000 Da. (Vigneswaran *et al.*, 2004). These unique characteristics enable UF membranes to allow the passage of water and low-molecular-weight solutes, while retaining the macromolecules, which have a larger size than the pore size of the membrane (Sablani *et al.*, 2001). The major dominating mechanism in UF separation is sieving. UF membranes have been amply used in water and wastewater treatment processes, as well as in the pharmaceutical and liquid food industries.

2.4.4 Microfiltration (MF)

MF is the oldest filtration process, and it has been applied in a variety of industrial applications, such as biotechnology and the pharmaceutical industry (Haneda *et al., 2006*). Compared to the other membranes, this membrane has the largest pores and the highest permeability, ranging from 0.1 μm to 10 μm (Fabris *et al.*, 2007). Therefore, lower pressure is applied and less energy is consumed than in other membrane filtration processes. MF is applied to separate fine particles, colloids, and micro-organisms (Fabris *et al.*, 2007). The principal mechanism involved in particle retention is therefore sieving.

2.4.5 Membrane fouling

Among all membrane processes, fouling is one that presents major challenges in membrane applications, because it causes significant loss of productivity as flux declines, a possible decrease in permeate quality, and an increase in operational cost (higher energy demand and a shorter membrane life)(Akbari *et al.*, 2002).

Fouling is produced by the accumulation of rejected inorganic or organic components, colloids, bacteria or suspended solids, which can generate membrane pore plugging and external pore blocking (Van der Bruggen *et al.*, 2002). When fouling occurs, an increase in applied pressure and the need for frequent cleaning or replacement becomes an essential option. Membrane fouling has been amply investigated by numerous researchers (Kwon *et al.*, 2006; Lee *et al.*, 2004; Peng *et al.*, 2004; Rice *et al.*, 2006; Shon *et al.*, 2004).

Fouling can be reversible (external) or irreversible (pore blocking fouling). Reversible fouling occurs when the membrane recuperates the flux after cleaning (Van der Bruggen *et al.*, 2002). Contrarily, irreversible fouling occurs in three different ways:

- Particle pore blocking, which has approximately the same size as the pore size;

- Incomplete pore blocking (intermediate fouling);
- Standard pore blocking, meaning the pores are continuously narrowed by particles smaller than the pore size (Knyazkova and Maynarovich, 1999).

The types of membrane fouling include (Van der Bruggen *et al.*, 2002):

- Scaling: precipitation of inorganic salts in the feed water;
- Colloidal fouling: clay minerals, colloidal silica, iron, aluminum, manganese oxides, organic colloids and suspended matter, and calcium carbonate precipitates;
- Chemical reaction of solutes and the membrane boundary layer or with the membrane polymer;
- Adsorption of low-molecular-weight solutes at the membrane polymer;
- Bacteria fouling.

Principally a serious problem in NF and RO systems is scaling formation. As mentioned before, scaling is produced when spare inorganic compounds exceed their solubility product and precipitate on the membrane surface, thereby decreasing membrane permeability. Therefore higher feed pressure must be applied in order to maintain the desired flux, and consequently the membrane must be cleaned more frequently, thus increasing the operational cost of the membrane. The most common compounds in scaling formation are calcium carbonate, calcium sulphate, silica, calcium phosphate and barium sulphate (Bremere *et al.*, 1999; Schaefer *et al.*, 2004). Figure 2.2 shows the scale formation mechanism for NF membranes (Shon *et al.*, 2004).

The precipitation mechanism of scaling depends on many factors, such as pH, temperature, and the presence of different metal ions in the bulk solution that will provoke concentration polarization. However, it involves two major mechanisms (Bremere *et al.*, 1999; Schaefer *et al.*, 2004):

- Surface crystallization: When minuscule particles (nuclei) are formed at specific sites, for example in the pores and/or at the membrane surface (blockage of the membrane surface), a decline in flux is produced;
- Bulk crystallization: The forming ions diffuse to the crystal surface and attach themselves to the membrane surface, leading to a decline in flux.

No reliable methods of predicting and/or monitoring scaling in RO and NF membrane systems exist. On the other hand, several alternatives exist to reduce scale formation, such as increasing the fluid velocity, adding antiscalants, performing chemical pretreatments, and applying microfilters to remove organic particles.

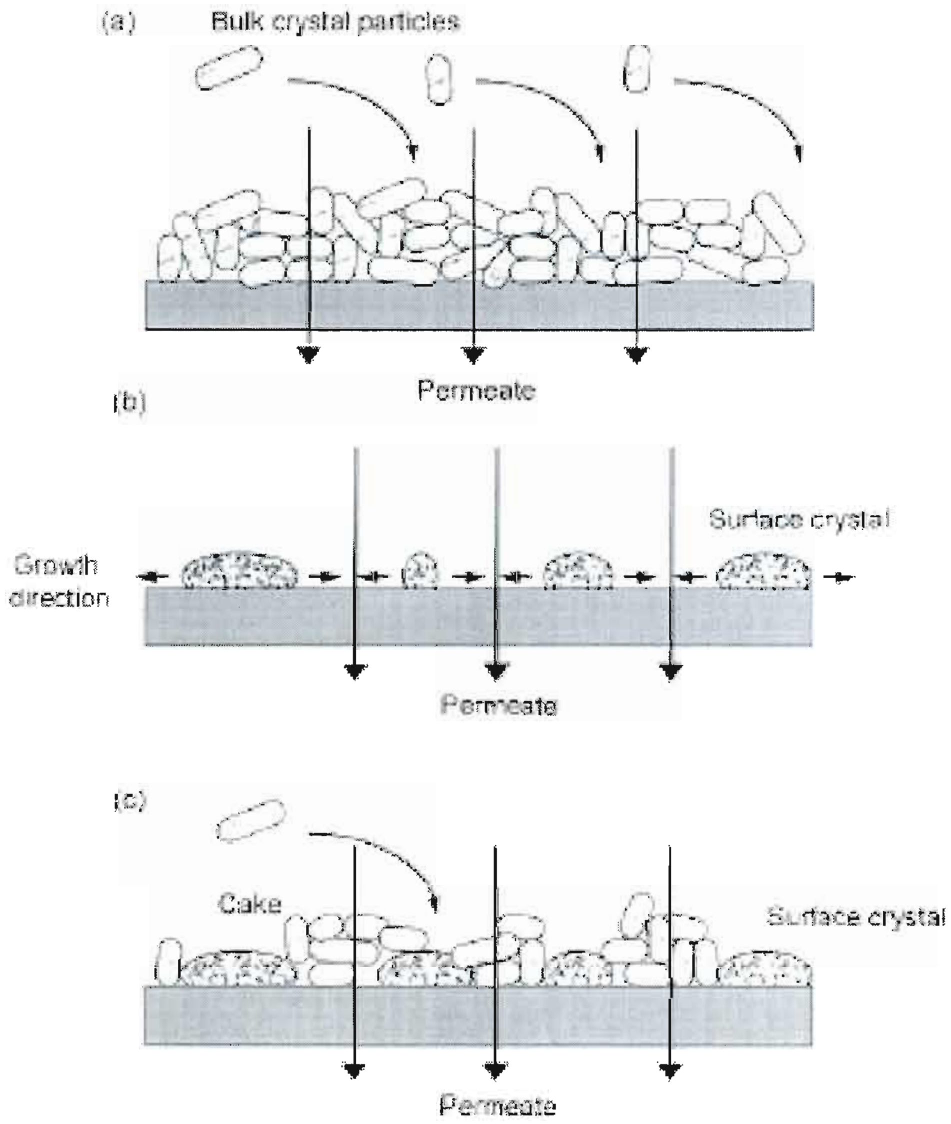

Figure 2.2 Scale formation mechanisms in NF. (a) Cake formation by bulk crystallization. (b) Surface blockage by surface crystallization. (c) Both mechanisms

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CHAPTER III

TREATMENT OF AN ACIDIC LEACHATE CONTAINING METAL IONS BY NANOFILTRATION

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3.1 Abstract

An acidic leachate obtained from a contaminated soil was generated using hydrochloric acid (HCl) as a soil washing agent and treated by nanofiltration membranes. This solution was studied in terms of different parameters, such as transmembrane pressures and flow rate, to evaluate membrane permeabilities and ion separation. The experimental results showed that the application of NF membranes is a promising alternative for the removal of metal ions from washing-solutions. For example, both membranes demonstrated a retention capacity higher for multivalent ions such as Al^{3+}, Ca^{2+}, Mg^{2+} and Mn^{2+} (between 84 and 100%) compared to monovalent ions such as K^+ and Na^+ (less than 68%). Additionally, variation in dynamic permeability using the acidic leachate solution due to concentration polarization is presented. Furthermore, the permeation of NaCl-H_2O solutions at different feed pH values (5.8, 3.7 and 2.2) was investigated.

This study will not only outline a process for treating contaminated soils and waste waters directly but will also offer a new approach to treating industrial residues produced during mining or leather processes.

Keywords

Leachate; NF membranes; Dynamic permeability; Metal ion removal; pH

3.2 Introduction

Enormous quantities of pollutants are discharged into the soil as a result of different human activities such as dumping of hazardous substances, wastes from industrial or/and chemical processes, and the spillage of different pesticides and fertilizers (Sikdar *et al.*, 1998) which represent a long-lasting source of contamination.

The principal contaminants found in the soil are the following: organic compounds (such as trichloroethylene (TCE), polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs)) and inorganic compounds such as toxic metals (e.g. cadmium (Cd), copper (Cu), zinc (Zn) and lead (Pb)) (Sikdar *et al.*, 1998). Both types of contaminants represent a great environmental concern because of their toxicity and persistence, affecting soil fertility and the complete ecosystem.

The main differences between them is that organic pollutants can be degraded by natural process while toxic metals are difficult to treat using biological chemical or physical treatments (Bosecker, 2001). In addition, the soil-metal remediation is one of the most difficult tasks for environmental engineering (Sun *et al.*, 2001).

The most frequent method for toxic metal-remediation is soil washing (Meunier *et al.*, 2002). Soil washing is an ex-situ technology characterized as inexpensive (Kuhlman and Greenfield, 1999). It is based on the desorption of pollutants using inorganic acids, organic acids, surfactants, biosurfactants, and the use of chelating agents or oxidative agents (Masscheleyn *et al.*, 1999; Mulligan *et al.*, 2001). These chemical agents help to increase the metal solubility and raise the cation concentration in the leachate produced (Davis and Singh, 1995). The result of this process is a complex waste water solution rich in metal ions (especially cations) that have to be decontaminated and/or disposed carefully.

It is therefore important to apply reliable remediation technologies in conjunction with soil washing to deal with the contaminants. Those techniques can include precipitation, coprecipitation, electrodeposition, electrocoagulation, membrane processes (e.g. reverse osmosis, nanofiltration, ultrafiltration and microfiltration), adsorption and biosorption, activated carbon adsorption (Patterson, 1989) or a combination of them. Among them, membrane processes, and particularly NF, can be promising alternatives for the removal of contaminants from wash-solutions of polluted soils. This process can bring about a successful wash-solution treatment which not only produces high quality permeates but which also can be run at lower pressures compared to RO membranes with lower operating costs.

For that reason, the principal objective of this study was to evaluate the effectiveness and feasibility of nanofiltration membranes (using two commercially-available NF membranes Desal 5 and NF-270) applied to an acidic leaching from contaminated soil.

3.3 Materials and methods

This research was divided in two phases. The first phase is the generation of the acidic leachate from a polluted soil. The second phase is the treatment of this solution by NF membranes.

3.3.1 Experimental soil

The soil sample was collected from the Pointe-aux-Lièvres site in Quebec, Canada. Some characteristics of the soil are summarized in Table 3.1. The fraction of soil (sand, silt and clay) superior to 20 µm (but less than 2 mm), which was obtained with a hydrocyclone, has been used for this work. The separation of the soil in fractions > 2 mm and < 2 mm was accomplished by sieving.

Table 3.1 Characteristics of soil used in this study

Component	Sand	Silt	Clay
Particle size (%wt)	73	21	6

3.3.1.1 Washing procedure

The extraction of metals from soils was performed using hydrochloric acid (HCl). This inorganic acid was used due to its inexpensive cost and because it is one of the most effective soil-washing agents (Neilson *et al.*, 2003). The leachate was prepared as follows:

Preparation of HCl leachate

500 g of soil were added to 5 L of water agitated by a variable speed mixer at 800 rpm (rotations per minute) with a stainless steel propeller (SS-316L, Labcor Technical Sales, Montreal, QC., Canada) fixed to a caframo RZR50 rotor (Labcor Technical Sales).

To this suspension was added 160 mL of HCl until a pH of 2 was obtained. This leachate was agitated for 2 hours. 5 mL of the reactant Percol E-10, an anionic polymeric solution (Ciba Specialty Chemicals Canada Inc., Mississauga, Ont.), was added to facilitate the decantation. This leachate was passed through a filter whatman no 4 (Whatman Bioscience Inc., Newton, MA, USA) under a vacuum, to remove large particles from the leachate solution. This acidic leachate was not subjected to pre-treatment to remove any type of foulants, including suspended solids or organic and inorganic colloids, as it was a virtually colorless solution. Subsequent to the generation of the acidic leachate, this solution was subjected to the treatment with NF membranes.

3.3.1.2 Membranes materials

The commercial nanofiltration membranes used in this study were Desal 5 membranes, manufactured by GE-Osmonics (Minnetonka, MN, USA). Desal 5 is a polymeric membrane, in which a polyamide selective layer is supported on a polysulfone layer (Bandini *et al.*, 2005). It is a positively charged membrane, with an iso-electric point of 4 and a pH resistance (20°) between 2-11 (Hagmeyer and Gimbel, 1998; Tanninen *et al.*, 2004). The other membrane used was NF-270 supplied by FilmTec Corporation (FilmTec Corporation, Dow Chemical Co., Midland, MI), which is a semi-aromatic piperazine-based polyamide layer on top of a polysulphone micro porous support reinforced with a polyester non-vowen backing layer. NF-270 is a negatively charged membrane (pH 3.5 and 7.7), with an iso-electric point of 3.3 and pH resistance (20°) between 3-11 (Hagmeyer and Gimbel, 1998).

3.3.2 Experimental set-up

The experiments were carried out in a laboratory scale set-up. The schematic diagram of the filtration equipment is illustrated in Figure 3.1. This apparatus was designed to test different membranes using the same operating conditions and also to test solutions using low pHs.

In this study, the experiments were realized in a batch mode with recirculation of substances. The feed solution from the tank was pumped through 4 different membrane cells (made of polyvinyl chloride (PVC)), obtaining itself a retentate that went back into the tank and a permeate that was collected into a beaker for permeate flux calculation. This permeate was not recirculated into the system. The effective membrane surface area of each membrane was 1.26×10^{-3} m^2.

The membranes tested were two of each type (NF-270 (4), (5) and Desal 5 (4), (5)) used for comparison purposes. Supplementary details about the experimental set-up can be found in the investigation made by Nöel *et al.*, (2000).

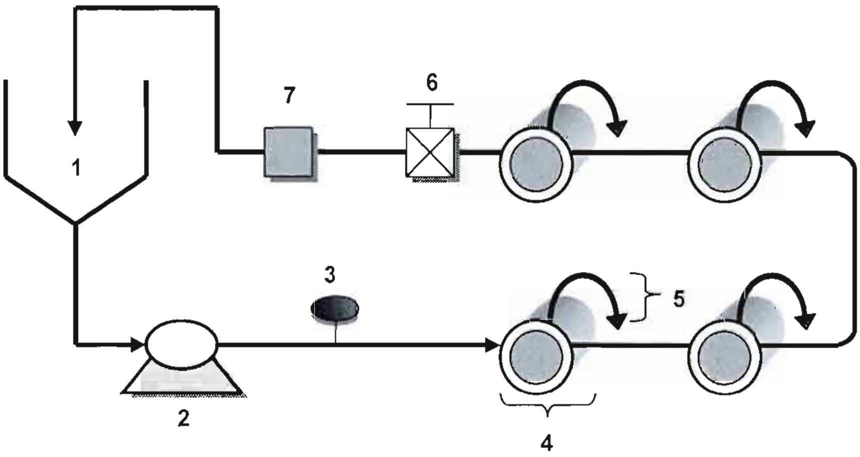

Figure 3.1 Schematic diagram of NF set-up

1. feed tank, 2. pump, 3. manometer, 4. membrane cell, 5. permeate outlet, 6. pressure valve, 7. flowmeter

3.4 Methodology

The membranes were characterized in terms of pure water permeability, dynamic permeability, and rejection of ions present in the solutions.

Before starting the experiments, the membranes were pressurized or compacted using deionized water at room temperature. The operating conditions used for membrane compaction were high pressure (1×10^6 Pa) and a constant recirculation flow rate (0.32×10^{-4} m^3/s) until the pure water permeability (A_{tpw}) was constant.

After the compaction, the pure water permeability of each membrane was measured before and after the test of each solution. The pressures used were 0.5×10^6, 0.8×10^6 and 1×10^6 Pa with a constant recirculation flow rate (0.32×10^{-4} m^3/s).

Following the measure of pure water permeability (A_{ipw}) the dynamic permeability (A_{id}) of the membranes was determined using NaCl-water solutions at different pHs (neutral, 3.7 and 2.2) adjusted with HCl at constant NaCl concentration (3.42×10^{-2} mol/l) and the principal solution of this study, the acidic leachate solution. The operating conditions--pressure and recirculation flow rate--utilized to measure dynamic permeability were the same as pure water permeability. The permeate flux values for pure water and the inorganic solutions including the leachate at different operating pressures were measured and plotted against applied pressure. It is important to note that the slope of the curve (straight line) was the value to determine the membrane permeabilities.

After the measure of membrane permeability, the system was rinsed with deionized water to diminish the experimental errors. The sequence of experiments is presented in Table 3.2

Table 3.2 Values of permeability (A_{ipw}) and dynamic permeability (A_{id}) of the membranes

	NF-270 ($\times 10^{-14}$)(4)		NF-270 ($\times 10^{-14}$)(5)		Desal 5 ($\times 10^{-14}$)(4)		Desal 5 ($\times 10^{-14}$)(5)	
	A_{ipw} (m)	A_{id} (m)	A_{ipw} (m)	A_{id} (m)	A_{ipw} (m)	A_{id} (m)	A_{ipw} (m)	A_{id} (m)
1. Compaction								
2. Water	2.51		2.61		0.72		0.69	
3. NaCl		2.37		2.45		0.93		0.87
4. Water	2.42		2.51		0.88		0.81	
5. NaCl + HCl		2.20		2.29		0.91		0.84
6. Water	1.82		1.74		0.86		0.79	
7. NaCl + HCl		1.71		1.81		1.21		1.13
8. Water	1.74		1.92		1.02		0.94	
9. Leachate		2.02		2.11		1.43		1.29
10. Water	1.72		1.85		1.13		1.03	

3.4.1 Reference solute

The reference solute used to prepare the inorganic solutions was NaCl. As mentioned before, HCl was used for pH adjustments. The chemicals were analytical grade, purchased from the Aldrich Chemical Company, Milwaukee, WI.

3.4.2 Sample analysis

The chemical analysis of the soil and aqueous solutions coming from feed and permeate were determined by a conductivity meter (model CDM 81, Radiometer, Copenhagen, Germany), a pH meter (Fisher Acumet model 915, Pittsburgh, PA), and plasma emission spectroscopy with a simultaneous (ICP-AES), Varian model (Varian Canada, Inc., Mississauga, Ont.). Quality controls were performed with certified liquid samples (multi-elements standard, catalogue number 900-Q30-002, lot number SC0019251, SCP Science, Lasalle, Quebec) to ensure the conformity of the measurement apparatus.

3.5 Calculation methods

3.5.1 Pure water permeability (A_{ipw})

Pure water permeability (A_{ipw}) through a membrane was calculated using the following equation:

Equation 3.1 $$A_{ipw} = \frac{\mu J_p}{\Delta P}$$

Where μ is water viscosity, J_p is water permeate flux and ΔP is the transmembrane pressure.

J_p was defined by:

Equation 3.2 $$J_p = Q_p / S_m$$

Where Q_p is the permeate flow rate and S_m is the surface of the membrane.

3.5.2 Dynamic permeability (A_{id})

According to Lebrun and Xu (1999), the transport of an inorganic solution through the membranes (A_{id}) was calculated by:

Equation 3.3 $A_{id} = \frac{\mu J_p}{\Delta P_{e_{ff}}}$

Where $\Delta P_{e_{ff}} = \Delta P - \Delta \Pi$

Equation 3.4 $\Delta \Pi = \Pi(X_{A2}) - \Pi(X_{A3})$

Where $\Delta P_{e_{ff}}$ is the effective pressure gradient and $\Delta \Pi$ is the difference in osmotic pressure between the molar fraction of the concentrated boundary (X_{A2}) and the permeate solutions (X_{A3}). When the circulation velocity is high enough to reduce the concentration polarization on the surface of the membrane, X_{A2} tends towards X_{A1} (molar fraction of the feed and in the reservoir) and therefore $\Delta P_{e_{ff}} = \Delta P_a$. ΔP_a is the apparent gradient pressure.

Thus:

Equation 3.5 $\Delta P_a = \Delta P - \Pi(X_{A1}) + \Pi(X_{A3})$

Consequently:

Equation 3.6 $\Delta P_a = \Delta P_{e_{ff}} + \Pi(X_{A2}) - \Pi(X_{A1})$

For diluted solutions, the osmotic pressure was calculated in correspondence with the concentration values in the feed and permeates using Van't Hoff's equation:

Equation 3.7 $\Pi = \sum iRTC$

Where $\sum_i$ is the number of ions per molecule of solute, R is the universal gas constant, T is the absolute temperature and C is the concentration of the inorganic solution (mol/l).

3.5.3 Global and intrinsic separation factor (f, f')

The global separation factor (f) of the solutes was calculated by the next equation:

Equation 3.8 $$f = \frac{X_{A1} - X_{A3}}{X_{A1}} = 1 - \frac{X_{A3}}{X_{A1}}$$

This equation was also used to calculate the rejection of individual ions. The Intrinsic separation factor (f') was expressed by:

Equation 3.9 $$f' = \frac{X_{A2} - X_{A3}}{X_{A2}} = 1 - \frac{X_{A3}}{X_{A2}}$$

Where X_{A2} is the molar fraction of the solute in the membrane surface.

3.6 Results and discussion

3.6.1 Composition of the leachate

Soil-washing is a difficult task due to the strong bonds presented between soil and metals. The efficacy of this method depends on the capability of the extractants to dissolve the metals from a soil-washing solution (Tejowulan and Hendershot, 1998).

Table 3.3, shows the effectiveness of the soil washing treatment using HCl as an extractant in removing different type of metal ions. The main characteristics of the acidic leachate are listed in the same table.

As shown in this table, the acidic leachate is contaminated with a great variety of metal ions. Particularly the leachate is a virtually colorless solution characterized by a high conductivity, partly due to the presence of hydrochloric acid (HCl) used as a soil-washing agent.

Table 3.3 HCl leachate characterization before NF treatment

Parameter	Value
pH	1.97
ORP (mV)	456
Conductivity (ms/cm)	13.55
TOC (mg/l)	15.9
Ions (mol/l)	
H^+	1.07×10^{-2}
Al^{3+}	8.02×10^{-4}
As^{5+}	9.34×10^{-7}
B^{3+}	3.14×10^{-5}
Ba^{2+}	1.97×10^{-5}
Ca^{2+}	5.39×10^{-2}
Cd^{2+}	5.33×10^{-7}
Cr^{3+}	1.15×10^{-6}
Cu^{2+}	3.35×10^{-5}
Fe^{2+}	3.31×10^{-5}
K^+	2.44×10^{-4}
Mg^{2+}	2.44×10^{-3}
Mn^{2+}	1.97×10^{-4}
Na^+	6.91×10^{-4}
Ni^{2+}	2.73×10^{-6}
PO_4^{2-}	2.50×10^{-4}
Pb^{2+}	9.00×10^{-5}
SO_4^{2-}	4.53×10^{-4}
SeO_4^{2-}	1.39×10^{-4}
Zn^{2+}	2.45×10^{-4}

3.6.2 Membrane characterization

3.6.2.1 *Water and dynamic permeability*

Permeability values of NF-270 and Desal 5 membrane coupons at different feed solutions are shown in Table 3.2. It can be seen that the NF-270 membrane type displays superior permeate fluxes compared to the Desal 5 membrane (experiment 2, on Table 3.2). These data give emphasis to the disparity between the behaviour of the two membranes.

Comparing the values of initial and final water permeability, it is clear that the feed concentration can influence the membrane permeabilities. For Desal 5 (4) and (5) membrane, it was observed that A_{ipw} values increased 56.9% and 49.3% respectively, over the initial A_{ipw} value (experiment 2 and 10, on Table 3.2). This behavior suggest that the presence of ions in the solution screens the charge density of the membrane, changing pore size and thus increasing membrane flux (swollen effect) (Hamza *et al.*, 1995).

The opposite behavior was presented by NF-270 (4) and (5) membranes, where A_{ipw} decreased 31.5% and 29.1% respectively (experiment 10, on Table 3.2). This decrease in A_{ipw} indicated that the NF-270 membranes underwent an irreversible shrinkage that affected not only the pore structure (reduction of pore size) but also the nature of the pore surface (Ortega *et al.*, 2005).

3.6.2.2 *Dynamic permeability of a binary system: NaCl-H$_2$O*

An experiment with NaCl-H$_2$O at neutral pH was carried out to characterize the membranes. As shown in Figure 3.2, for both membranes, a linear increase of the permeate flux (μJ_p) was presented according to the applied pressure (ΔP_a). In this particular case, this linear evolution suggests that the recirculation flow rate was high enough to remove the particles on the surface of the membranes. For that reason, the differences in osmotic pressure of the bulk and the boundary solution were considered equal ($\Pi X_2 \approx \Pi X_1$). It was assumed, for both membranes, that the intrinsic separation factor was equal to the overall separation factor $f \approx f'$.

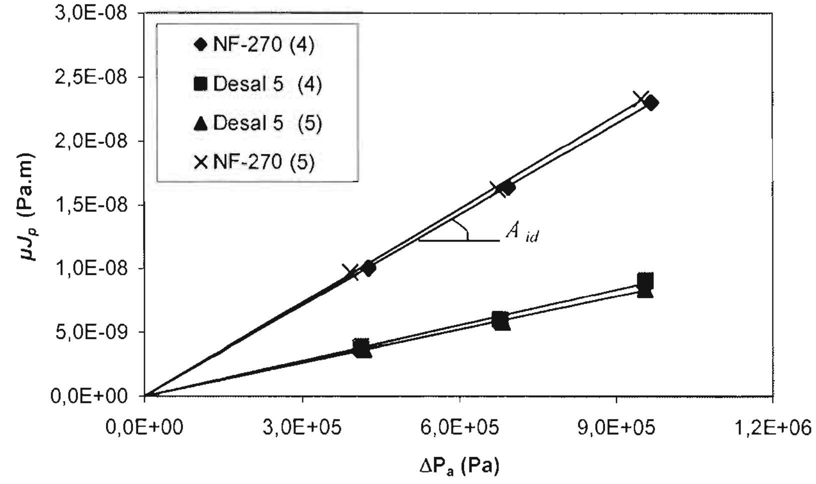

Figure 3.2 **Permeate flux vs. apparent transmembrane pressure for NaCl (experiment 3). Salt concentration = 3.42 × 10^{-2} mol/l; pH = neutral, Q_c = 0.32 m^3/s; 22 < T (°C) < 27**

3.6.2.3 *Salt separation at different pH values*

Salt rejections of Desal 5 and NF-270 membranes at different pH and pressure values are shown in Figures 3.3 to 3.5. The separation factors for the sodium chloride solution (tank and permeate) were obtained as a function of their conductivity.

The separation factor of the solutions varying the pH indicates that the membrane is greatly influenced by the electrolyte concentration and by the acidic characteristics existing in the feed solution. Generally, it was observed that the membrane rejection went through a minimum values as feed pH decreased. For example, in the case of NF-270 (4), the highest separation was obtained at 42.5%, for the run conducted at pH = 5.8 and the lowest separation approximately at 2.4% at the lowest pH (2.2). For Desal 5 membranes the differences in separation were small (Figures 3.3 to 3.5).

In general, the higher the electrolyte concentration, the higher the osmotic pressure and the lower the permeate flux (Xu and Lebrun, 1999). This behavior was shown by NF-270 membranes, where the lowest permeability values were obtained at low pH (2.2) due to the effect of the osmotic pressure (experiments 3, 5 and 7, on Table 3.2). This behaviour was expected since the dynamic permeability value of a membrane decreased when the concentration increased. In this case it is assumed that NF-270 membrane underwent preferential sorption.

On the other hand, Desal 5 membrane coupons displayed a slight increase in dynamic permeability compared with the values of water permeability (experiments 3, 5 and 7, on Table 3.2). This membrane appears to be dependent upon the presence of electrolytes. According to Lebrun and Xu (1999), in the presence of ions, the pore size may induce dynamic changes in permeability.

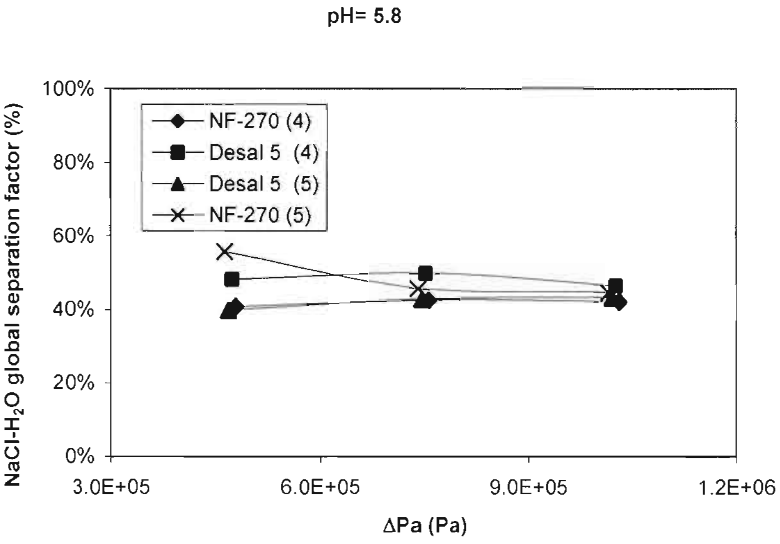

Figure 3.3 Overall separation factor of $NaCl-H_2O$ vs. apparent transmembrane pressure. Salt concentration = 3.42 × 10^{-2} mol/l; pH = 5.8, Q_c = 0.32 m^3/s; 22 < T (°C) < 27

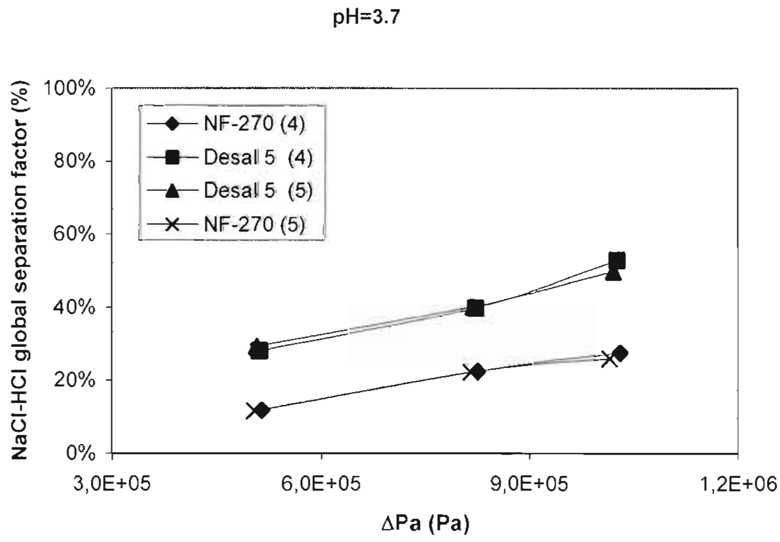

Figure 3.4 Overall separation factor of NaCl-HCl vs. apparent transmembrane pressure. Salt concentration = 3.42 × 10^{-2} mol/l; pH = 3.7, Q_c = 0.32 m^3/s; 22 < T (°C) < 27

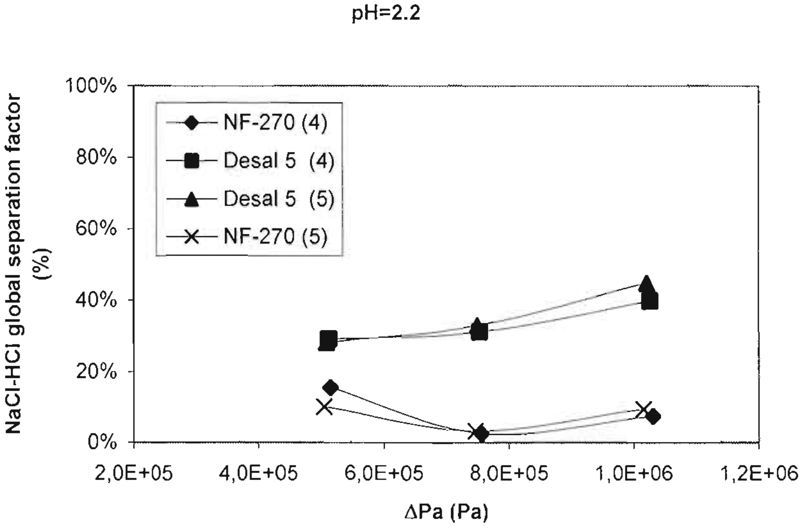

Figure 3.5 **Overall separation factor of NaCl-HCl vs. apparent transmembrane pressure. Salt concentration = 3.42 × 10^{-2} mol/l; pH = 2.2, Q_c = 0.32 m^3/s; 22 < T (°C) < 27**

3.6.2.4 *Na^+ retention*

Figures 3.6 to 3.9 show the retention of Na^+ at different pH values. In the case of Desal 5 membranes, as the pH decreased, an increase in Na^+ retentions was observed. Similar behaviour has been described by several authors (Bandini *et al.*, 2005; Hagmeyer and Gimbel, 1998; Quin *et al.*, 2004). In this case it is assumed that the feed pH affected the separation performance of the membrane. This behaviour possibly could be due to the fact that the surface of Desal 5 membrane was positively charged at pH below the iso-electric point and negatively charged at pH above the iso-electric point.

For NF-270, it was observed that the minimum retention was presented at pH around 3.8, close to the iso-electric point of the membrane. This membrane displayed its normal behaviour, acting as a positively charged membrane at pH below the iso-electric and as a negatively charged membrane at pH above the iso-electric point.

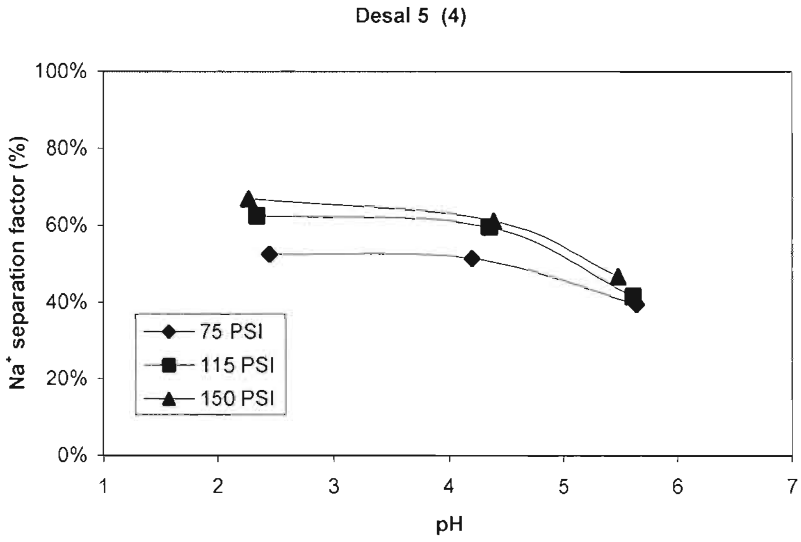

Figure 3.6 Na$^+$ separation factor (%) vs. pH for the membrane Desal 5 (4). Salt concentration = 3.42 × 10^{-2} mol/l; pH = 5.8, 3.7 and 2.2, Q_c = 0.32 m^3/s; 22 < T (°C) < 27

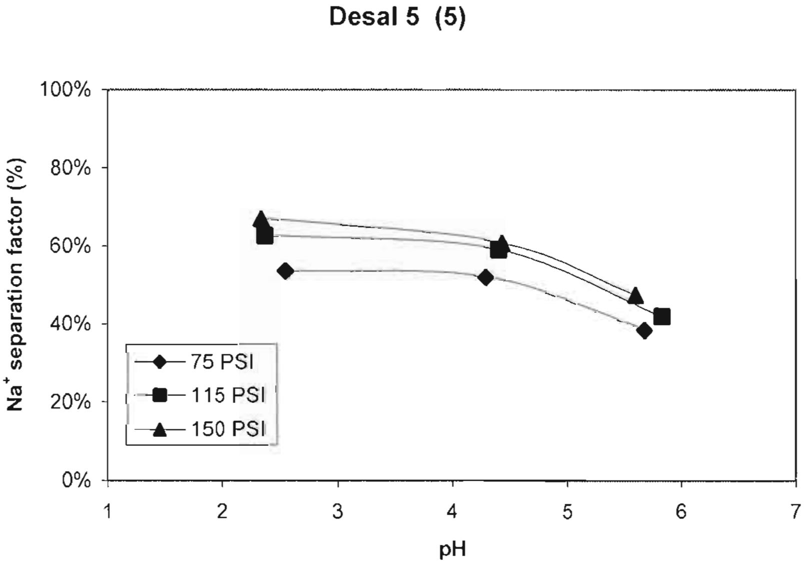

Figure 3.7 Na$^+$ separation factor (%) vs. pH for the membrane Desal 5 (5). Salt concentration = 3.42 × 10^{-2} mol/l; pH = 5.8, 3.7 and 2.2, Q_c = 0.32 m^3/s; 22 < T (°C) < 27

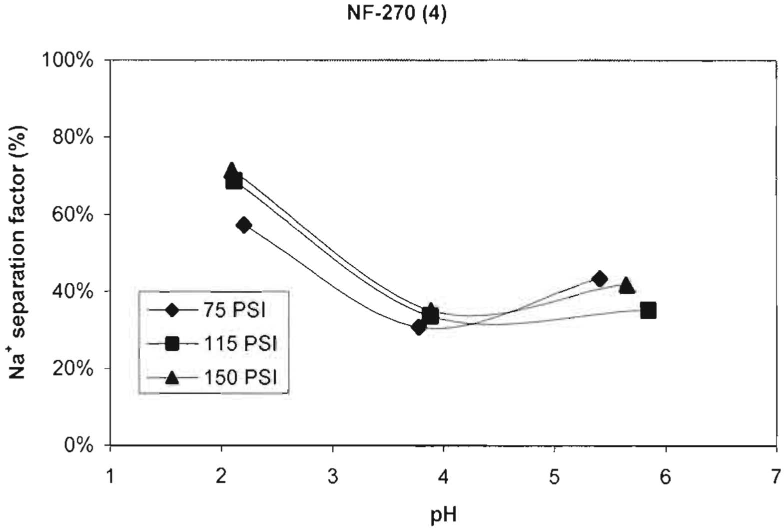

Figure 3.8 Na$^+$ separation factor (%) vs. pH for the membrane NF-270 (4). Salt concentration = 3.42 × 10^{-2} mol/l; pH = 5.8, 3.7 and 2.2, Q_c = 0.32 m^3/s; 22 < T (°C) < 27

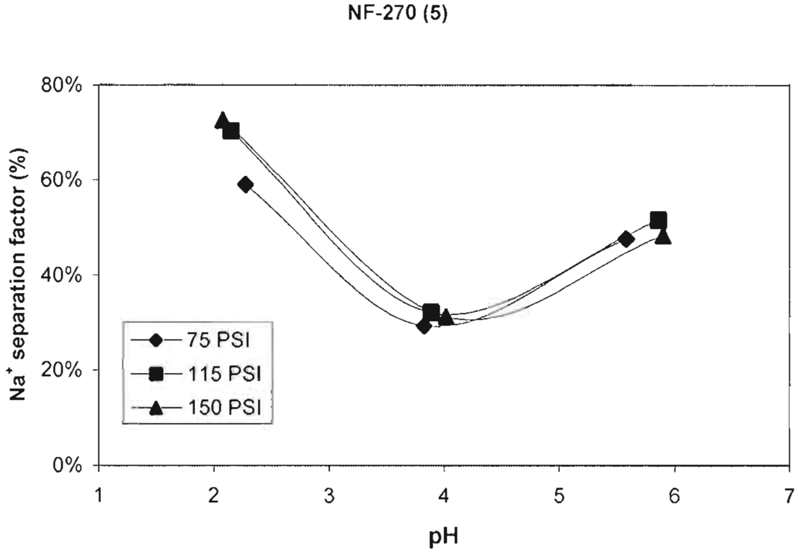

Figure 3.9 Na$^+$ separation factor (%) vs. pH for the membrane NF-270 (5). Salt concentration = 3.42 × 10^{-2} mol/l; pH = 5.8, 3.7 and 2.2, Q_c = 0.32 m^3/s; 22 < T (°C) < 27

3.6.2.5 *Acidic retention*

The retention values of H^+ ions at different pH values are shown in Figures 3.10 to 3.13. In general, the results obtained in these experiments for Desal 5 membrane 4 and 5 shows that H^+ rejection went through a maximum value, which approximately corresponds to a pH of 4.3 (close to the membrane iso-electric point), showing after that a decrease that went to a minimum retention (negative rejection) obtained at high pH values. This tendency has been observed in other investigations (Bandini *et al.*, 2005; Quin *et al.*, 2004).

In this particular case where the membrane charge was influenced by the pH, it is assumed that Desal 5 membrane was acting as a negatively charged membrane at high pH values, and, consequently, the H^+ rejection increased as the H^+ concentration increased, decreasing the concentration of H^+ in the permeate (Bandini *et al.*, 2005).

In the case of NF-270 membranes, a negative rejection of H^+ ions was generally observed. This behaviour suggests that the membrane surface rejects Na^+ leading it to enhance the permeation of H^+.

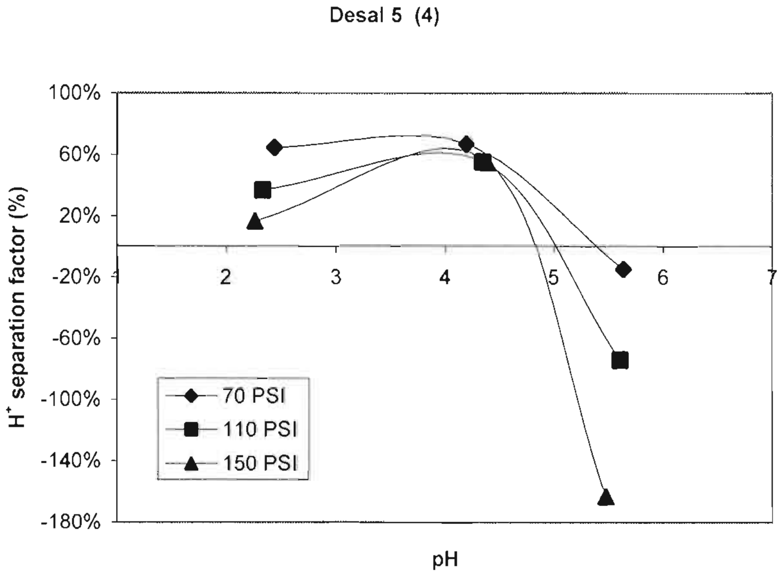

Figure 3.10 H⁺ separation factor (%) vs. pH for the membrane Desal 5 (4). Salt concentration = 3.42 × 10^{-2} mol/l; pH = 5.8, 3.7 and 2.2, Q_c = 0.32 m³/s; 22 < T (°C) < 27

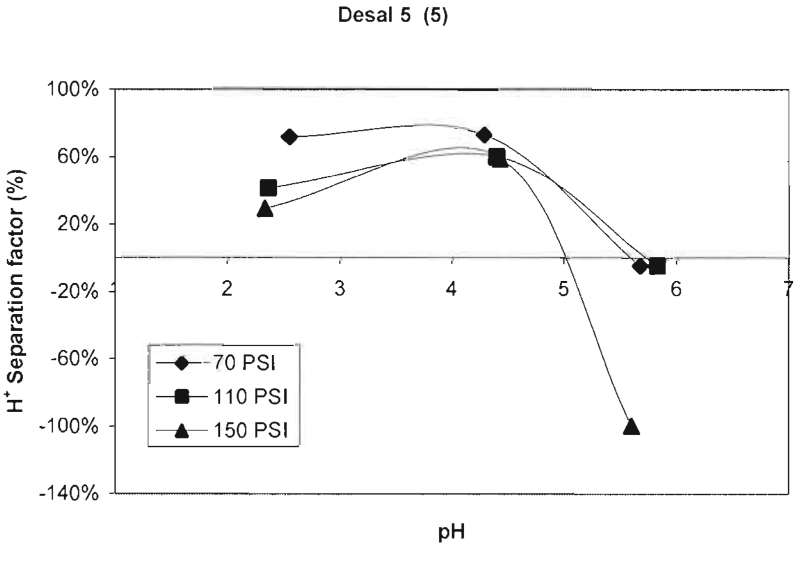

Figure 3.11 H⁺ separation factor (%) vs. pH for the membrane Desal 5 (5). Salt concentration = 3.42 × 10^{-2} mol/l; pH = 5.8, 3.7 and 2.2, Q_c = 0.32 m³/s; 22 < T (°C) < 27

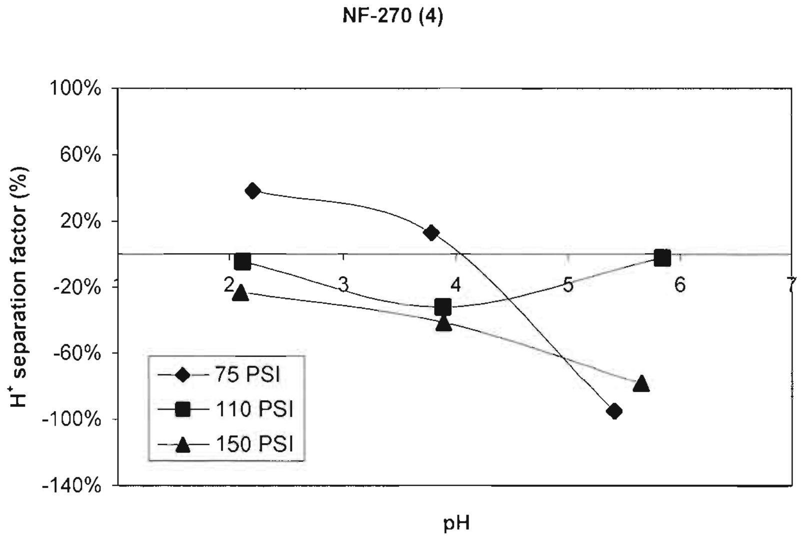

Figure 3.12 H$^+$ separation factor (%) vs. pH for the membrane NF-270 (4). Salt concentration = 3.42×10^{-2} mol/l; pH = 5.8, 3.7 and 2.2, Q_c = 0.32 m^3/s; 22 < T (°C) < 27

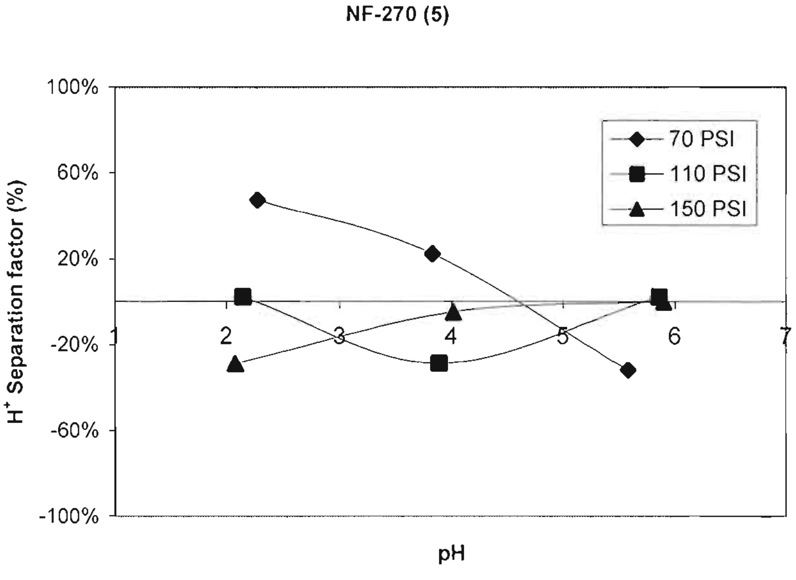

Figure 3.13 H$^+$ separation factor (%) vs. pH for the membrane NF-270 (5). Salt concentration = 3.42×10^{-2} mol/l; pH = 5.8, 3.7 and 2.2, Q_c = 0.32 m^3/s; 22 < T (°C) < 27

3.6.3 Nanofiltration of the acidic leachate

3.6.3.1 Dynamic permeability of the acidic leachate

Membrane fouling was investigated by measuring pure water fluxes before and after the filtration of the acidic leachate solution. As shown in Table 3.2, for all membranes, an increase in dynamic permeability was observed (Experiment 9, on Table 3.2). This behaviour was attributed to the influence of concentration polarization and high osmotic pressure on the surface of the membrane produced by the presence of inorganic components that generated changes in pore size caused by the electrostatic repulsions within the membrane pore structure, resulting from variations in solution chemistry. Furthermore, this behaviour is corroborated in Figure 3.14. In this particular case as it was not observed a linear increase of the permeate flux (μJ_p) according to the applied pressure (ΔP_a), it is assumed that all the membranes were affected by the high concentration of electrolytes on the surface of the membranes.

After the run with the acidic leachate solution, it was observed that the increase in dynamic permeability was reversible due to the pure water permeability measured following this experiment was recovered (experiments 9 and 10, on Table 3.2).

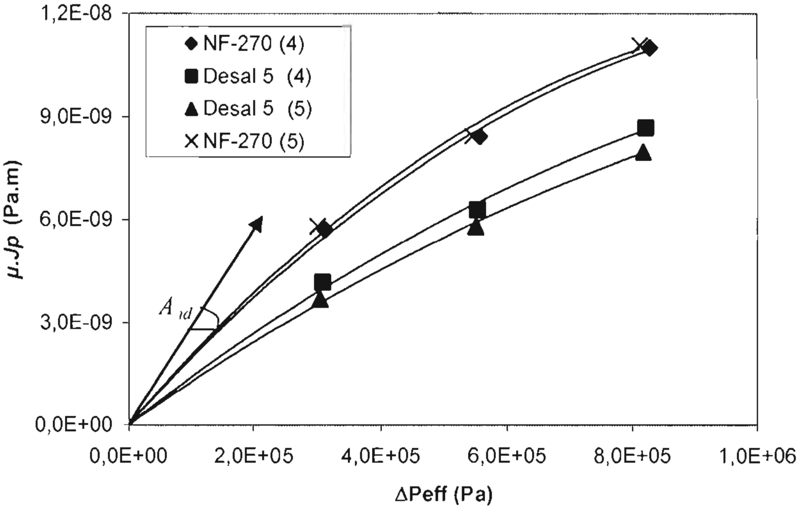

Figure 3.14 **Permeate flux vs. effective pressure for the acidic leachate solution. pH = 1.97, Q_c = 0.32 m³/s; 22 < T (°C) < 27**

3.6.3.2 Separation of metals ions from leachate solution by NF membranes

The separation efficiency of the NF membrane process in the removal of metal ions from the acidic leachate is presented in Table 3.4.

This table shows that the membrane treatment was effective in the removal of Al^{3+}, Ca^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+} and Zn^{2+} with recuperation between 84% and 100%. This implies the effective application of NF in the metal ion removal. Other ions that presented high to moderate retentions were K^+, Na^+ and PO_4^{3-}. Additionally, metal ions such as As^{3+}, B^{3+}, Cd^{2+}, Cr^{3+}, Mg^{2+}, Ni^{2+}, Se^{2+}, SO_4^{2-} and Pb^{2+} were found in the feed solution. These separations depended on the characteristics of the membranes used and the acidic characteristics and cation concentration of the leachate solution, as well as the ion size.

As the pH of the feed solution can change the nature of the membrane surface charge, it can consequently affect the membrane retention performance (Hagmeyer and Gimbel, 1998). In this case the high retention presented by the cations suggests that both membranes were acting as positively charged membranes due to the highly acidic conditions and high concentration of the feed solution, leading to a repulsion of cations induced by charge effects. Furthermore, this behaviour was presented in the permeation of NaCl at different pHs.

Another factor that could influence the retention of cations in the membranes was the presence in the leachate solution of multivalent ions or metal complexes that were easily retainable by the membrane due to their sizes.

Table 3.4 Separation factors of ions (%) present in the acidic leachate

Membrane	Pressure (PSI)	Ion separation factor (%)									
		Al^{3+}	Ca^{2+}	Cu^{2+}	Fe^{2+}	K^+	Mn^{2+}	Na^+	PO_4^{3-}	Zn^{2+}	H^+
NF-270 (4)	75	100	97.7	93.0	92.4	60.7	98.1	55.5	72.8	95.3	20.6
	110	100	98.4	95.0	95.5	68.3	98.7	67.5	72.4	96.0	50.5
	150	100	98.3	94.5	96.0	66.0	98.5	64.5	70.7	95.5	23.3
NF-270 (5)	75	100	98.4	95.5	92.5	64.7	98.7	60.8	73.2	95.8	24.1
	110	100	98.9	96.4	95.5	68.9	99.0	61.4	71.0	96.0	50.5
	150	100	99.1	94.9	93.4	50.9	99.2	58.2	68.2	94.4	28.4
Desal 5 (4)	75	100	98.9	91.3	90.8	48.7	99.1	42.0	70.3	92.3	36.9
	110	100	99.3	93.5	94.2	51.2	99.4	47.7	63.9	93.1	56.8
	150	100	99.5	91.8	96.6	51.2	99.5	63.2	71.6	94.1	31.6
Desal 5 (5)	75	100	98.4	92.0	84.0	52.1	98.7	49.7	78.2	93.8	36.9
	110	100	99.0	93.4	85.9	38.7	99.1	46.5	65.6	92.6	60.6
	150	100	98.9	94.7	93.4	60.6	99.2	59.1	67.3	94.4	37.6

3.6.4 Soil washing, NF membranes and industrial application

The presence of toxic and hazardous compounds is the main reason to apply reliable process to decontaminate soils and waste-waters. However, some processes have been demonstrated to be expensive and inappropriate, generating more contamination. Particularly waste-waters coming from soil washing are difficult to treat by some methods. These waste-waters are complex solutions, rich in metal ions, which, due to their composition, are comparable to industrial waste-waters (Peters, 1998). Therefore, the use of soil washing combined with membrane filtration can be a solution to the contamination problem. However, literature concerning the application of soil washing with NF membranes is scarce.

The two processes described in our research constitute reliable processes that can be applied at the industrial level. There are a number of industrial benefits: (1) the use of some inorganic acids, such as HCl, used as a soil washing agent is inexpensive. HCl is considered one of the most effective soil-washing agents (Neilson *et al.*, 2003). (2) the application of NF membranes requires lower pressures compared to RO (according to its application). Therefore less energy is required for the process. Generally, the capital cost of membranes tends to be high, while, on the other hand, the operating cost is comparatively low (Sikdar *et al.*, 1998). (3) It is possible to reuse the acidic water during the process. (4) The use of NF membranes allows the fractioning of pollutants. NF is able to separate monovalent ions from multivalent ions, and it also allows acid recuperation. Consequently, they can be applied in further processes. Those characteristics make of soil washing and principally NF membranes successful processes in the purification of waste water streams.

However, it is important to take into account that the application of pressure-driven membrane processes as nanofiltration generates large volumes of concentrated liquid wastes that need to be disposed or discharged carefully. For that reason, those concentrate waste waters need an adequate treatment as a function of its origin and composition (Van der Bruggen *et al.*, 2003).

3.7 Conclusions

These experimental results have demonstrated the feasibility of using NF membranes applied to an acidic leachate solution coming from contaminated soil. This investigation has been performed using two commercial membranes, Desal 5 and NF-270. These membranes have been characterized in terms of permeability and retention of several ions. Principally Desal 5 membrane coupons showed good performance in terms of membrane permeability. This membrane, in the presence of electrolytes, displayed an increase in dynamic permeability. On the other hand, the NF-270 membrane displayed a decrease in permeability. Furthermore, it was observed that the feed pH of the solutions significantly influenced the charge of the membrane as observed in some experiments. It is possible that the acidity of the solution contributed to the membrane charge formation.

Using the acidic leachate solution, both membranes demonstrated high retention capacity, especially with multivalent ions rather than monovalent ions. Furthermore, in using this solution, it was observed that the dynamic permeability for all the membranes increase due to the high presence of ions provoked by the concentration polarization on the surface of the membrane.

Finally, these results obtained might offer a new approach in treating complex industrial residues.

Abbreviations and Symbols

A_{ipw}	Pure water permeability of membrane, (m)
A_{id}	Dynamic solution permeability of membrane, (m)
C	Concentration, (mol/l)
$f, f,$	Overall and intrinsic separation factor, (dimensionless)
J_p	Solution permeate flux, (m/s)
M	Molar concentration (mol/l)
ORP	Oxydoreduction potential, (mV)
P	Pressure, (Pa)
P_a	Apparent pressure (Pa)
ΔP_{eff}	Effective pressure (Pa)
Q_c	Feed flow rate, (m^3/s)
Q_p	Permeate flow rate, (m^3/s)
S_m	Membrane area, (m^2)
T	Temperature, (K)
TOC	Total organic carbon, (mg.O_2/l)
X	Molar fraction
X_{A1}	Molar fraction of the feed
X_{A2}	Molar fraction of the concentrated boundary
X_{A3}	Molar fraction of the permeate

Greek letters

Δ	Gradient
μ	Fluid viscosity, (Pa.s)
Π	Osmotic pressure, (Pa)
$\sum_i$	Number of ions per molecule of solute

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CHAPTER IV

REMOVAL OF METAL IONS FROM AN ACIDIC LEACHATE SOLUTION BY NANOFILTRATION MEMBRANES

Desalination

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4.1 Abstract

This paper presents the feasibility of the application of two commercial nanofiltration (NF) membranes (Desal 5 and NF-270) in the removal of metal ions from an acidic leachate solution generated from a contaminated soil using H_2SO_4 as a soil washing agent. The experimental results of soil washing indicated that H_2SO_4 is highly effective in removing metal ions from contaminated soil. Following this process, the treatment of this acidic solution by nanofiltration membranes showed good metal ion rejection (between 62 to 100%), where divalent ions were better rejected than monovalent ions. For characterization purposes, the membrane experiments were conducted using K_2SO_4 solutions at different pHs. Membrane performance criteria were evaluated according to membrane permeability and ionic retention in the tank and permeate, taking into account different operating conditions such as pressures, flow rate and pH.

These results demonstrated the effectiveness and feasibility of the application of nanofiltration treatments in the cleaning-up of contaminated water residues generated during soil washing processes.

Keywords

Nanofiltration; Soil washing; Acidic leachate; Ionic separation factor; Dynamic permeability

4.2 Introduction

Every year, millions of tons of metals are generated and spilled into the environment, making an enormous impact on it. In 2002, industries worldwide released 22 000 tons of cadmium, 93 900 tons of copper, 783 000 tons of lead, and 135 000 tons of zinc (Singh *et al.*, 2003).

Although metals are naturally present in soils, this contamination is attributed to human activities such as vehicle emissions, use of fertilizers and pesticides, mining activities, and, principally, industrial processes (Kiem *et al.*, 2003). Once released into the soil, they are mobilized either by leaching or by uptake into plants, persisting for many years because metals are not biodegradable and are generally not mobile (Vassilev *et al.*, 2004). In high concentrations, metals can affect all groups of organisms and different ecosystems, including microbial activities (Baath, 1989). These wastes are dumped arbitrarily, without waste management techniques. For example, in the United States, approximately 1200 sites on the National Priority List (NPL) contain a mix of organic-metal contamination, of which 63% are polluted with metals (Mulligan *et al.*, 2001). In Quebec (Canada), according to the Ministère de l'Environnement et de la Faune du Québec (MEFQ, 2001), 5125 sites are polluted, and 11% of these sites are contaminated with metals.

During the last decades, several technologies have emerged that try to give innovative solutions to the soil contamination problem. Some examples are soil washing, soil flushing, vitrification, bioremediation, phytoremediation, or a combination of them (Mulligan *et al.*, 2001). However, despite numerous promising decontamination options, many technologies have not been successfully implemented. This is because some of them are inadequate to reduce the metal concentration to acceptable regulatory standards, or because of the extreme cost of the removal process, excavation and landfill disposal, or simply due to disappointing results (Mulligan and Eftekhari, 2003). For that reason, much effort has been made to find ways to remove metals from soil. One of the most common and simple treatments for soil metal remediation is soil washing (Meunier *et al.*, 2003). This technique extracts metals from contaminated soils by solubilizing them in a washing solution (Barona *et al.*, 2001; Peters, 1999). This technique usually uses washing agents such as inorganic acids, organic acids, bases, chelating agents, or a combination of them (Mulligan and Eftekhari, 2003). However, the problem with the application of these reagents is that they generate secondary waste products that may require additional waste-water treatments.

For that reason, in the search for waste water techniques, there has been a growing interest during the last decade, for "cleaner" treatments such as membrane filtration (reverse osmosis, nanofiltration, ultrafiltration, and microfiltration). Principally the application of NF membranes after soil treatment has been seen as a favorable option due to the fact that soil treatment operations (e.g., soil washing) generates large volumes of contaminated water (Sikdar *et al.*, 1998).

Hence, the present work evaluates the performance of two commercial nanofiltration membranes (Desal 5 and NF-270) for the removal of metal ions from an acidic leachate solution generated from contaminated soil.

4.2.1 Nanofiltration

Nanofiltration with a molecular weight cut-off (MWCO) ranging between 200 and 1000 g/mol, displays separation characteristics between reverse osmosis and ultrafiltration membranes (Ku *et al.*, 2005). The major separation mechanism in salt separation using NF process can be explained in terms of steric (organic solutes) and/or charge effects (inorganic solutes) (Schaep *et al.*, 1998). Principally charge effect is responsible of the removal of ions from waste waters. Other factors that could influence membrane performance are the electrolyte concentration and the acidic characteristics existing in the feed solution (Bandini *et al.*, 2005).

4.3 Experimental

This section is divided into two parts: generation of the acidic leachate solution coming from contaminated soil, followed by membrane characterization and nanofiltration experiments of the acidic leachate solution, to evaluate membrane performance.

4.3.1 Site information

Contaminated soil from the Pointe-aux-Lièvres site located in Quebec, Canada was collected and used for this work. The fraction of soil used was superior to 20 µm and less than 2 mm. The initial metal concentrations in the soil were as follows: 1.4 mg/kg of Cd, 120 mg/kg of Cr, 175 mg/kg of Cu, 457 mg/kg of Mn, 80 mg/kg of Ni, 817 mg/kg of Pb and 565 mg /kg of Zn. Cu, Pb and Zn concentrations were above the criteria B given by the Ministry of Environment and Fauna of Quebec (MEFQ, 1999) which are, respectively, 100, 500 and 500 mg/kg. For that reason, this soil cannot be used for agricultural, residential or recreational purposes.

4.3.2 Soil experimental procedure

500 g of soil was added to 1.5 l of water agitated by a variable speed mixer at 800 rpm (rotations per minute) with a stainless steel propeller (SS-316L, Labcor Technical Sales, Montreal, QC., Canada) fixed to a caframo RZR50 rotor (Labcor Technical Sales). To this suspension was added H_2SO_4 (36 N) until a pH of 3 was obtained. This leachate was agitated for 25 min. Following this procedure, 5 ml of the reactant Percol E-10, an anionic polymeric solution (Ciba Specialty Chemicals Canada Inc., Mississauga, Ont.), was added to facilitate the decantation.

This acidic solution was passed through a Whatman no. 4 membrane filter with a porosity between 20 and 25 µm (Whatman Bioscience Inc., Newton, MA, USA) under a vacuum, to eliminate any trace of soil particles from the leachate solution. The leachate was kept at room temperature until membrane filtration experiments were realized.

H_2SO_4 was used for this study as a soil washing agent not only for its inexpensive cost but also because in practice, acid washing is a frequent and effective method for metal-contamination removal (Meunier *et al.*, 2002; Rampley and Ogden, 1998).

4.3.3 Membrane procedure

The steps used in membrane experiments are as follows:

4.3.3.1 Membrane compaction

The membranes were compacted with distilled water for 3 hours at room temperature, a constant recirculation flow rate (1.01×10^{-4} m^3/s), and a pressure of 1.0×10^6 Pa.

4.3.3.2 Membrane pure water permeability (A_{ipw})

After membrane compaction, the pure water permeability of each membrane was measured before and after the test of each solution. The operating conditions for all the experiments were the following: three different pressures of 0.5×10^6, 0.8×10^6 and 1.0×10^6 Pa and a constant feed flow rate 1.01×10^{-4} m^3/s at room temperature. Pure water permeability was measured before and after the measurement of the dynamic permeability of each inorganic solution to evaluate membrane integrity in terms of permeability.

Between each NF run with a solution (K_2SO_4 (at different pHs) and acidic solution), the membranes were washed by circulating distilled water with a electric conductivity of ≤ 2 µS/cm, for approximately half an hour without pressure in order to minimize experimental errors.

The permeate flux values for pure water and the inorganic solutions, including the leachate, at different operating pressures were measured and plotted against applied pressure. The slope of the curve (straight line) was the value to determine the membrane permeabilities.

A_{ipw} was calculated using the following equation:

Equation 4.1 $$A_{ipw} = \frac{\mu J_p}{\Delta P}$$

Where μ is water viscosity, J_p is water permeate flux and ΔP is the transmembrane pressure.

J_p was defined by:

Equation 4.2 $$J_p = Q_p / S_m$$

Where Q_p is the permeate flow rate and S_m is the surface of the membrane.

4.3.3.3 *Membrane dynamic permeability (A_{id})*

Following the determination of the water permeability, the dynamic permeability and selectivity of each membrane was measured in the following order

K_2SO_4 + H_2SO_4 at pH 6.7, 3.7 and 2.2, and the principal solution of this study, the acidic leachate solution. The concentration of K_2SO_4 was kept constant (1.1×10^{-2} mol/l).

A_{id} was calculated by the next equation [17]:

Equation 4.3 $$A_{id} = \frac{\mu J_p}{\Delta P_e}$$

Where:

Equation 4.4 $$\Delta P_e = \Delta P - \Delta \Pi$$

Equation 4.5 $$\Delta \Pi = \Pi(X_{A2}) - \Pi(X_{A3})$$

Where ΔP_e is the effective pressure gradient and $\Delta \Pi$ is the difference in osmotic pressure between the molar fraction of the concentrated boundary layer (X_{A2}) and the permeate solutions (X_{A3}).

When there is no concentration polarization on the surface of the membrane, X_{A2} tends towards X_{A1} (molar fraction of the feed and in the reservoir), and, therefore, $\Delta P_e = \Delta P_a$. ΔP_a is the apparent gradient pressure.

Thus,

Equation 4.6 $$\Delta P_a = \Delta P - \Pi(X_{A1}) + \Pi(X_{A3})$$

Consequently,

Equation 4.7 $\Delta P_a = \Delta P_e + \Pi(X_{A2}) - \Pi(X_{A1})$

The osmotic pressure for dilute solutions was calculated using the Van't Hoff equation:

Equation 4.8 $\Pi = \sum iRTC$

where, $\sum i$ is the number of ions per molecule of solute, R is the universal gas constant, T is the absolute temperature, and C is the concentration of the inorganic solution (mol/l).

Rejection rate (f) was calculated using the following equation:

Equation 4.9 $f = \frac{X_{A1} - X_{A3}}{X_{A1}} = 1 - \frac{X_{A3}}{X_{A1}}$

4.3.3.4 *Membrane materials*

Two types of thin-film commercial nanofiltration membranes: Desal 5 and NF-270 were studied for their permeation and ionic selectivity. Desal 5 manufactured by GE-Osmonics (Minnetonka, MN, USA) is a polymeric membrane, in which a polyamide selective layer is supported on a polysulfone layer (Bandini *et al.*, 2005). NF-270 supplied by FilmTec Corporation (FilmTec Corporation, Dow Chemical Co., Midland, MI) is a semi-aromatic piperazine-based polyamide layer on top of a polysulphone micro-porous support reinforced with a polyester non-vowen backing layer. Supplementary details about the membranes characteristics are found in Table 4.1 (Hagmeyer and Gimbel, 1999; Tanninen and Nyström, 2002).

Table 4.1 Characteristics of the membranes used in this study

Membrane	**Desal 5**	**NF-270**
Manufactured	GE-Osmonics	Dow (FilmTec)
Isoelectric point	4	3.3
pH resistance (20°C)	2-11	3-10
Temperature resistance	90	45
Charge	positive	negative

4.3.3.5 Experimental set-up

The filtration experiments have been carried out at room temperature, in batch mode with recirculation of substances. The schematic representation of the equipment is illustrated in Figure 4.1.

In this investigation, the feed solution from the tank was pumped through 4 different membrane cells (made of polyvinyl chloride (PVC)), obtaining itself a retentate that went back into the tank and a permeate that was collected into a beaker for permeate flux and rejection rate calculation. This permeate was not recirculated into the system. The effective membrane area was 1.26×10^{-3} m^2. The same NF membranes were used in all experiments.

This apparatus was designed to test different membranes using the same operating conditions and also to test solutions using different pHs. Additional details of the experimental set-up were presented and described in the investigation made by Noël *et al.* (2000).

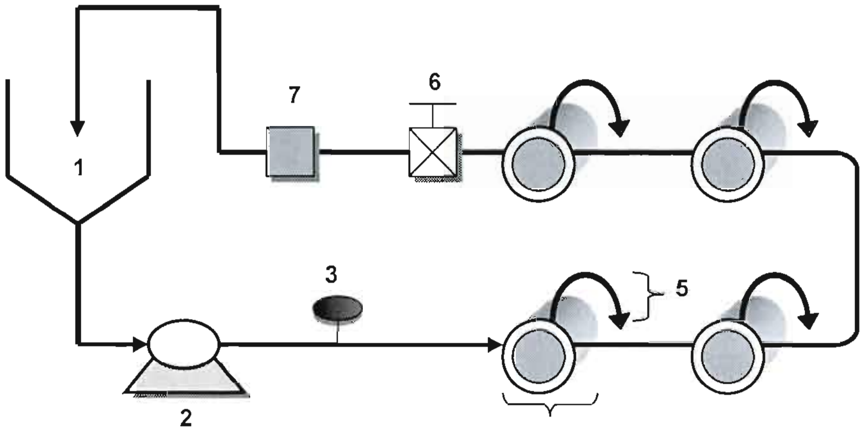

Figure 4.1 **Schematic diagram of NF set-up**

1. feed tank, 2. pump, 3. manometer, 4. membrane cell, 5. permeate outlet,
6. pressure valve, 7. flowmeter

4.3.4 Reference solutes

During membrane characterization, certified analytical grade K_2SO_4 and H_2SO_4 were used, purchased from the Aldrich Chemical Company, Milwaukee, WI. H_2SO_4 was used in the experiments to decrease the pH.

4.3.5 Analytical methods

All the solutions coming from feed and permeate used during this study were determined by a conductivity meter (model CDM 81, Radiometer, Copenhagen, Denmark), a pH meter (Fisher Acumet model 915, Pittsburgh, PA), and plasma emission spectroscopy with a simultaneous (ICP-AES), Varian model (Varian Canada, Inc., Mississauga, Ont.). Quality controls were performed with certified liquid samples (multi-elements standard, catalogue number 900-Q30-002, lot number SC0019251, SCP Science, Lasalle, Quebec) to ensure the conformity of the measurement apparatus.

4.4 Results and discussion

4.4.1 Characterization of the membranes

4.4.1.1 *Water permeability* (A_{ipw})

Initial and final water permeability for the membranes is reported in Table 4.2. This permeability was measured at different transmembrane pressures. As can be seen from Table 4.2, the membrane permeability is significantly different for the two membranes. The NF-270 membrane type exhibits higher permeate flux values compared to the Desal 5 membrane.

As presented in this table, NF-270 (6) and (7) showed a decrease in permeability of 28.2% and 36.8%, respectively. This behaviour suggests that the membranes underwent preferential sorption (irreversible phenomenon).

On the other hand, it was observed that the Desal 5 membranes presented an increase in permeability over the initial values (Table 4.2). This data suggests that the electrolyte solutions contributed to the increase in membrane permeability (swollen effect) (Hamza *et al.*, 1995).

The NF-270 membrane was more permeable during all the experiments than the Desal 5, as seen from whole permeability results (Tables 4.2 and 4.3).

Table 4.2 Values of initial and final water permeability (A_{ipw}) of the membranes

Membrane	A_{ipw} (m) (x 10^{-14})	
	Initial	**Final**
NF-270 (6)	2.55	1.83
NF-270 (7)	2.47	1.56
Desal 5 (6)	0.72	0.88
Desal 5 (7)	0.67	0.79

4.4.1.2 *Evolution of the dynamic permeability (A_{id})*

Generally it is observed for a membrane that in the presence of electrolyte solutions under the same operating conditions, the dynamic permeability (A_{id}) is lower than pure water permeability (A_{ipw}). This behaviour was presented for the NF-270 membrane coupons (Tables 4.2 and 4.3).

On the other hand, the Desal 5 membranes presented the opposite behaviour. It was observed that under the same operating conditions, the dynamic permeability was higher than pure water permeability (Tables 4.2 and 4.3). In this case the dynamic permeability increased as the electrolyte concentration increased (in function of pH). It seems that the membranes were dependent on the electrolyte solution. As presented in the investigation made by Lebrun and Xu, (1999), they proposed that the pores can suffer changes or dynamic changes due to the presence of ions in the solution.

Table 4.3 Values of dynamic permeability (A_{id})

Membrane	**A_{id} (m) (x 10^{-14})**		
	K_2SO_4	**$K_2SO_4 + H_2SO_4$ (pH=2.9)**	**$K_2SO_4 + H_2SO_4$ (pH=2.32)**
NF-270 (6)	2.26	2.01	1.96
NF-270 (7)	2.10	1.98	1.61
Desal 5 (6)	0.83	0.93	1.15
Desal 5 (7)	0.77	0.85	1.01

4.4.1.3 Ionic rejection

Figures 4.2 to 4.5 illustrate the rejection of K^+ and SO_4^{2-} ions at different pHs. It can be seen from these figures that both membranes exhibited an excellent retention of sulphate and potassium ions at pH=6.76 (>95%) and good to medium retention at pH=2.9 and 2.32.

In general it was observed that the rejection of SO_4^{2-} and K^+ decreased with the increasing of electrolyte concentration (in function of pH) (Figures 4.2 to 4.5). Similar data were obtained by the Desal 5 (6) and NF-270 (6) membrane coupons.

As observed in these figures, the membrane retention was dependent on the electrolyte concentration of the feed solution. In this case higher rejection at lower feed concentration and lower rejection at higher feed concentration was observed, characteristic of charged membranes (Xu and Lebrun, 1999).

For the Desal 5 membrane, generally similar retentions for SO_4^{2-} and K^+ ions at the same pH were observed (Figures 4.2 and 4.3). This behaviour can be attributed to the Donnan exclusion phenomena, where these close retentions keep the electroneutrality of the solution on both sides of the membrane. Similar behaviour has been observed by some authors using different solutions (Ku *et al.*, 2005; Mehiguene *et al.*, 1999).

At pH=6.76 for NF-270, similar retentions for SO_4^{2-} and K^+ ions are also presented. As mentioned before, in order to keep electroneutrality, SO_4^{2-} and K^+ are repelled by the membrane. However at pH < Ip (pH =2.9 and 2.32), as the membrane is charged positively, it is observed that the membrane repelled the co-ion (K^+), and the counter-ions are rejected (SO_4^{2-}) (Figures 4.4 and 4.5).

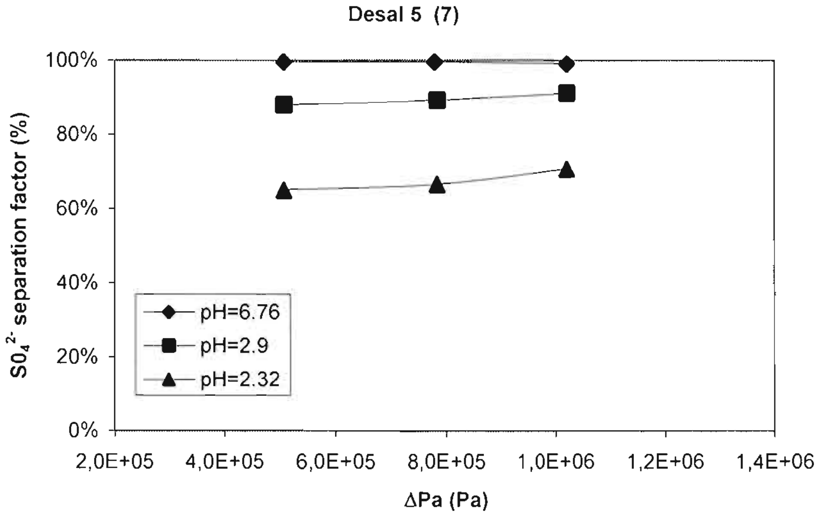

Figure 4.2 SO_4^{2-} separation factor vs. apparent transmembrane pressure for the Desal 5 membrane (7) at different pHs. Salt concentration = 1.1×10^{-2} mol/l; Q_c = 0.32 m³/s; 24 < T (°C) < 25

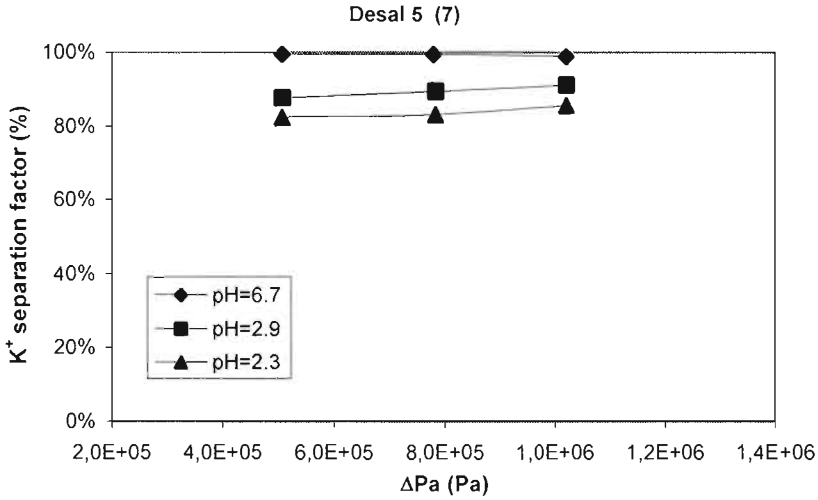

Figure 4.3 K^+ separation factor vs. apparent transmembrane pressure for the Desal 5 (7) membrane at different pHs. Salt concentration = 1.1×10^{-2} mol/l; Q_c = 0.32 m³/s; 24 < T (°C) < 25

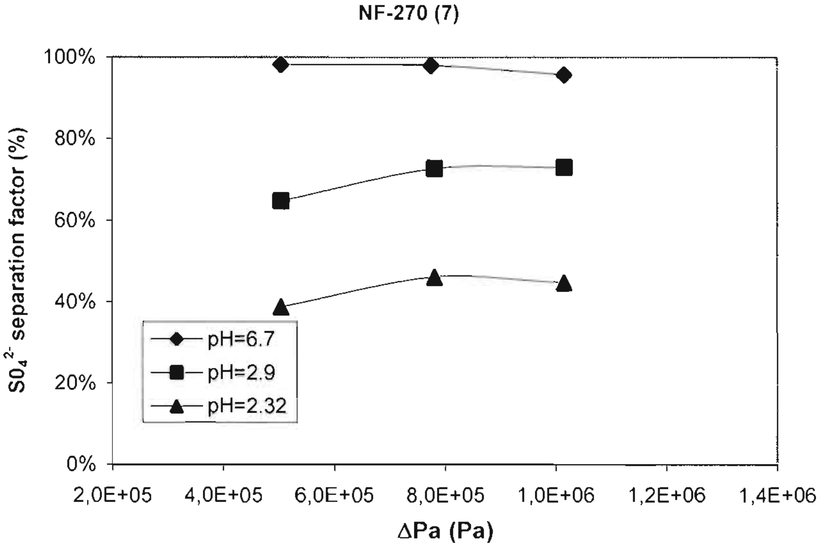

Figure 4.4 SO_4^{2-} separation factor vs. apparent transmembrane pressure for the NF-270 membrane (7) at different pHs. Salt concentration = 1.1×10^{-2} mol/l; Q_c = 0.32 m³/s; 24 < T (°C) < 25

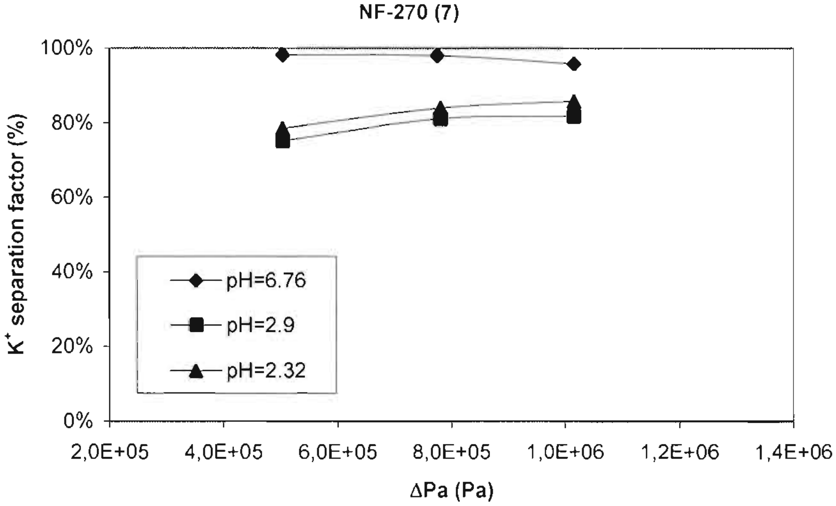

Figure 4.5 K^+ separation factor vs. apparent transmembrane pressure for the NF-270 membrane (7) at different pHs. Salt concentration = 1.1×10^{-2} mol/l; Q_c = 0.32 m³/s; 24 < T (°C) < 25

4.4.1.4 Acidic retention

Figures 4.6 and 4.7 represent the evolution retention of H^+ as a function of the applied pressure. From these figures, it can be seen that the membrane Desal 5 (7) presented the highest retention at pH=2.9 and lower retention of H^+ at pH 6.7. As this membrane is charged negatively at pH< Ip, the high ion retention presented by it at low pH suggests that due to the acidic solution, the protons are able to neutralize the negative sites on the membrane surface, thus reducing the anion repulsion effect caused by the membrane surface charge (Mehiguene *et al.*, 2000). On the other hand, the NF-270 (7) membrane presented an average H^+ retention. Figure 4.7 shows that an increase in pH results in an increase of membrane retention. It is assumed that the membrane surface charge becomes less negative as the pH increases.

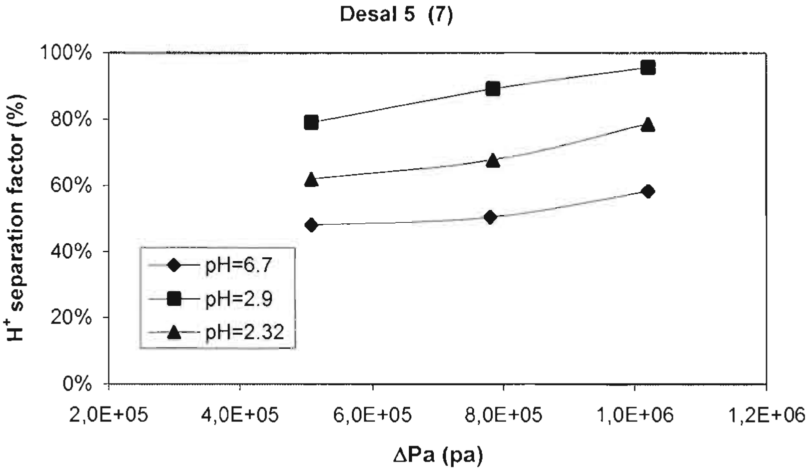

Figure 4.6 H+ separation factor vs. apparent transmembrane pressure for the Desal 5 membrane (7) at different pHs. Salt concentration = 1.1 × 10^{-2} mol/l; Q_c = 0.32 m^3/s; 24 < T (°C) < 25

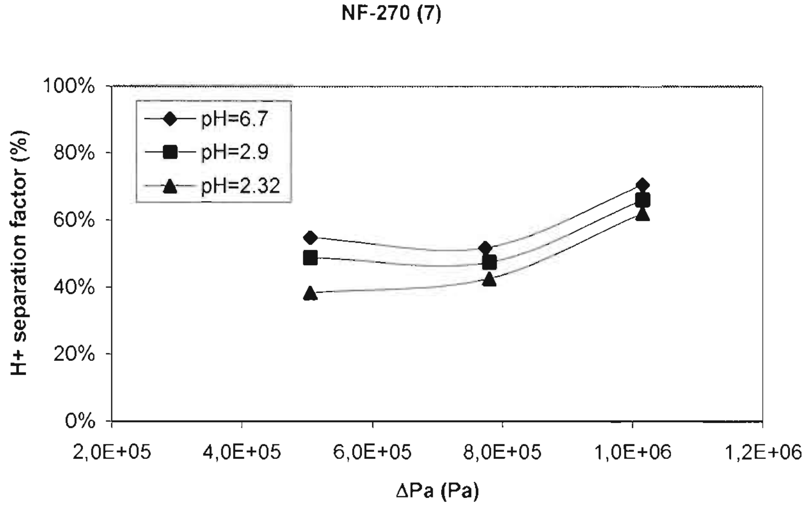

Figure 4.7 H+ separation factor vs. apparent transmembrane pressure for the NF-270 membrane (7) at different pHs. Salt concentration = 1.1 × 10^{-2} mol/l; Q_c = 0.32 m^3/s; 24 < T (°C) < 25

4.4.2 Soil washing treatment

Soil washing has been widely used for many years as a technique for decontaminating soil. As mentioned before, this method is a water-based soil treatment that consists of the extraction of organic and inorganic contaminants using a washing solution (Barona *et al.*, 2001; Peters, 1999; Sikdar *et al.*, 1998). Soil washing agents such as organic acids (citric acid, acetic acid, etc.), chelating agents (EDTA, ADA, NTA, DTPA), oxidative agents ($KMnO_4$, H_2O_2, etc) and principally inorganic acids (H_2SO_4, HCl, HNO_3, etc.), have been widely applied to extract metal ions from soil (Meunier *et al.*, 2002; Peters, 1999; Tuin and Tels, 1991). The result after this method is a multi-component system mixture, characterized by richness in organic and principally inorganic compounds.

Commonly the application of inorganic acids such as HCL, HNO_3, etc., or, as in this case, the use of H_2SO_4, is done to remove metal ions from soils; however, the particular washing solution applied to the soil can depend on the metal involved, the specific metal compound and the species involved in the removal (Peters, 1999).

4.4.2.1 Leaching of ions with H_2SO_4

Values of the acidic leachate solution characterization before NF treatment are depicted in Table 4.4. The results reported in this table indicate that the acidic leachate contains a variety of ions, indicative of the effectiveness of the washing solution (H_2SO_4). The electric conductivity presented by this solution principally came from the high concentration of H_2SO_4. The leachate produced is a yellowish solution due to the presence of humic acids. This acidic solution is not subjected to filtration pre-treatment for the removal of any type of contaminants.

Table 4.4 Characterization of the acidic leachate solution before NF treatment

Parameter	**Value**
pH	3.15
ORP (mV)	451
Conductivity (ms/cm)	3.36
TOC (mg/l)	19.4
Ions (mol/l)	
H^+	7.08×10^{-1}
As^{5+}	1.82×10^{-3}
B^{3+}	5.30×10^{-2}
Cr^{3+}	3.60×10^{-3}
Cu^{2+}	9.76×10^{-2}
Fe^{2+}	2.09×10^{-1}
K^+	6.73×10^{-1}
Mg^{2+}	5.92
Mn^{2+}	5.20×10^{-1}
Na^+	9.64
Ni^{2+}	1.09×10^{-2}
PO_4^{3-}	7.71×10^{-1}
Pb^{2+}	2.47×10^{-2}
SO_4^{2-}	3.26×10^{-1}
Zn^{2+}	7.87×10^{-1}

4.4.3 Membrane dynamic permeability of the acidic leachate solution

As presented in Figure 4.8, the flux increased with increasing pressure with no linearity. This evolution clearly indicates that the membranes are dependent on the solution concentration. This trend is possibly due to the presence of the accumulation of inorganic and organic molecules and suspended macromolecules on the membrane surface. This behaviour was expected due to the high concentration of the solution measured by electric conductivity (Table 4.4).

As can be seen from Table 4.5, the membranes perform differently. Membrane pore clogging by organic or inorganic compounds probably occurs particularly for the NF-270 membrane because the permeability was not recuperated after the run with deionized water.

On the other hand, for the Desal 5 membrane, it was observed that the dynamic permeability increased comparing to pure water permeability (Table 4.5). As mentioned before, the pores can suffer changes or "dynamic changes" due to the presence of ions in the solution, thus producing an increase in permeability (Lebrun and Xu, 1999). This behaviour indicates that the dynamic permeability of this membrane is dependent on the electrolyte solution. Similar behaviour has been observed by some authors using different solutions (Lebrun and Xu, 1999; Noël *et al.*, 2000).

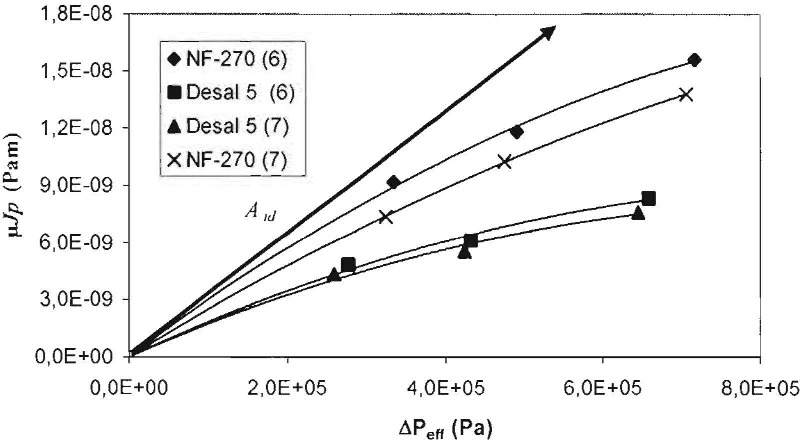

Figure 4.8 **Permeate flux vs. effective pressure for the acidic leachate solution. pH = 3.15, Q_c = 0.32 m³/s; 24 < T (°C) < 25**

Table 4.5 Values of dynamic permeability (A_{id}) and final water permeability (A_{ipw})

Membrane	A_{ipw}, **(m)** (x 10^{-14})	A_{id}, **(m)** (x 10^{-14})	A_{ipw}, **(m) final** (x 10^{-14})
NF-270 (6)	1.99	1.74	1.83
NF-270 (7)	1.71	1.52	1.56
Desal 5 (6)	0.86	0.99	0.88
Desal 5 (7)	0.76	0.92	0.79

4.4.4 Removal of metal ions: permeate quality

The permeate quality is expressed in terms of membrane retention during the nanofiltration of the acidic leachate solution. In this case, for all membranes the permeate obtained was a clear and colourless solution with relatively low amounts of ions measured by ICP-AES. Table 4.6 exhibits the permeation results. As presented in this table, in general divalent ions were better rejected than monovalent ions, a typical behaviour of charged membranes.

As the feed pH can considerably influence the ion rejection during filtration processes due to the change of membrane surface charge, in the case of Desal 5 it seems that the good ion retention indicates that the increased protons (due to the low pH) in the acidic solution might neutralize the negative sites on the membrane surface.

The high retention presented by NF-270 can be explained by the charge of this membrane. In this case, the cations are rejected by the membrane charge, as this membrane is positively charged at pH< Ip.

Those results present the efficacy of NF membranes in the treatment of soil washing solutions.

Table 4.6 Ionic separation factor of the acidic leachate solution

Membrane	Pressure (PSI)	Ion separation factor (%)							
		Cu^{2+}	Fe^{2+}	K^{+}	Mg^{2+}	Mn^{2+}	Na^{+}	SO_4^{2-}	Zn^{2+}
NF-270 (6)	75	99	100	85	100	100	87	90	100
	110	99	100	100	100	99	78	83	99
	150	100	100	100	100	100	98	100	99
NF-270 (7)	75	98	89	80	99	98	83	89	98
	110	100	100	100	100	100	98	100	99
	150	100	100	100	100	100	98	100	99
Desal 5 (6)	75	98	84	86	100	99	80	93	99
	110	98	100	69	100	99	62	89	100
	150	100	100	100	100	100	98	100	99
Desal 5 (7)	75	98	89	80	99	98	83	89	98
	110	100	100	100	100	100	98	100	99
	150	100	100	100	100	100	98	100	99

4.4.5 TOC analysis

It is difficult to specify the type of organic contaminants present in the soil and at the same time in the acidic leachate solution. However, in this type of contaminated soil, one of the major components of the total organic carbon is composed of non-specific humic-type substances principally humic acids such as tannins, lignins, fulvic acids, etc.

Figure 4.9 presents the removal of TOC retention as a function of the applied pressure. The result shows that all the membranes presented similar retentions (between 65 and 90%). As mentioned before, due to the yellowish color in the feed solution (acidic leachate) given by humic acids and soils containing humic-type substances, it is assumed that this retention is due to the presence of those organic components and mainly by humic acids due to their chelating ability to bind different metal ions.

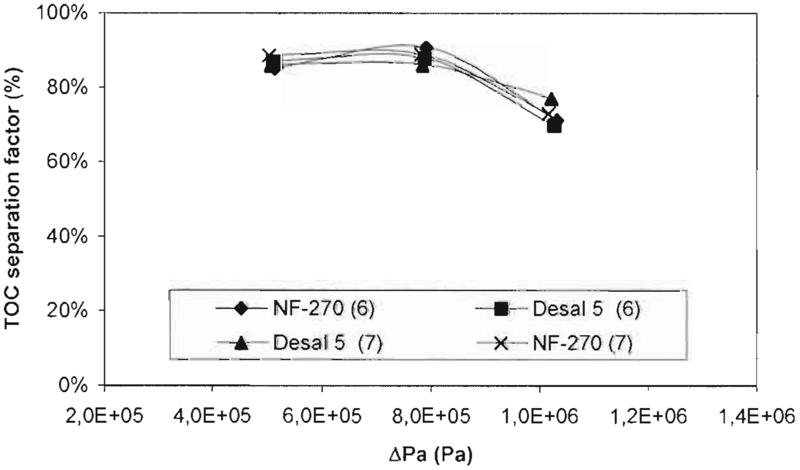

Figure 4.9 TOC separation factor (%) vs. apparent pressure for the acidic leachate solution. pH = 3.15, Q_c = 0.32 m³/s; 24 < T (°C) < 25

4.4.6 H^+ separation factor

During the filtration of the acidic leachate solution, H^+ retention increased with an increase in pressure for both membranes, showing negative retentions as depicted in Figure 4.10. As presented in this figure, the retention of H^+ ions was slightly higher for the Desal 5 than for the NF-270 membrane. This behaviour suggests that in acidic conditions, the positive surface charge rejects cations, leading to enhanced permeation of acid (Tanninen *et al.*, 2004).

This negative proton retention when the membrane is positively charged has been investigated by several authors (Bandini *et al.*, 2005; Childress and Elimelech, 2000; Hagmeyer and Gimbel 1999; Tanninen and Nyström, 2002) and this behaviour has been attributed to the higher mobility of the H^+ compared to other cations in solution. This low retention of acid and the high retention of metal ions, suggest the possibility of acid recuperation through NF treatment.

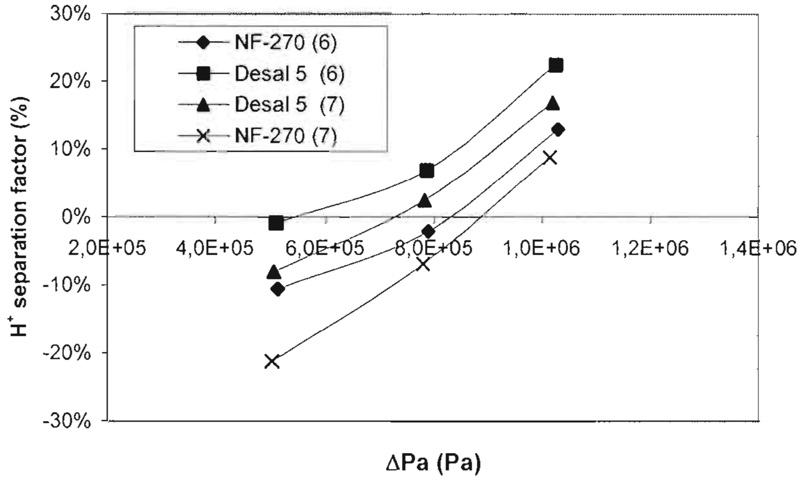

Figure 4.10 H^+ separation factor (%) vs. apparent pressure for the acidic leachate solution. pH = 3.15, Q_c = 0.32 m³/s; 24 < T (°C) < 25

4.4.7 Soil washing integrated to NF process

Several studies, at both laboratory and industrial scale, have investigated the performance of the membrane process (RO, NF, UF) on the separation of organic and inorganic pollutants from waste waters coming from soil treatments. These results have demonstrated the effectiveness of incorporating membrane processes into soil treatments (Peters, 1998, 1999; Linde and Jönsson, 1995; Volchek *et al.*, 2002).

Soil washing techniques have been characterized to be an economical and feasible process due to the application of effective and low cost chemicals (particularly the use of inorganic acids). The application of this method can lead to the reduction of the volume of hazardous materials and at the same time the transformation of contaminants to non-hazardous substances (Peters, 1999; Semer and Reddy, 1996).

On the other hand the advantages of the application of NF membranes among other filtration processes not only are higher fluxes, low operating pressures, relatively low operation and maintenance cost but also higher removal efficiency of organic and inorganic components, reducing the volume of waste products and a possibility for acid reuse (Lu *et al.*, 2002; Semer and Reddy, 1996; Volchek *et al.*, 2002). For that reason, the combination of soil treatments in the NF process can bring about the removal and recovery of contaminants from a great variety of aqueous streams and a total water recirculation in the system, eliminating the negative problems related with the release of trace contaminants into the environment as a result of soil washing processes (Volchek *et al.*, 2002).

4.5 Conclusions

The removal of pollutants from soils is one of the most challenging environmental tasks. For that reason, this study was intended to evaluate two NF membranes for the recovery of ions coming from contaminated soil. The experimental results have successfully demonstrated that the use of the washing solution H_2SO_4 has a high extraction efficiency in the removal of ions from contaminated soils. During the application of NF membranes in the treatment of the acidic leachate solution, the commercial membrane showed high ion selectivity. Additionally it demonstrated a good removal of TOC during the filtration experiment (65 to 90%). During the filtration experiments, the Desal 5 membrane demonstrated an increase in dynamic permeability, showing its dependence to the electrolyte solutions. On the other hand, the NF-270 membrane presented an opposite behaviour: a decrease in dynamic permeability. These results indicate that the best candidate for the removal of metal ions was Desal 5, which presented good membrane permeability combined with good ion retention and acidic resistance.

During this investigation it has been demonstrated that the application of nanofiltration processes will bring about the elimination of metal ions from waste waters, a possible recovery of acid during the process and a reduction of the amount of inorganic and organic waste.

Abbreviations and Symbols

A_{ipw}	Pure water permeability of membrane, (m)
A_{id}	Dynamic solution permeability of membrane, (m)
C	Concentration, (mol/l)
f, f'	Overall and intrinsic separation factor separation, (dimensionless)
I_p	Isoelectric point
J_p	Solution permeate flux, (m/s)
M	Molar concentration (mol/l)
ORP	Oxydoreduction potential, (mV)
P	Pressure, (Pa)
P_a	Apparent gradient pressure (Pa)
P_e	Effective pressure gradient (Pa)
Q_c	Feed flow rate, (m^3/s)
Q_p	Permeate flow rate, (m^3/s)
S_m	Membrane area, (m^2)
T	Temperature, (°C)
TOC	Total organic carbon, (mg.O_2/l)
X	Molar fraction
X_{A1}	Molar fraction of the feed
X_{A2}	Molar fraction of the concentrated boundary layer

X_{A3}	Molar fraction of the permeate

Greek letters

Δ	Gradient
μ	Fluid viscosity, (Pa.s)
Π	Osmotic pressure, (Pa)
$\sum i$	Number of ions per molecule of solute

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CHAPTER V

EFFECTIVENESS OF SOIL WASHING, NANOFILTRATION AND ELECTROCHEMICAL TREATMENT FOR THE RECOVERY OF METAL IONS COMING FROM CONTAMINATED SOIL

Water research

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5.1 Abstract

This research was conducted to integrate soil washing, nanofiltration membranes and electrochemical treatment as feasible methods for the remediation of contaminated soils. For this investigation, two acidic leachates (pH=2) were prepared using HCl and H_2SO_4-NaCl as soil-washing agents. The results of the soil washing indicated that HCl and the combined H_2SO_4-NaCl were effective for the extraction of ions resulting from a contaminated soil. It was observed that both leachates presented similar chemical compositions. Following this procedure, the leachate solutions were pre-filtered by microfiltration, followed by nanofiltration using the Desal 5 membrane. The experiment results showed that nanofiltration membranes presented a high ion-retention rate for the two leachates. In general, better retentions were observed with the leachate prepared with HCl than H_2SO_4-NaCl. In order to treat the concentrate resulting from the nanofiltration treatment, it underwent an electrochemical procedure (electrochemical deposition) as an alternative method for safe disposal. The results showed a high reduction of toxic ions, such as Pb and Cu, from the solution.

These three processes applied in conjunction not only indicated that the treatment of solutions heavily-contaminated with inorganic pollutants resulting from contaminated soils were feasible, but also suggested the possibility of treating different types of heavy industrial effluents.

Keywords

Soil washing; Leachate; Nanofiltration; Sulfuric acid; Hydrochloric acid; Sodium chloride; Ion removal; Electrochemical treatment

5.2 Introduction

The cleanup of soils contaminated with toxic ions has been one of the most difficult tasks, due to its toxicity and the long-lasting adsorption of ions by soils. For example, in Western Europe there are 1 400 000 sites contaminated with inorganic and/or organic pollutants (ETCS, 1998). According to the US EPA, 31 000 sites in the United States are contaminated with metals, and according to the Ministère de l'Environnement et de la Faune du Québec (MEFQ, 2001), 5 125 sites are polluted in Canada, in the province of Quebec, 11% of which are contaminated with inorganic pollutants.

Among many technologies used to decontaminate soils with inorganic pollutants, soil washing has been one of the most-used treatments because of its rapid remediation process (Tuin and Tels, 1990) and its low cost in comparison to other remediation techniques (Kuhlman and Greenfield, 1999). The successful application of this technique depends mainly on the use of the washing agent. The following chemicals are the most-used washing solutions for extracting metals from soils:

(1) EDTA (Ethylenediaminetetraacetic acid) is the most commonly used chelate agent, due to its strong metal-complexing ability (Norvell, 1991). Its efficiency relies on the solubilization of poorly available metals in soils, such as Pb, Cr and Cu (Sarret *et al.*, 2001). It is expensive and toxic, and presents a low level of biodegradability (Dirilgen, 1998; Finzgar *et al.*, 2006). (2) NTA (Nitrilotriacetic acid) is highly biodegradable under environmental conditions. It is also toxic and considered a class II carcinogen (Peters, 1999). It is not recommended for soil cleanup (Davis and Singh, 1995). (3) HCl (hydrochloric acid) is a very efficient reagent for the removal of Pb, Zn, Cd and, in some cases, Cu and Ni. HCl is the most-used acid in ion-metal recuperation (Tampouris *et al.*, 2004). Applied in-situ, HCl can alter soil properties, due to mineral dissolution and increased mobility of contaminants (Neilson *et al.*, 2003). It presents a low cost. (4) HNO_3 (nitric acid) is effective in the removal of inorganic pollutants from the soil. As an acid, it is lethal to soil micro-flora and destructive to the physical and chemical properties of soil, due to mineral dissolution (Neilson *et al.*, 2003). (5) H_2SO_4 (sulphuric acid) is a very

efficient and economical reagent for the removal of ions from soil (Djedidi *et al.*, 2005). (6) Citric acid is a nontoxic acid that forms relatively strong complexes. It is easily biodegradable, but it presents a lower effectiveness in the removal of metal ions (Di Palma and Mecozzi, 2007).

The problem with soil washing is the production of a complex solution that requires an additional treatment. Therefore, it is important to remove leached ions from soil leachates.

Among the many liquid-separation techniques, nanofiltration (NF) is an attractive approach for the treatment and removal of contaminants from wastewaters. NF is able to separate different ions according to their valence, and it has the ability to remove inorganic substances through electrostatic interactions between the ions and membranes. With the application of NF, it is possible to obtain an outstanding quality of permeate. On the other hand, the concentrate represents a barrier, due to its high concentration of pollutants.

An alternative and effective process to reduce the levels of pollutants in the concentrate is an electrochemical treatment. This technique allows a decrease in the amount of metallic sludge produced, by generating compact and less voluminous sludge, thereby resulting in a cost-saving process (Rajeshwar and Ibanez, 1997). This process can work at different pHs according to the characteristics of the electrodes (Subbaiah *et al.*, 2002). It has been amply applied to treat municipal and industrial effluents (Meunier *et al.*, 2004). During the investigation performed by Djedidi *et al.* (2005) and Beauchesne *et al.* (2005), the effectiveness of the electrochemical process in treating acidic soil leachates strongly-loaded with several ions was demonstrated.

The objective of this study was to evaluate the performance of soil washing, nanofiltration membranes and the electrochemical treatment as remediation strategies for soil and wastewater contaminated with toxic ions.

5.3 Soil methods

5.3.1 Site description

Soil samples used in the experiments were collected from the Pointe-aux-Lièvres site located in Quebec City (QC, Canada). It was chosen as a typical soil contaminated with inorganic and organic pollutants, due to industrial activities. The fraction of soil used was superior to 20 µm and less than 2 mm (Meunier *et al.*, 2004). Supplementary details about the soil can be found in the investigation carried out by Meunier *et al.*, (2002).

5.3.2 Washing procedure

The extraction of metals from soils was performed using two different methods.

- **Hydrochloric acid (HCl).** The leachate was prepared as follows: 2 kg of soil was added to 20 l of water, agitated by a variable speed mixer at 800 rpm with a stainless steel propeller (SS-316L, Labcor Technical Sales, Montreal, Canada) fixed to a Caframo RZR50 rotor (Labcor Technical Sales). To this suspension, 640 ml of HCl (Fisher scientific, ASC reagent) was added until a pH of 2 was obtained. This leachate was agitated for about 2 h. A volume of 20 ml of a polymer solution (1 g l^{-1} of Percol E-10, an anionic polymer made of sodium acrylate and acrylamid copolymer, Ciba Specialty Chemicals Canada Inc., Mississauga, Canada) was added to facilitate the solid/liquid separation. This leachate was filtered using Whatman no. 4 membrane (Whatman Bioscience Inc., Newton, MA, USA) under a vacuum to remove soil particles from the solution.

- **Sulphuric acid and NaCl (H_2SO_4-NaCl).** H_2SO_4 and NaCl were in combination, based on their successful application as a solubilized agent (Djedidi *et al.*, 2005). To prepare the saline leachate, 6 kg of soil was added to 18 l of water, agitated by a variable speed mixer at 800 rpm with a stainless steel propeller fixed to a Caframo RZR50 rotor. Subsequently, 6.5 kg of NaCl was added, followed by H_2SO_4 (36 N) (Fisher scientific, ASC reagent) until a pH of 2 was obtained. This leachate was agitated for about 25 min. A volume of 5 ml of a polymer solution (1 g l^{-1} of Percol E-10) was added to facilitate the settling. This leachate was passed through a Whatman no. 4 membrane under a vacuum.

Following this procedure, the solutions were pre-filtered through microfiltration (MF) using a pore size of 2 µm (GE-Osmonics, Minnetonka, MN, USA) for the removal of suspended solids and high-molecular-weight colloidal compounds to minimize NF membrane blocking.

5.4 Nanofiltration membrane

The selected nanofiltration membrane was a Desal 5 manufactured by GE-Osmonics. This membrane is a polymeric membrane, in which a polyamide selective layer is supported on a polysulfone layer (Platt *et al.*, 2004). According to the manufacturer, it is a positively-charged membrane, having an iso-electric point of 4, a pH resistance (20 °C) between 2 and 11 (Hagmayer and Gimbel, 1998; Tanninen *et al.*, 2004) and a molecular weight cut-off of the membrane of 200-300 Da.

5.4.1 NF pilot-scale for soil washing experiment

The performance of the tubular Desal 5 membrane was evaluated in a filtration equipment manufactured by Hayka Industry (Montreal, Canada). The equipment was made for operation in acidic conditions. The schematic diagram of the filtration equipment is illustrated in Figure 5.1.

In this study, the experiments were realized in a batch mode with recirculation of substances. Each filtration experiment was done with the same membrane. During the experiments, the feed solution from the tank was pumped to the membrane, obtaining a concentrate that was recycled the feed tank and a permeate that was not recirculated into the system (Fischer, 2006). The effective surface area of the membrane was 2 m^2.

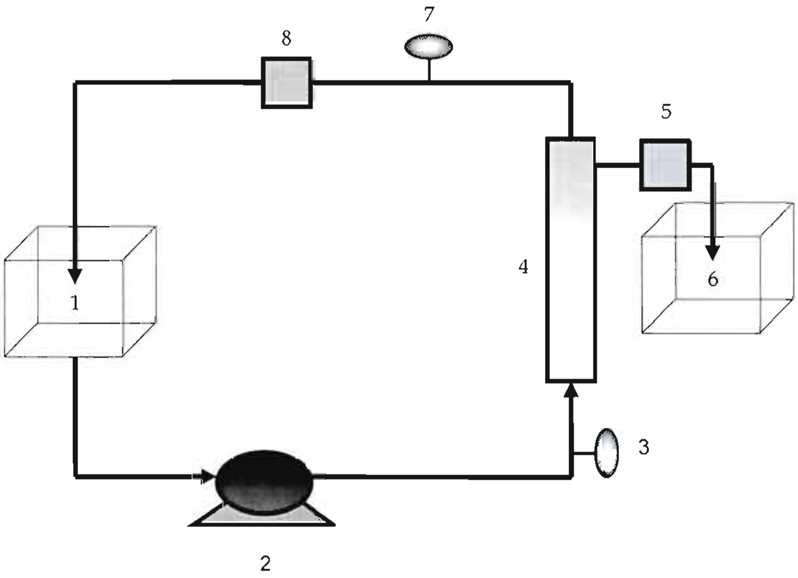

Figure 5.1 **Schematic diagram of NF set-up**

1. Feed tank 2. Pump 3. Pressure valve 4. Tubular membrane 5. Permeate flowmeter 6. Permeate 7. Pressure valve 8. Concentrate flowmeter

5.4.2 Determination of water permeability (A_{ipw})

Membrane permeability was determined using distilled water that was measured before and after testing each inorganic solution. The pressures used were 3.45 × 10^5, 6.89 × 10^5 and 1.03 × 10^6 Pa with a constant recirculation flow rate of 1.21 × 10^{-4} m^3 s^{-1} at room temperature.

The determination of water permeability (A_{ipw}), dynamic permeability of solutions (A_{sd}) and ionic separation factor (f) can be found in the investigation made by Lebrun and Xu, 1999.

5.4.3 Determination of dynamic permeability (A_{id})

Dynamic permeability of the membranes was determined using the two acidic leachates. For the HCl leachate, the operating conditions —pressure and recirculation flow rate— were 1.72 × 10^6 Pa and 1.87 × 10^{-4} m^3 s^{-1} respectively. For the H_2SO_4-NaCl leachate, the same pressure was used for the HCl run and a recirculation flow rate of 2.23 × 10^{-4} m^3 s^{-1}. Between each NF run, the membrane was washed with deionized water in order to avoid experimental errors.

5.5 Electrochemical treatment

The electrochemical treatment was conducted using the concentrate (approximately 1.5 l of each leachate) coming from the NF treatment. For this experiment, it was used a batch electrolytic cell made of acrylic material with a dimension of 12 cm (width) x 12 cm (length) x 19 cm (depth). The electrode sets (anode and cathode) consisted of eight parallel pieces of metal plates each, having a surface area of 220 cm^2, situated 1.5 cm apart and submerged in the soil leachate. Titanium coated with platinum (Ti/Pt) was used as the anode, whereas stainless steel (SS, 316L) was used as the cathode. Four anodes and four cathodes alternated in the electrode pack. The electrodes were installed on a perforated acrylic plate placed 2 cm from the bottom of the cell. Mixing in the cell was achieved by a Teflon-covered stirring bar installed between the perforated plate and the bottom of the cell. A working volume varying from 1.3-1.5 l was used for all experiments. Samples of 10 ml were drawn at 30 min intervals and monitored for pH and residual metal concentration. Between the assays, electrolytic cells (including the electrodes) were cleaned with 5% (v v^{-1}) hydrochloric acid solution and then rubbed with a sponge and rinsed with tap water.

The anode and cathode sets were connected to the negative and positive outlets of the DC power supply Xantrex XFR40-70 (Aca Tmetrix inc., Mississauga, Canada). The current of 3.0 A was held constant for each run with a retention time of 90 min. The electric current was divided between all the electrodes. The anode and cathode electrodes were not consumed during the electrolysis. The diagram of the electrolytic cell can be found in the investigation made by Beauchesne *et al.*, (2005).

5.6 Analysis of the samples

The conductivity of the solutions coming from the feed and permeate was determined by a conductivity meter (model CDM 81, Radiometer, Copenhagen, Denmark). The pH of the solutions was measured using a pH meter Fisher Acumet model 915 (Pittsburgh, PA, USA). The ions in solutions were measured by a Varian ICP-AES (model Vista-AX, Varian Canada Inc., Mississauga, Canada). Quality controls were performed with certified liquid samples (multi-elements standard, catalogue number 900-Q30-002, lot number SC0019251, SCP Science, Lasalle, Canada) to ensure the conformity of the measurement apparatus. To determine the metal concentration in sludge resides (generated during electrolysis), the latter was first digested in HNO_3, HF, and $HClO_4$ according to APHA *et al.* (1999).

5.7 Economic aspects

The economic study of electrochemical treatment incorporated only energy consumption and sludge disposal. The energy consumed was estimated at a cost of 0.06 USD kW h^{-1}. The disposal cost for the residual sludge, including, transportation (excluding drying costs) were evaluated at 300 USD t^{-1} of dry residue by assuming that the residues were considered as hazardous materials. The total cost was assessed in terms of U.S. dollars (USD) spent per cubic meter of treated effluent (USD m^{-3}).

5.8 Results and discussion

5.8.1 Soil washing

During this study, a pH of approximately 2 was preferred to extract the metals from the soil. The main mechanisms for metal removal under acidic conditions are dissolution and solubilization enhanced by low pH, and dissolution of specific soil components containing metals (Neale *et al.*, 1997).

The two leachates obtained during this investigation were complex solutions containing different inorganic pollutants, varying in concentration (Table 1). Both solutions presented a brownish-yellow color as a result of the natural organic matter dissolved in water. Principally, the high conductivity of H_2SO_4-NaCl leachate was partly due to the presence of NaCl added to the leachate (6.5 kg). As depicted in Table 1, these results indicate that strong acids are not always able to remove a great amount of ions from the soil. Some acids tend to attract metal ions better than others. This tendency depends on many factors such as the nature of the soil, the solvent used, the ionic and acid concentration, the metal mobilization, and so on. This explains the low concentrations that can be observed in Table 5.1. Nevertheless, the high concentration of calcium compared with the other ions could be to the dissolution of carbonates that result in the high release of Ca in the solution (Di Palma and Ferrantelli, 2005). In addition, it can be observed from Table 5.1 that Pb, considered a toxic ion for the environment, obtained better results using H_2SO_4-NaCI than HCl. In fact, some studies have demonstrated that NaCl is a good solubilization agent (Nedwed and Clifford, 2000; Djedidi *et al.*, 2005). As the authors mentioned in their investigation, chloride ions are able to react with Pb to form soluble salt complexes such as $PbCl_4^{2-}$, $PbCl_3^-$ or $PbCl_{2\ (aq)}$. Also, the lower extraction presented by Pb could be to the fact to the higher humic substance content in the leachate solutions. COOH groups on humic substances have higher affinity for Pb than other groups on mineral surfaces (Hohl and Stumn, 1976).

5.8.2 Leachate treatment by NF membrane

As both the HCl and H_2SO_4-NaCl leachates were highly contaminated with inorganic contaminants, the samples were treated with a Desal 5 membrane in order to study membrane performance in terms of ionic retention and membrane permeability. It was observed that both permeates consisted of clear and colourless solutions.

Table 5.2 shows that both leachates contain a high salt concentration containing different ions. Conductivity was reduced by more than 50% for both leachates (HCl leachate final conductivity 6.1 mS/cm and H_2SO_4-NaCl 144 mS/cm), and many inorganic ions were retained by more than 65%.

Table 5.1 Chemical composition of HCl and H_2SO_4-NaCl leachates before NF treatment

Parameters	HCl leachate	H_2SO_4-NaCl leachate
pH	2.4	2.2
ORP (mV)	545	514
Conductivity (mS/cm)	26.6	317
NH_4 (mg/l)	149	156
Ions (mol/l)		
H	3.98×10^{-3}	6.31×10^{-3}
Al	4.77×10^{-3}	4.61×10^{-4}
B	9.62×10^{-5}	1.31×10^{-4}
Ba	7.57×10^{-6}	6.56×10^{-6}
Ca	1.17×10^{-1}	3.93×10^{-2}
Cd	3.02×10^{-6}	6.11×10^{-6}
Co	3.52×10^{-6}	2.58×10^{-6}
Cr	4.78×10^{-6}	1.87×10^{-6}
Cu	1.38×10^{-4}	1.54×10^{-4}
Fe	4.26×10^{-5}	1.44×10^{-5}
K	8.19×10^{-4}	7.61×10^{-3}
Mg	8.47×10^{-3}	9.80×10^{-3}
Mn	6.39×10^{-4}	1.55×10^{-3}
Na	2.06×10^{-3}	3.38
Ni	1.22×10^{-5}	2.31×10^{-5}
P	4.24×10^{-4}	1.94×10^{-4}
Pb	4.10×10^{-4}	2.29×10^{-3}
S	9.53×10^{-4}	5.97×10^{-2}
Se	1.40×10^{-6}	2.91×10^{-6}
Si	3.49×10^{-3}	1.22×10^{-3}
Zn	1.33×10^{-3}	3.41×10^{-3}

Table 5.2 Ionic separation factor (%) for the HCl and H_2SO_4-NaCl leachates

Ion	HCl leachate (%)	H_2SO_4-NaCl leachate (%)
Initial conductivity (mS/cm)	26.6	317
NH_4	-1.3	-9.2
H	-127.9	35.7
Al	98.4	91.7
Ba	67.7	38.0
Ca	84.2	42.6
Cd	-7.2	27.4
Co	87.1	69.4
Cr	97.2	88.3
Cu	23.4	11.8
Fe	98.2	96.7
K	-41.8	-0.4
Mg	92.2	79.2
Mn	86.2	66.6
Na	5.6	5.8
Ni	89.0	76.6
Pb	-107.2	35.8
S	96.5	88.7
Si	12.9	2.7
Zn	-4.1	19.8

5.8.2.1 HCl leachate

In general, Table 5.2 shows that metals such as Co, Cr, Fe, Mn and Ni were better rejected than K and Na, which are relatively harmless for the environment. This low retention presented by K and Na were due to the characteristics of the Desal 5 membrane. On the other hand, the high retention presented by some metals was due to its binding with functional groups, provoking the repulsion of co-ions by the membrane surface and the retention of counter-ions, satisfying the electroneutrality condition. Also, due to its binding the degree of retention rose due to a heightened repulsion by the membrane (sieving mechanism). Another reason that could influence the ion retention was the diffusion coefficient. Some ions, such as K^+, Na^+, Ca^{2+} and Mg^{2+} with diffusion coefficients of 1.96×10^9, 1.33×10^9, 0.79×10^9, 0.71×10^9 m^2 s-1 respectively (Atkins, 1990), show that the higher the diffusion coefficient, the lower the retention rate.

Moreover, it was observed a negative rejection of H. This behaviour may be attributed to the Donnan effect. This effect was possibly responsible for the low retention presented by K and Na. This phenomenon was also observed in the investigation made by Volchek *et al.* (2002) and Bandini *et al.* (2005). The negative retention presented by some ions can be possible when mixed solutions that contain sufficient amounts of easily-retainable multivalent ions or organics are filtered by NF (Gilron *et al.*, 2001). In addition, a negative retention for ammonia was observed. This retention was expected, considering the molecular weight cut-off of the membrane (200-300 g mol^{-1}). According to Marttinen *et al.*, (2002), the retention of ammonium salts in NF depends on the size of the complex.

5.8.2.2 H_2SO_4-NaCl leachate

Retention values for H_2SO_4-NaCl after NF treatment are also depicted in Table 5.2. As the retention of metal was strongly dependent on the pH, due to a stronger binding with the polymeric ligands, it was observed that some ions were retained by the membrane in high percentage (for example Al, Cr, Fe, Mg and S). In this case the pH is able to protonate and deprotonate not only the functional groups of the membrane but also the molecules present in the solution (Teixeira *et al.*, 2005). Consequently this will change the membrane charge, membrane pore size and consequently membrane performance (Teixeira *et al.*, 2005). Additionally, this behavior can be attributed to different mechanisms: (1) electrostatic repulsion between ions and the membrane surface charge; (2) changes in the solution viscosity (this solution presented high concentration of NaCl used during the soil washing); or (3) the diffusion coefficients (Childress and Elimelech, 2000).

Finally, no negative retention value for H was observed. It was probably due to the metal salt concentration that influenced the acid permeation. In addition, as this solution contained a large amount of S ions, which probably affected the filtration of Cu, K and Na ions through the membrane (Donnan exclusion phenomenon).

Also, NH_4 presented a negative retention (-9.2 %). The retention of ammonium salts in NF depends on the size of the complex (Marttinen *et al.*, 2002).

5.8.2.3 Membrane integrity

The integrity of the membrane was investigated by measuring pure water permeability before and after filtration of the two leachates. Table 5.3 presents the data obtained during the experiment. It was observed that the feed concentration of the two leachates influenced the membrane permeability. In this case, a decrease in final water permeability of about 16.1% was observed. This decreased could be due to the osmotic pressure build-up created by the retained salts, the accumulation of molecules and suspended macromolecules on the membrane surface, or the shielding of the membrane charge by the high ionic strength. Another factor that could influence the osmotic pressure build-up was the operating pressure. In this case, the applied operating pressure was 1.72×10^6 Pa (it was kept constant), which was not high enough to overcome the osmotic pressure of the concentrated leachate.

During the run of H_2SO_4-NaCl leachate, a reduction in membrane permeability of 61.3% was observed. This behavior can be explained by the soluble inorganic compounds which become supersaturated and then precipitated, and which finally produced a membrane surface blockage. Principally NaCl influenced this phenomenon, because the concentration of the salt (6.5 kg) added was higher of its solubility degree. The decline of the flux due to inorganic scaling could be dependent on the membrane properties, the module geometry, the feed characteristics, the type of solute and the operating conditions and the salts present in the solution (Shaalan, 2002). It is difficult to know what kind of salts provoked the salt precipitation for this leachate, but the most common salts found in inorganic scaling are calcium sulfate ($CaSO_4$), calcium carbonate ($CaCO_3$) and silica (SiO_2) (Lee and Lueptow, 2003).

Table 5.3 Values of permeability (A_{ipw}) and dynamic permeability (A_{id}) of Desal 5 membrane

Parameters	Values (x 10^{-14})
Initial water permeability (A_{ipw})	1.55
HCl leachate (A_{id})	1.22
Water permeability (A_{ipw})	1.43
H_2SO_4-NaCl leachate (A_{id})	0.95
Water permeability (A_{ipw})	1.30

5.8.3 Electrochemical treatment of the NF concentrate

In order to maximize the removal of metal ions from the NF concentrate, the solutions were treated by electrochemical treatment using insoluble electrodes (titanium coated with platinum used as the anode and stainless steel used as the cathode). The chosen metals were Cu, Mn, Ni, Pb, and Zn, because they are compounds frequently found at many hazardous waste sites.

Table 5.4 presents the experimental procedure applied during the assays, and Table 5.5 compares the initial and residual metal concentrations in H_2SO_4-NaCl and HCl leachates. For example lead (537 mg/l) and zinc (195 mg/l) had the highest initial concentration in the H_2SO_4-NaCl leachate. By comparison, 28 mg/l of Pb and 97 mg/l of Zn, were initially recorded in the HCl leachate. In both leachates, nickel had the lowest initial metal concentration. At the end of the treatment, more than 97% of Pb, Mn and Cu were reduced in H_2SO_4-NaCl leachate, compared to 88% of Pb, 64% of Cu and 93% of Mn removed from HCl leachate. The yield of Zn removal from the two leachates was quite similar. In general, the electrochemical treatment was more effective in removing metals (Pb, Cu, Mn, and Ni) from the H_2SO_4-NaCl leachate than from the HCl leachate. In fact, the best percentages of metal removal using the H_2SO_4-NaCl leachate resulted from metal deposition on cathode electrodes (equation 5.1) and from the capacity of the electrolytic cell to produce enough hydroxides ions (equation 5.2) to compensate the acid-buffer and make the H_2SO_4-NaCl leachate more alkaline compared to the HCl leachate. This is the reason why the pH increased from 2.74 to 7.24 in the H_2SO_4-NaCl leachate and from 3.42 to 4.98 in the HCl leachate. When the H_2SO_4-NaCl leachate was brought to pH=7.24, an amount of 5.70 kg/m^3 of metallic sludge was produced in the electrolytic cell, compared to 0.93 kg/m produced while the HCl leachate was brought to pH=4.98.

Equation 5.1 $Me^{z+} + ze- \dashrightarrow Me_{(s)}$

Equation 5.2 $2H_2O_{(l)} + 2e- \Leftrightarrow H_{2(g)} + 2OH^-$

Where Me represents the metal (Pb, Cu, Mn, Ni or Zn) and z is the valence of the metal. When metals were formed and deposited on cathodes electrodes (cathodic deposition); a thin layer of metals was visually seen on the surface of cathode electrodes. When the pH gradually increased, metals were also removed by precipitation and co-precipitation (equation 5.3):

Equation 5.3 $Me^{z+} + zOH^- \to Me(OH)_{z(s)}$

The high metallic sludge produced in the H_2SO_4-NaCl leachate, was probably due to the high amount of NaCl (6.5 kg) added to produce this leachate. A high amount of mineral salt in an effluent often induces a large quantity of solid generated during a physical-chemical treatment. It is worth noting that during electrolysis, some metallic complexes such as MnO_2 and PbO_2 could be formed in solution and precipitated out with sludge. Such compound formation resulted from Mn^{2+} and Pb^{2+} ions oxidation in solution by means of hypochlorous acid (HClO) generated during electrolysis (equations 5.4 and 5.5).

Equation 5.4 $Mn^{2+} + HClO + H^{+} \rightarrow Mn^{4+} + Cl^{-} + H_2O$

Equation 5.5 $Pb^{2+} + HClO + H^{+} \rightarrow Pb^{4+} + Cl^{-} + H_2O$

Once oxidized, manganese and lead react with hydroxide ions in solution forming MnO_2 and PbO_2, respectively (equations 5.6 and 5.7).

Equation 5.6 $Mn^{4+} + 2H_2O \rightarrow MnO_2 + 4H^{+}$

Equation 5.7 $Pb^{4+} + 2H_2O \rightarrow PbO_2 + 4H^{+}$

In fact, HClO formation resulted from chloride ions oxidation at the anode (Ti/Pt). It is well-known that, hypochlorous acid production takes place on anode electrodes when the electrolyte solution contains chloride ions. This HClO formation, at the end of the electrolysis, could explain the relatively high oxidoreduction potential (ORP) values presented during HCl (1020 mV) and H_2SO_4-NaCl (873 mV) leachate treatment. Before treatment, 332 mV and 346 mV values were respectively measured (Table 5.4).

Fig. 5.2 shows the change in pH during the treatment of the H_2SO_4-NaCl and the HCl leachates, and Figs 5.3 and 5.4 compare the C/C_0 ratio against time (C_0 and C are respectively the initial and residual metal concentration in the leachates). It took 60 min for the H_2SO_4-NaCl leachate to reach a pH around 7.0, whereas 90 min was required to slightly increase the pH to 4.0 in the HCl leachate. The HCl leachate was less sensitive to pH variation than the H_2SO_4-NaCl leachate. Thus, during the first 60 min of the treatment, the decrease in the C/C_0 ratio in the HCl leachate was mainly attributed to cathodic reduction (Fig. 5.3), the pH was stable during this period. However, over 60 min of treatment, the pH slightly increased and a small fraction of metal precipitated as metallic sludge. Fig. 5.3 also shows that Pb and Mn were the easiest metals to remove from the HCl leachate, followed by Cu, while Ni and Zn were the most difficult metals to remove from the solution. According to the Electrochemical Motive Force (EMF) series, the order of metals deposition should be as follows: Cu > Pb > Ni > Zn > Mn (Bard *et al.,* 1985; Vanysek, 2006). However, this order of metal deposition can be influenced by many parameters, such as the pollutant concentration, the redox potential of the pollutant, competitive cathode reactions and the affinity existing between the pollutant and cathode electrodes, etc. In addition during an electrochemical treatment, as the concentration of pollutant increases in the solution, the depurative efficiency increases (Persin et Rumeau, 1989; Meunier *et al.,* 2004). By comparison, for the H_2SO_4-NaCl leachate (Fig. 5.4), Ni and Zn remained the most difficult metals to remove from the solution, while Pb, Cu, and Mn were easily reduced. The C/C_0 ratio decreased faster than in the HCl leachate treatment. The maximum decrease of C/C_0 was obtained between 30 to 60 min, followed by a steady state or a slight decrease. However, when the pH increased from 2.7 to 4.9 after 30 min of treatment, the residual metals started precipitating out. With a 60 min of treatment period was reached the optimum metal removal, the energy consumption should be reduced by stopping the treatment at this time while treating H_2SO_4-NaCl leachate.

Table 5.5 presents the yields of metal precipitation, the yields of deposited-metal and the yields of remained-metal in solution. The amount of metal retained on the cathode electrodes, was calculated by a mass balance between the initial and the final state:

Equation 5.8 $M_{\text{int}} = M_{dep} + M_{res} + M_{pre}$

Where, M_{int} (mg) is the amount of initial metal in solution (before treatment), M_{res} (mg) is the amount of residual metal in solution (after treatment), M_{pre} (mg) is the amount of metal in sludge residues, and M_{dep} (mg) is the amount of metal deposited on the cathode electrodes. The best performance of metals reduced on the cathode electrodes were recorded during the HCl leachate treatment, more than 50% of Mn and Pb was formed and deposited on the cathode electrodes, followed by 35% of Zn and Cu, and 25% of Ni. By comparison, using H_2SO_4-NaCl leachate, metals were mainly removed by electrochemical precipitation; more than 80% of Pb, Cu and Mn were precipitated as sludge, follow by 69% of Ni and 6.3% of Zn. Less than 30% of metals (Pb, Cu, Mn, Ni and Zn) were deposited on cathode electrodes while treating H_2SO_4-NaCl leachate.

Also, it was compared the cost of electrochemical treatment while treating H_2SO_4-NaCl leachate versus the HCl leachate. The treatment of the H_2SO_4-NaCl leachate involved a total cost of 2.48 USD per cubic meter of treated leachate, compared to 1.05 USD m^{-3} recorded during the treatment of the HCl leachate. These costs included only, energy consumption and metallic sludge disposal. The energy consumed was estimated at a cost of 0.06 USD kW h^{-1}, and the disposal cost for the metallic sludge including transportation and charges for hazardous waste disposal, was evaluated at 300 USD t^{-1}.

Table 5.4 Metal recovery from NF concentrates using electrochemical treatment

Parameters	**NF concentrates**	
	HCl leachate	**H_2SO_4-NaCl leachate**
Volume treated (l)	1.5	1.3
Current intensity (A)	3.0	3.0
Treatment time (min)	120	120
Initial pH	3.42	2.74
Final pH	4.98	7.24
Conductivity (mS/cm)	16.8	85.5
Initial ORP (mV)	332	346
Final ORP (mV)	1020	873
Energy consumption (kWh m^{-3})	14.1	14.9
Metallic sludge (kg/m^3)	0.93	5.70
Energy cost (USD m^{-3})	0.84	0.89
Sludge disposal cost (USD m^{-3})	0.28	1.72
Energy and disposal cost (USD m^{-3})	1.12	2.62
Removal yields (%)		
Pb	88	99
Cu	64	98
Mn	93	99
Ni	30	84
Zn	38	30

Table 5.5 Distribution of the metals after electrochemical treatment

Parameters	**HCl-leachate**					**H_2SO_4-NaCl leachate**				
	Pb	Cu	Mn	Ni	Zn	Pb	Cu	Mn	Ni	Zn
Solution										
Initial metal conc. (mg/l)	27.7	59.3	69.1	1.90	96.6	537	22.7	124	3.20	195
Residual metal conc. (mg/l)	3.32	21.3	4.90	1.31	60.3	7.28	0.50	1.38	0.51	136
Initial metal (mg) (M_{int})	41.6	89.0	104	2.80	145	698	29.5	161	4.20	254
Residual metal (mg) (M_{res})	4.81	30.7	7.11	1.90	87.4	9.09	0.61	1.73	0.64	170
Metal fraction (%)	11.6	31.6	6.90	67.7	60.3	1.30	2.10	1.10	15.3	67.1
Metallic sludge residues										
Metal conc. (mg/g)	11.4	20.3	24.9	0.16	5.59	87.8	3.39	19.3	0.41	2.29
Metal precipitated (mg) (M_{pre})	15.4	27.3	33.3	0.20	7.50	616	23.9	136	2.90	16.1
Metal fraction (%)	37.0	30.7	32.4	7.50	5.20	88.3	80.9	84.2	68.5	6.30
Electrode surface (cathode)										
Metal deposited (mg) (M_{dep})	21.4	30.9	63.0	0.7	49.9	72.5	5.00	23.7	0.60	67.4
Metal fraction (%)	51.4	34.7	60.8	24.8	34.5	10.4	17.1	14.7	12.2	26.6

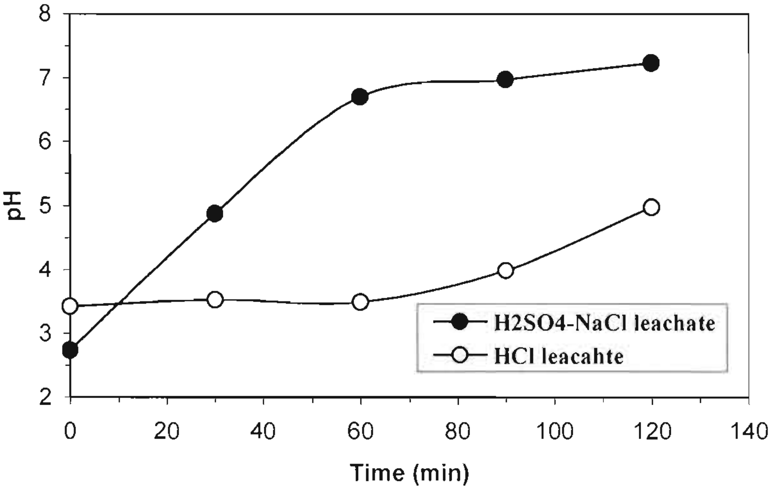

Figure 5.2 Change in pH during electrochemical treatment of H_2SO_4-NaCl and HCl leachates

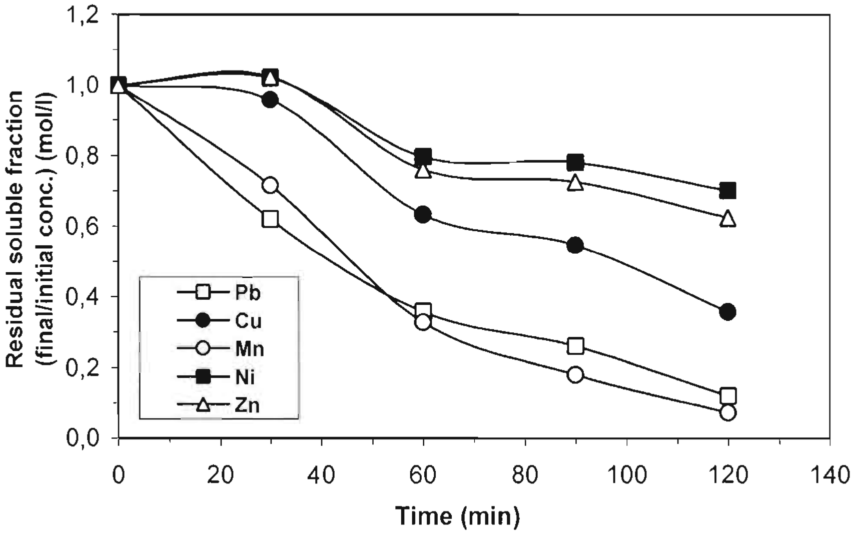

Figure 5.3 Metal removal from HCl leachate using electrochemical treatment

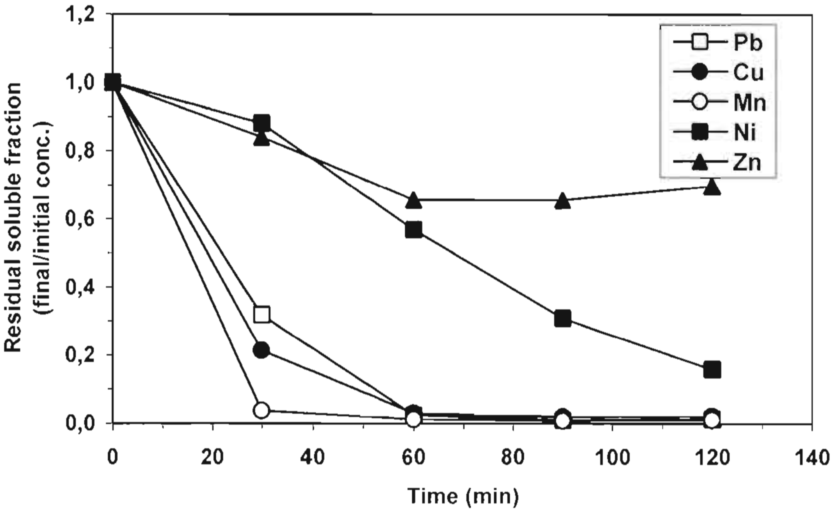

Figure 5.4 Metal removal from H_2SO_4-NaCl leachate using electrochemical treatment. (•) Cu, (○) Mn, (■) Ni, (□) Pb, (▲) Zn

5.9 Conclusions

The laboratory experiments presented herein have demonstrated that soil washing, nanofiltration membranes and electrochemical recovery are promising methods for the remediation of soils contaminated with metal ions. Soil-washing results demonstrated the effectiveness of the washing agents (HCl and H_2SO_4-NaCl) on the removal of pollutants from contaminated soil. For both leachates it was observed similar chemical compositions. The NF treatment presented good ion separation for both leachates and also negative retention of some ions due to the Donnan effect, which affected the retention of monovalent ions. However higher ion retentions rates were observed using the HCl leachate.

Finally, the electrochemical deposition demonstrated the feasibility of treating the NF treatment concentrate. This process showed a good reduction of Pb, Mn and Cu, approximately 97%, in the H_2SO_4-NaCl leachate, compared to a reduction of 88% of Pb, 64% of Cu and 93% of Mn removed from the HCl leachate.

The next step of this work should be the study of the treatment of both leachates (HCl leachate and H_2SO_4-NaCl leachate) using electrocoagulation process. Then, an economical study should be carried out to critically demonstrate the economical advantage of electroreduction application (including cost energy, metallic residues disposal cost and the cost required to built the electrochemical reactor) compared to electrocoagulation.

Abbreviations and Symbols

A	Amperes
A_{ipw}	Pure water permeability of membrane (m)
A_{id}	Dynamic solution permeability of membrane (m)
TOC	Total organic carbon (mg O_2/l)
f, f'	Overall and intrinsic separation factor (dimensionless)
J_p	Solution permeate flux (m/s)
M	Molar concentration (mol/l)
ORP	Oxydoreduction potential (mV)
P	Pressure (Pa)
Q_c	Feed flow rate (m^3/s)
Q_p	Permeate flow rate (m^3/s)
rpm	Rotations per minute
S_m	Membrane area (m^2)
T	Temperature (°C)
USD	United States Dollars
X	Molar fraction

Greek letters

Δ	Gradient
μ	Fluid viscosity (Pa.s)
Π	Osmotic pressure (Pa)
$\sum_{i}$	Number of ions per molecule of solute

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CHAPTER VI

GENERAL DISCUSSION

Research conducted in the past few years has demonstrated that the combination of soil washing and membrane filtration, such as NF membranes, can be advantageous thanks to the possibility of accelerating the extraction of pollutants from the soil, reducing the amount of liquid wastes produced during soil washing and recuperating reagents (ex. the inorganic acids) used to extract metals from soil. However, to reach this point, it is necessary to apply effective washing agents that produce satisfactory results in the extraction of metals from the soil as well as a good membrane filtration that will be able to decontaminate the leachate without decreasing its flux. With this in mind, this investigation explored different topics, such as effectiveness of the washing solutions, effect of the solution pH on the membrane, membrane performance and it is introduced a new technology: electrochemical treatment in order to treat the concentrate coming from the nanofiltration treatment. Hence, the discussion from this research is summarized below.

6.1 Soil washing

A variety of remediation methods have been employed for soil clean-up with toxic metals. Among all of them, soil washing is particularly effective in removing metals from soils (Mulligan *et al.*, 2001).

Our experimental results demonstrated that soil washing using inorganic agents (at low pH) can facilitate the metal extraction, because some metals can precipitate at a high pH. This removal can be dependent on many factors, such as target pollutants, soil, concentration and type of acid used. This extraction is controlled by the dissolution of the metal-mineral bond, followed by the dispersion of the pollutant metal in the washing liquid. However, the application of strong acids does not show their extraction capacity. Some acids tend to attract metal ions better than others. For that reason, it was observed that some metals were better extracted under the influence of HCl, H_2SO_4 or the combination of H_2SO_4-NaCl. Generally, H_2SO_4 presented a better extraction capacity, compared with HCl. Many studies had used HCl at different concentrations to extract metals contained in soil, and showed excellent performance especially in the case of Pb and Zn (Davis and Singh, 1995; Nael *et al.*, 1997; Reed *et al.*, 1996; Tokunaga and Toshikatsu, 2002; Van Benschoten *et al.*, 1997). On the other hand, for H_2SO_4, few studies have been conducted regarding the application of soil washing (Moutsatsou *et al.*, 2006; Tokunaga and Toshikatsu, 2002). For the application of the combined H_2SO_4-NaCl as a washing agent, the results demonstrated a slight improvement in the removal efficiency of some ions, such as Pb, Fe, K and Mn, compared to the HCl leachate. Removing Pb from soils was particularly important because it is a contaminant well-known to bind strongly to soil surfaces and inner-layer surfaces complexed with mineral-surface oxides (VanBenschoten *et al.*, 1997). In our investigation, a higher Pb concentration was observed using H_2SO_4-NaCl. This behaviour was probably due to the presence of the NaCl salt that is a good solubilization agent, due to its capacity to form chloride ions with different metals and to form soluble salt complexes particularly with Pb (Djedidi *et al.*, 2005; Nedwed and Clifford, 2000).

6.2 Membrane filtration

During this investigation, it was observed a reduction of the volume of contaminated water and low concentration of toxic metals in the permeate, which contribute to be a cost-effective and competitive technology. Conversely, it was observed membrane fouling that helped to decrease the membrane performance and probably for future membrane use to increase membrane operation cost. It is important to note that few studies have been made in order to investigate soil washing in conjunction with membrane process.

Due to the solution pH, it was observed that the membranes became positively-charged in acidic conditions, thus attracting anions and rejecting cations. For that reason, as the membrane was highly-affected by the solution, the charge formation on the membrane surface became relevant in determining rejection properties. Several studies have demonstrated that in binary and multicomponent systems, the membrane's performance is influenced not only by the concentration of ions, but also by the acidic characteristics existing in the feed solutions (Childress and Elimelech, 1996; Hagmeyer and Gimbel, 1998; Lipp *et al.*, 1994; Nyström *et al.*, 1995). In the case of H^+ ion, a negative rejection for the two leachates was observed, while metal salts were retained in order to obtain electroneutrality. This behaviour suggested the higher mobility of H^+, compared to other cations in solution, and also suggest the possibility to recuperate the acid in NF treatment.

Finally when the H_2SO_4-NaCl solution was filtered, a salt precipitation (scale formation or crystallization fouling) was observed in the filtration system. This behaviour was due to the amount of salt added to the solution (6.5 Kg). The scales precipitated from the feed stream onto the membrane surface. As the feed solution was ten times more concentrated, this precipitation was likely due to some sparingly soluble salts that became supersaturated during the NF process, causing a scale precipitation problem. This precipitation provoked a decrease in the membrane permeability, membrane rejection and possibly membrane lifespan. Some experimental studies have demonstrated that the major components of scaling are calcium carbonate, calcium sulfate, silica, calcium phosphate and barium sulphate in addition to ferric and aluminum hydroxides (Bremere *et al.*, 1999; Dydo *et al.*, 2004; Van de Lisdonk *et al.*, 2000). As in this case, the presence of these multivalent ions probably blocked the membrane's pores. Another factor that could have affected the scale formation was the operating conditions. However, scarce information was found regarding how the effect of the operating conditions in membrane scale formation plays an important role in membrane performance.

6.3 Electrolytic treatment

This process effectively removed metals from the waste solution and reduced the amount of metallic sludge produced by generating compact and less voluminous sludge, resulting in a cost saving. The best percentages of metal removal using the H_2SO_4-NaCl leachate resulted from metal deposition on cathode electrodes and from the capacity of the electrolytic cell to produce enough hydroxides ions to compensate the acid-buffer and make the H_2SO_4-NaCl leachate more alkaline compared to the HCl leachate.

In addition, it was interesting to see that electrochemical treatment is an economically competitive alternative. The treatment cost of the two leachates was compared in terms of energy consumption and metallic sludge disposal. The treatment cost of the H_2SO_4-NaCl leachate was \$2.48 USD per cubic meter of treated leachate, compared with \$1.05 USD m^{-3} for the HCl leachate.

6.4 Contributions to the knowledge

The next contributions fulfill in part the main objective of this research that was the application of a membrane process for the removal of metal ions resulting from an acidic leachate produced during soil decontamination.

Based on the results from different experiments, this research work offers the following contributions:

- This project is one of the very first applications of a combined treatment such as soil washing, nanofiltration membrane and electrochemical treatment in order to treat a metal-contaminated soil. Also the innovative application of the electrochemical treatment was used to prevent secondary contamination resulting from the NF concentrate;
- This experiment offers the possibility to establish most favorable conditions for membrane operations in order to treat charged effluents.

6.5 Recommendation for future works

Based on the experience of this research, the following recommendations can be made for future studies:

- Determination parameters of soil washing such as effective physical sizing for the removal of pollutants, as well as types and concentration of washing agents in order to compare the efficiency of washing agents and at different concentrations;
- Recuperation and recycling of the acid applied to extract the ions using membrane filtration;
- Investigation of the membrane surface charge as a function of pH in order to understand membrane charge (Zeta potential studies);
- Morphology studies of the soil in order to investigate the presence of different metal complexes;
- Although this investigation has been conducted on a laboratory scale, pilot studies are needed to quantify the overall treatment cost associated with the proposed treatments.

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CHAPTER VII

CONCLUSIONS

The removals of metals ion from a contaminated soil induced by different technologies were investigated. The experimental results demonstrated that the technologies used during this investigation were simple methods and effective in the minimization and recuperation of toxic metals. Consequently, these technologies are example of sustainable environmentally friendly technologies, because metals were recovered safely without environmental contamination.

Firstly, during the soil washing treatment, it was observed that H_2SO_4 presented a better extraction capacity, compared with HCl. On the other hand the combined H_2SO_4-NaCl as a washing agent, the results showed a slight increase in the removal efficiency of some ions.

Secondly, the membrane filtration showed a reduction of the volume of contaminated water and low concentration of toxic metals in the permeate, which contribute to be competitive and a cost-effective technology. In contrast, it was observed an irreversible permeability, which helped to decrease the membrane performance and membrane life.

Finally, the electrochemical deposition demonstrated the feasibility of treating the NF concentrate. This process showed a good reduction of Pb, Mn and Cu, approximately 97%, in the H_2SO_4-NaCl leachate, compared to the HCl leachate. This technology presented low cost.

The processes presented in this investigation can be applied not only to decontaminate leachates produced by soil-washing techniques, but also to decontaminate wastewaters having similar and more complex mixtures of pollutants, resulting from waste from industrial, municipal, or groundwater origins.