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INVESTIGATION OF POLYETHERSULFONE (PES) HOLLOW FIBER MEMBRANE FOR THE TREATMENT OF ACID MINE DRAINAGE

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A research report submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in partial fulfilment of the requirements for the degree of Master of Science in Engineering

Johannesburg, 2014

DECLARATION

I declare that this report is my own unaided work, unless otherwise stated. It is being submitted to the Degree of Master of Science to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

_____

Velinjani Mthethwa

_____day of _____year_____

Abstract

Efforts in treatment of acid mine drainage (AMD) have been fraught with limitations for the mining industry. Membrane filtration technology is a new alternative employed to treat AMD in this work. A commercially available polyethersulfone (PES) hollow fibre nanofiltration membrane was investigated for its likelihood for the treatment of AMD. The system was configured in a cross flow set up and effects of pH, feed flowrate and operation time were explored in relation to the membrane performance (rejection and flux). Acid mine collected from site had a very high concentration of Iron (1.055 mg/L), sulphate (3639.301 mg/L) and high levels of hardness due to magnesium ions (523.011 mg/L). Also, heavy metals were in trace amounts. Experimental results showed that the maximum rejection of iron was 96.28 % at a pH of 4.37, maximum feed flowrate of 872ml/min and the iron permeate concentration was within the potable water standards (less than 0.100mg/L) inferring suitability of the membrane for AMD amelioration at the aforementioned pH. Furthermore, maximum rejection of sulphate ions was 97.30% at a pH of 6.55 and maximum feed flowrate. In addition, the membrane was efficient in curbing the hardness (91.99 % rejection) of the AMD to the accepted water standards at the pH of 4.37. The reduction of hardness levels, iron, and sulphate concentrations by the membrane were attributed to steric (size) exclusion and electrostatic interaction mechanisms. Although the membrane had a large surface area ($2m^2$), the flux was not that high (ranged from 3 - 4.5 L/m^2hr). Further studies on modification of the polyethersulfone polymer matrix within the realm of enhancing its hydrophilicity henceforth flux are desirable.

Acknowledgements

This work would not have been possible without the aid and goodwill of several people. In particular, I am thankful to Professor Sunny Iyuke and Bavon Nkazi for their invaluable supervision and help through the whole course of my Masters (research and coursework). Tumi Dons, Sydney Mthombo and Sola Masola displayed remarkable generosity in making this work possible. I would also like to express appreciation to my colleagues, Phillip Chafa, Mpendulo Ncongwane, Langa Moyo, Tsholofelo Rankwane, Benjamin Obuala, Moitshudi Segoatlhe, Seetsa Lekeletsane and Melusi Nkosi for their enlightening conversations and making my stay extraordinary at Wits. I am thankful to my own family and friends for their encouragement and limitless support. Finally, I am grateful to the Chemical Industries Education and Training Authority (CHIETA) for financial support.

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List of abbreviations and symbols

AMD - Acid mine drainage

DIW- De-ionised water

DWAF- Department of Water Affairs

Ec - Electrical conductivity

HF- Hollow fibre

ICP-OES - Inductively coupled plasma optimised emission spectrometry

IC - Ion chromatography

LOD- Limit of detection

NF- Nanofiltration

PES-Polyethersulfone

SEM-Scanning electron microscopy

Std.dev - Standard deviation

R (%) - Rejection in percentage

RE - Reverse osmosis

C- Concentration

J - Solute flux

L - Mass transfer coefficient

CHAPTER 1

1 INTRODUCTION

Acid mine drainage (AMD), its concomitant risks and consequences have in the past years spawned an area of interest and concern. AMD is an austere environmental pollution problem which is usually an aftermath of pyrite oxidation or other sulphide containing ores in mining waste, ore tailings, and overburden (Peppas et al.,2000; Akcil and Koldas,2006). AMD is enriched with iron, aluminium, sulphate, and heavy metals such as cadmium (Cd), mercury (Hg), lead (Pb), and in some cases thorium (Th) and uranium (U) nuclides (Envangelou, 1995; Azapagic, 2004). If not mitigated, AMD can weave into water courses and have consequences that are far reaching and long term and these incorporates destruction of eco-systems and endangering human health (Zhong et al., 2006).

With regard to the South African context, various areas have been reported to have the problem of AMD and this includes the Witwatersrand basin, Mpumalanga and Kwazulu-Natal Coal fields and the O'Kiep Copper district (Department of water affairs, 2010). An ad hoc measure of implementing intervention in these areas has to be spearheaded with urgency since the status quo is at a degree of graveness. This is averred by the recent crisis in Mpumalanga where 17 000 people in the town of Carolina lived for months with no drinkable water (McCarthy and Humphries, 2013). The situation is further aggravated by the fact that South Africa (SA) is a water scarce country while on the other hand AMD has already polluted water courses in the old West rand mines, and threatens the water courses of the eastern and central Witwatersrand basin (Nepfumbada and Keet, 2011).

Conventional methods for treatment of AMD are either not effective or too expensive which results in huge amounts left unremedied (Akcil *et al*., 2006). However, membrane filtration has gained much drive in terms of research and application as one of the promising and eminent ways for elimination of water contaminants (Celik et al., 2011; Maphutha et al., 2013; Ulbricht et al., 2007). Notwithstanding that, since the dawn of membrane technology, separation, concentration and purification have become industrially pertinent and efficient unit operations due to the outstanding separation efficiency of membranes (Arthanareeswaran et al., 2004). Furthermore, their ease to use, inexpensiveness, nominal energy and space requirements makes

them laudable in separation processes (Baker, 2004). In this study, the utilisation of polyethersulfone (PES) membrane in treating acid mine drainage is investigated. What makes it attractive for such an application is its inherent characteristics which incorporates, physical toughness, wide pH tolerance (hence compatibility with the lower pH of acid mine drainage) and heat stability (Johnson,2002).

1.1 Membrane technology

With on-going research and applications, membrane technology has emerged as a very promising substitute to the conventional methods (Hilal et al., 2005). It is an effective technology for a wide range of wastewaters due to its easy operation, inexpensiveness, high separation efficiency, low energy consumption and it does not require integrated steps, that is, no need for further purification (Zhong et al., 2006). Different membranes are used for specific purposes.

In this study, a PES membrane is investigated for its applicability in the treatment of AMD. Several literatures have averred PES as a high performance membrane because of its resistance to chemical attack, toughness and wide temperature use (Thominette et al., 2006; Yadav et al., 2009; Birly and Martyn, 1982; Zondervan et al., 2007). The polyethersulfone polymer constitutes of phenylene rings joined to sulfonyl (SO_2) and ether linkages as shown in Figure 1.1.

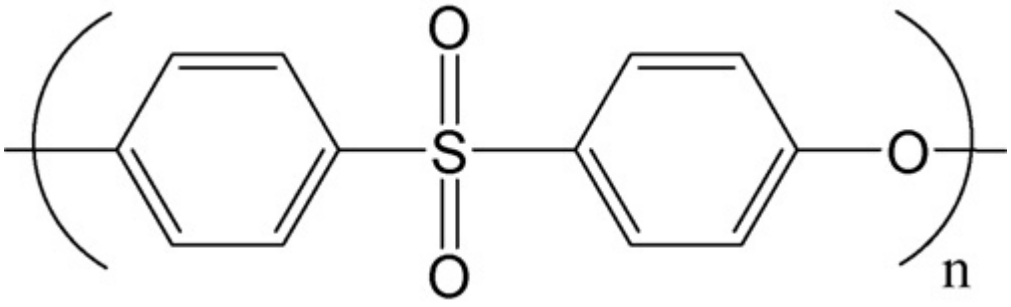


Figure 1.1: Polyethersulfone structure (Arkhangelsky et al., 2007)

The sulfonyl group confers stiffness with a high glass transition temperature and, together with the ring structures, make the membrane chemically resistance and relatively hydrophobic

(Arkhagelsky et al., 2007). The ether linkages make the polymer less hydrophobic and more flexible, hence more amenable to processing (Johnson, 2002; Arkhangelsky et al., 2007).

1.3 Hypothesis

In this study, it is postulated that nanofiltration using polyethersulfone hollow fibre membrane has a potential to treat acid mine drainage due to the innate characteristics of the membrane.

1.4 Validation of study and expected contribution to knowledge

Numerous research studies have been reported on treatment of waste water and desalination using nanofiltration, but studies on treatment of AMD are seldom available yet it is a major global conundrum. Consequently, there exists an enormous space to explore the use of nanofiltration for AMD treatment since conventional methods are not much effective. Accordingly, this study is expected to contribute significantly to the knowledge base of using membrane technology in AMD treatment, especially using the PES membrane and thus providing a new technology. Furthermore, the study will provide a tangible foundation in understanding the PES membrane in AMD treatment and this knowledge is vital in further studies concerning enhancing or optimisation for better AMD treatment using nanofiltration (e.g., incorporating new functional groups or nanoparticles).

1. 5 Purpose of study

The main purpose of the study is to investigate the use of a polyethersulfone hollow fibre membrane for the treatment of AMD through the following objectives;

- To evaluate the rejection of metals by the membrane
- To evaluate the rejection of anions more specifically sulphate ions which contribute to the acidity of mine waters.
- To investigate the effect of pH and feed flowrate on rejection performance
- To monitor the flux of the PES membrane with time (fouling proneness)

1.6 Outline of the project

In this Chapter (Chapter 1), an overview of the environmental problem AMD is imposing especially in South Africa is presented. It includes some introductory comments on membrane technology and also it provides the reason for the utilisation of the polyethersulfone membrane in this study. In the subsequent chapters, literature is reviewed in Chapter 2 to provide background knowledge in AMD formation, prevalent technologies employed to curb AMD proliferation with emphasis on the advantages and disadvantages of these technologies. Further, an extensive literature is reviewed in exposition to the aims of this study. Furthermore, Chapter 3 explains the experimental procedure and method of analysis used while Chapter 4 furnishes the results and discussions. Lastly, Chapter 5 presents the conclusion and recommendations unfolded by the study.

CHAPTER 2

2 LITERATURE REVIEW

2.1 Background

2.1.1 Acid mine drainage formation

AMD is formed by exposure of sulphide bearing minerals to oxidising conditions. In the presence of oxygen and water, the sulphide bearing rock oxidises to form a sulphate rich drainage (Evangelou and Zhang, 1995). There are numerous types of sulphide minerals and hence the constituent of AMD differs from one place to another due to variable mineralogy. One of the most common sulphides bearing rock is pyrite (FeS_2) and it is oxidised in the following manner (Singer and Stumm, 1970; Blodau, 2006):

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad (2.1)$$

Further, oxidation of sulfide to sulphate solubilizes Fe^{2+}, which in turn is oxidized to Fe^{3+}:

$$4Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(l) \quad (2.2)$$

Sometimes the Fe^{3+} ions can precipitate:

$$Fe^{3+}(aq) + 3H_2O\ (l) \rightarrow Fe(OH)_3(s) + 3H^+(aq) \quad (2.3)$$

Or additional pyrite oxidized to form extra Fe^{2+} ions:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (2.4)$$

The dissolved ions H^+ and SO_4^{2-} increase the acidity of the water. The acidity can leach other metals and hence contribute to increased heavy metal loads in watercourses (Singer and Stumm, 1970). Other sulphide minerals like chalcocite (Cu_2S) and pyrrhotite (FeS) undergo the same oxidation process but in different stoichiometric ratios (Johnson and Hallberg, 2005).

2.1.2 Prevalent technologies in place for acid mine drainage mitigation

In South Africa, the main technology used for AMD treatment is neutralisation (Visser et al., 2001). In this method, the sulphate is precipitated as gypsum by the addition of limestone and likewise, the metals as hydroxides. Separation is effected by gravity. This technique results in large amounts of sludge polluted with metals, and also its labour intensive and very expensive (Al-Zoubi et al., 2010). Also, the sulphate content that remains usually exceeds the environmental stipulations for such water being directed to receiving bodies (Akcil and Koldas, 2006). In addition, limestone is inefficient in highly concentrated ferrous AMD hence such environment renders neutralisation ineffective (Akcil and Koldas, 2006).

With regard to neutralisation, much research has been done in trying to improve efficiency of the method. Numerous researchers both local (SA) and international have utilised variable chemicals in place of lime ($Ca(OH)_2$) or limestone ($Ca(CO_3)$) for AMD neutralisation (Feng et al.,2004; Petrik et al.,2003). Petrik et al (2003) investigated the use of fly ash from SA as the neutralisation agent in place of lime. On the other hand, Feng et al (2004) used blast furnace slag as substitute for limestone. The authors' findings were that the process is only viable at increased pH which poses a challenge at lower pH.

Another conventional method is biological treatment for AMD whereby sulphate-reducing bacteria is utilised to raise pH and remove metals. Reactors which use different carbon substance to reduce metal sulphide precipitates are employed (Wakao, 1979). The effectiveness of this technique diminishes as carbon substances are used up in the reactor. Research on use of other various carbon substances is still going on.

Furthermore, another technique used is the control of AMD migration which prevents ingress of AMD into other areas. This include, averting seepage of hydrological water into polluted areas, surface water diversion from affected areas, groundwater infiltration deterrence into polluted areas and organized placement of AMD producing waste (Johnson and Hallberg,2005). Diversion usually entails the use of ditches which become cumbersome in terms of maintenance over a long period of time. In addition, wetlands are often seen as having a potential for treatment of AMD. Some wetlands can remove some heavy metals. They are a multifaceted ecosystem which can effect a change in water chemistry (Hedin and Hyman, 1989). However,

much care has to be in place for the use of wetlands and research is still much in progress for its use (Adam et al, 2012).

Another method that has been investigated for AMD amelioration is the cation exchange process whereby solvent extraction is used to extract ions of interest (Riveros, 2004). This method promises not solely removal of toxic metals from AMD, but also the likelihood of recovery of valuable metals (Akcil and Koldas, 2006). However, the huge costs of the process in comparison with its shortfall to handle vast amount of AMD renders this technological solution presently unrealistic (Al-Zoubi and Omar, 2009).

With the genesis of membrane technology for removal of contaminants in water, nanofiltration membranes have been developed, utilised and displayed very promising outcomes in AMD treatment (Al-Zoubi and Omar, 2009).

2.2 Membrane separation processes

The primordial purpose of a membrane is to act as a physical barrier, selectively permitting the passage of particular constituents of a determined mixture and retention of others, implying the concentration of one or more constituents in permeate and retentate (Strathmann, 1990). The selectivity of the membrane is a function of its pore size, the dimension of the elements of interest, as well as the solute diffusivity within the matrix and also the associated electrostatic charges (Scott, 2003; Cheryan, 1998). The common membrane separation processes are, microfiltration, ultrafiltration, nanofiltration and reverse osmosis (Cheryan, 1998). They are all pressure driven and one of the factors that distinguish them is the separation due to particle size (Matsuura, 1994). The separation processes are described as follows (United States Environmental Protection Agency, 2008):

Microfiltration- it is used to remove most suspended solids and living material but cannot retain any type of dissolved solute. It is effective in rejection of particulates that are not less than 100 nm.

Ultrafiltration- it is effective only to the 10nm size range which makes it suitable for rejection of groundwater colloids, viruses and most proteins.

Nanofiltration- used to remove material in the 0.5-10nm range and will reject most of ions in mixtures especially multivalent ions with water being able to pass through and also monovalent ions. The removal of multivalent ions is usually higher than monovalent ions.

Reverse Osmosis – it is able to reject almost all material, except water and simple organic species. It is effective in removing monovalent ions.

Even though reverse osmosis can remove all material in a determined mixture including monovalent ions, nanofiltration was preferred in this study over reverse osmosis due to the following advantages (Rautenbach and Groeschl, 1990):

- Low energy costs
- Low operating expenses

2.3 Aspects of membrane processes

There are two principal hitches associated with membrane operations which affect permeate flow or flux; concentration polarisation, which is reversible, and fouling which is typically an irreversible process (Lee et al., 1984; Bian et al., 2000). Conventionally, fouling is a serious problem than concentration polarisation; however, both have to be restricted in enhancing membrane performance (Lee et al., 1984).

Normally in the first stage of nanofiltration, that is, the first few minutes, a sharp decrease in permeate flowrate is witnessed and this is due to concentration polarisation (Cheryan, 1998). The polarisation can quickly proliferate until a polarised gel layer is established (Chen et al., 1997). The subsequent stage occurs slowly whereby flux continues to decrease owing to the effect of interactions between the solute and material used in membrane fabrication and this is ascribed to the several modes of membrane fouling. In the last stage, the process is fairly stationary, a phase ensues where permeate flow decreases very slow, remaining more or less constant due to consolidation of fouling and particle deposition (Daufin and Marshall, 1995).

2.3.1 Concentration polarisation

When membrane separation is taking place, there is usually an increase in local concentration of solute on the membrane surface and this effect is known as concentration polarisation (Mattiasson and Sivik, 1980). Usually, when particles with larger dimensions than the diameter of the membrane pore are rejected and accumulate on membrane surface, a concentration profile is entrenched within a film spawned by the hydrodynamic conditions (Figure 2.1). With elevated concentrations of solute within the membrane surface, the solute will diffuse back to the solution in accordance with Fick's law of diffusion (Schafer et al., 2004). Additionally, when the feed concentration of particles is sufficiently high, a polarised gel layer is formed (Mulder, 1995; Chen et al., 1997).

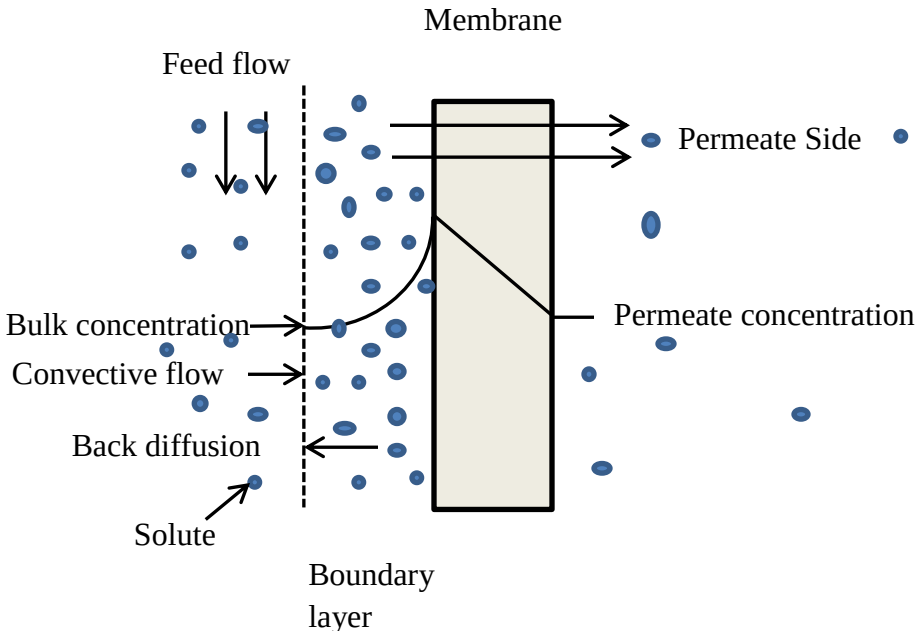


Figure 2.1: Concentration polarisation (Schafer et al., 2004)

Concentration polarisation is concomitant with the subsequent undesirable aspects (Mattiasson and Sivik, 1980);

- Can result in chemical attack on membrane material if concentration build-up of solute materialise on membrane surface. This can alter the membranes composition and thus its separating characteristics.
- If concentration of the feed is high, precipitation or formation of a gel layer on membrane surface can occur and this would increase the hydrostatic resistance of the process.

Concentration polarisation is usually taken to be reversible and could be avoided by means of flowrate or velocity alteration and pulsation (Zeman and Zydney, 1996; Ma et al., 2000).

2.3.2 Fouling

Fouling is "the loss of performance of a membrane due to deposition of suspended or dissolved substances on its external surface, at its pore openings, or within the pores" (Koros et al., 1996). Furthermore, it is also defined as an irreversible flux decline which can only be amended by chemical cleaning (Mattiasson and Sivik, 1980). Fouling is different and more complex than concentration polarisation as in the latter flux declines can be reversed with clean water (Lee et al., 1984). The origins of fouling are summarised as follows (Schafer et al., 2004).

- Adsorption at membrane polymer by low molecular mass substances
- Deposition of fine or colloidal matter on membrane pores
- Precipitation on membrane surface by substance that have exceeded their solubility
- Reaction of solution constituents with membrane polymer
- Reaction of solution constituents at membrane boundary layer
- Formation of an irreversible gel layer of macromolecular solution constituents

Attenuation of fouling can be achieved by proper membrane material selection, pre-treatment by means of surfactants, enzymes, and polymers (Chen et al., 2004). Irrespective of the aforementioned, fouling can also be reduced by all means that eliminate or limit concentration polarisation (Zeman and Zydney, 1996).

In addition, the membrane performance is also affected by its configuration (tubular modules, flat sheet, hollow fibres and spiral wound). Excellent membrane performance with respect to good flux and retention of the preferred solute must be balanced with respect to its features such as cost, propensity for fouling, ease of cleaning and substitution (Porter, 1990).

2.4 Nanofiltration

Nanofiltation together with reverse osmosis were primarily developed for production of potable water from brackish and saline waters (Yu et al., 2001). However, these techniques have become the standard technologies employed for public and industrial water purification. Numerous membranes are available and their separation efficiencies differ. Eriksson et al.(2005) point out that nanofiltration is used for treatment of water in Saudi Arabia, Umm Lujj plant whereby total hardness is reduced from 7500 to 220 ppm, total dissolved solids from 45 500 to 28 200 ppm while sulphate, calcium and magnesium rejection is 99%, 92% and 98%, respectively.

Extensive research has been going on in treatment of water using membrane filtration technique. However, few studies have been done in treatment of AMD using membrane technology. Betrand et al (1997) investigated the use of nanofiltration for treatment of a hard and low sulphated acid mine water using an NF70 membrane (polyamide nanofiltration membrane, Dow Company) in France. The findings attested that the NF70 membrane can eliminate hardness to the required potable water standards (98% reduction). Again in South Africa, an outstanding study by Visser et al (2001) explored the performance of commercial nanofiltration membranes (inclusive of the NF70, used by Betrand et al., 1997) for the elimination of sulphate, calcium, sodium and chloride ions in an acidic environment. This study established that under neutral pH conditions, the sulphate rejection was up to 99% while at lower pH values (acidic conditions) performance declined which was due to availability of HSO^-_4 ions and the likelihood of membrane charge shift from negative to positive. The former, that is, the study by Betrand et al (1997) focused solely on the removal of hardness from acid mine water and it implores the quest for further studies on the effect of pH on membrane performance in different environment and this can be of crucial help in knowing if membrane can be adaptable to a wider pH range since the constituents of AMD are cumulative and hence there can be change of pH with time. The latter, that is, research by Visser et al (2001) concluded that under acidic conditions the

performance of the membrane dwindled due to the aforementioned reasons and likewise it supplicates research on South African acid mine drainage using other different membranes and hence the focus underhand is on polyethersulfone membrane which has excellent attributed characteristics under a wide range of conditions. In addition, both studies did not investigate the rejection of heavy metals which is also one of the chief concerns in acid mine drainage. Numerous researchers investigated the effect of concentration and pressure in rejection of salts as a single phase and likewise as a mixture utilising variable nanofiltration membranes (Hilal et al., 2005; Al-Zoubi and Omar, 2009).

In a study entitled treatment of acid mine drainage (AMD) by ultra-low pressure reverse osmosis and nanofiltration, Zhong et al (2006) evaluated the use of reverse osmosis and nanofiltration processes for acid mine drainage with the consideration of pH, pressure and operating temperature. One of the prime rational of doing the study was that membrane filtration relative to the conventional methods is the only technique that can be used not only to treat AMD but also the liquid concentrate can be reclaimed and hence, recovery of valuable materials and prevention of ecological degradation. Results showed rejection of heavy metal ions and total conductivity were above 97% and 96% respectively using RO while on the other hand the process removed about 90% of heavy metal ions and decreased total conductivity by 48% when using a nanofiltration membrane.

Contrary, results from a study by Alzoubi et al (2010) showed that nanofiltration membranes are more suitable for AMD treatment relative to reverse osmosis due to high rejections and flux. In the study, Alzoubi et al. employed two different nanofiltration membranes, that is, an NF99 (thin film polyamide in polyester) and DK (thin film composite membrane) while on the other hand a thin film composite membrane was used for reverse osmosis (RO). Results showed that nanofiltration technique had a rejection of heavy metals greater that 98% for both membranes while RO had about 94%. In terms of sulphate rejection DK membrane (nanofiltration) and RO had a 92% rejection of sulphate while the NF99 had 86%. In addition, nanofiltration technique had the lowest energy consumption and higher flux relative than RO. The study concluded that treatment of AMD using nanofiltration is more plausible than using reverse osmosis.

In another study, the use of a polyamide nanofiltration membrane in acid mine water was investigated for the rejection of heavy metals (Munoz et al., 2006). The results showed that the

membrane was effective in rejection of zinc in a wide concentration and pH range (above 90% in all cases) while the other heavy metals, that is, cadmium and lead which are deemed carcinogenic and highly toxic did not exhibit the same characteristics. This further leaves room for the utilisation of other membrane like PES in the rejection of heavy metals like Cd and Pb. Hardly research has been done where the PES membrane was investigated for the treatment of acid mine drainage. Ali et al (2005) used polyethersulfone membrane for the treatment of aquaculture wastewater which was characterised by the concentrations of phosphorus and ammonium. Results showed that the PES membrane was capable to remove ammonium and phosphorus at percentages of 85.70 and 96.49 respectively at a pressure range of 4 to 8 bar which inferred that PES membranes has a great potential to be used for the treatment of aquaculture wastewater.

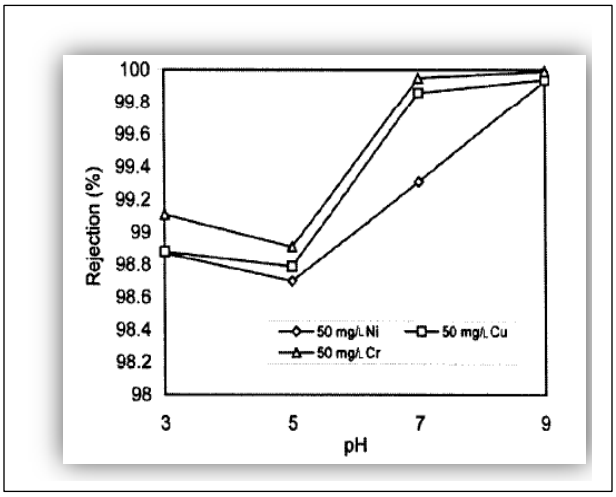
Recently, an ingenious study by Maphutha et al (2013) used a novel nano-composite membrane for treating oil-containing waste water. In this study, a polysulfone matrix comprising of carbon nanotube and polyvinyl chloride was developed and this membrane was capable to have oil rejection of 97%. Furthermore, the membrane had excellent properties which incorporated an upsurge of 119%, 77% and 258% for tensile strength, young's modulus and toughness, respectively. It is worth noting that in the study polysulfone was used which is a similar polymer as polyethersulfone which is used in this study. Both polysulfone and polyethersulfone exhibit the same properties with the latter having low protein retention while the former additionally contains isopropyliden (Enrico and Giorno, 2010). In another recent study, Celik et al (2011) synthesized a polyethersulfone/carbon nanotube for filtration of natural water investigating its fouling, flux, natural organic matter rejection and ease of cleaning characteristics. In both studies by Maphutha et al (2013) and Celik et al (2011) the membranes were not used for AMD remediation even though they seem to have a great potential due to the anti-fouling characteristics inherent in them. Polyethersulfone has never been investigated for its use in treatment of acid mine drainage and this study seeks to use the PES membrane so to produce a basis for further research which might be modification of the polymer with certain functional groups for better performance.

Nanofiltration separation mechanism hinges on electrostatic interactions and sieving effects (Qin et al., 2004). The electrostatic interactions are amid the membrane surface charge and ions in the

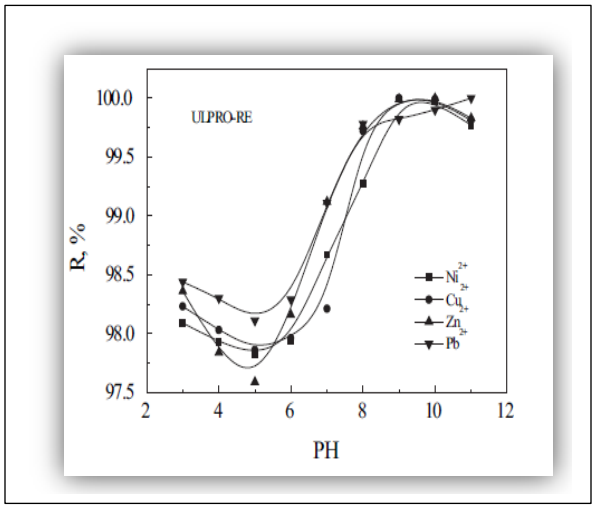
system (Ernst et al., 2000). Membrane surface charge and the resulting potential (zeta potential) are governed by the feed pH of the system due to protonation and de-protonation of functional groups over a pH range (Hagmeyer and Gimbel ,1999). Numerous studies concentrating on the relationship between feed pH, ion rejection, and membrane charge, concur on the major effect of pH, and that minimum rejections are usually obtained at the isoelectric point (IEP) (Artug, 2007; Qin et al., 2004; Al-Rashdi et al.,2013). The isoelectric point is the pH at which a certain molecule or surface has no net electrical charge (Qin et al., 2004). Accordingly, at the IEP, only sieving effects are the mode of separation hence minimal rejection. The IEP of commercially available nanofiltration membranes range between 3 to 5 and thus brackets the pH range of most AMD solutions (Childress and Elimelech 1996; Tanninen et al., 2004; Artug, 2007). Comprehension of IEP and AMD pH is vital in maximizing the rejection of ions and recovering of valuable metals. The rejections of ions such as sodium, iron, magnesium, chloride and heavy metals has been reported to upsurge with conditions favoring membrane surface charge that repulse electrostatically the ions of interest (Childress and Elimelech,2000; Ozaki et al.,2002; Tanninen and Nystrom,2002).

Ozaki et al (2002) investigated the effect of pH on membrane rejection of heavy metals (Ni, Cu and Cr) and found that rejection decreased with feed pH and increased after a minimum point was reached (Fig 2.2 (a)). It was gathered that the membrane is negatively charged in neutral and alkaline media, positively charged in an acidic environment, and have an IEP in a certain pH range. Higher rejection of metals at pH 3 was most likely due to electrostatic repulsions between the positively charged membrane surface and the metal ions. Maximum rejection was at the pH range of 7-9. The probable reason could be that at elevated pH metal ions may perhaps form complexes with OH^- and lead to insoluble hydroxide formation hence formation of a larger molecule which cannot easily permeate (Ozaki et al., 2002).

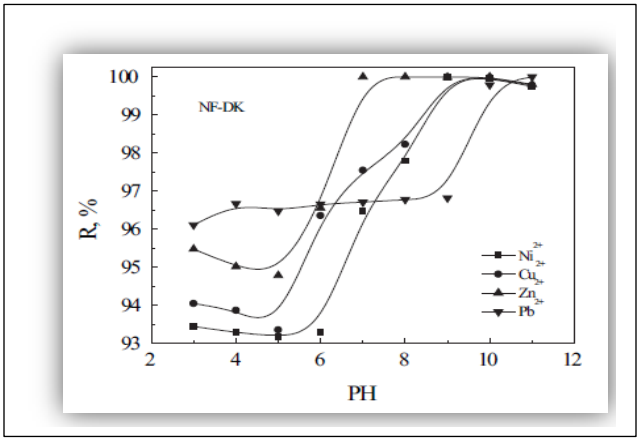
Zhong et al (2007) compared the use of reverse osmosis and nanofiltration for the treatment of acid mine drainage. Again the effect of pH on rejection of heavy metal ions ($Ni^{2+,}$ Cu^{2+}, Zn^{2+} and Pb^{2+}) was investigated and it is presented in Figures 2.2 (b) and 2.2 (c). The heavy metals were successfully removed by both membranes. Similarly, as observed by Ozaki et al., rejection was found to decrease with feed pH and increase after a minimum point (Figure 2.2 (a)). The higher rejection of metal ions at lower pH was also attributed to electrostatic repulsions.



(a)



(b)



(c)

Figure 2.2: Effect of pH on rejection of heavy metals: (a) Nanofiltration membrane on rejection of nickel, chromium and copper; (b) Reverse Osmosis on rejection of nickel, copper, zinc and lead; (c) Nanofiltration membrane on rejection of nickel, copper, zinc and lead

It is worth mentioning that much of the literature employed flat sheet membranes with the dead end filtration system whereas in this study the hollow fibre (HF) configuration and cross flow filtration scheme is utilised. One of the main advantages of hollow fibre filters is that they are scalable directly from research and development volumes to whole production and furthermore, their self-supporting assembly, large surface area per unit and flexibility of usage are the prime

indicators for their potential to aid in water purification processes. Cross flow filtration enhances product recovery owing to retentate recirculation. Praneeth et al (2012) synthesised a PES hollow fibre membrane for clarification of surface water and results showed a turbidity rejection of 95.4%.

CHAPTER 3

3 EXPERIMENTAL METHODS AND MATERIALS

3.1 Materials

The membrane used in this study was a nanofiltration PES 180 HF module from Hydelena Corporation. The membrane specifications are shown in Table 3.1.

Table 3.1: Membrane Specification

Characteristics	***PES Membrane***
Membrane configuration	Hollow fibre
Membrane material	Polyethersulfone
Membrane model	HF 180
Surface area	2 m^2
Allowable operating pH	2-12

The hollow fibre was utilised since this configuration is well-regarded over the flat sheet in most separation/filtration processes due to its mentioned advantages. The hollow fibre configuration is employed in virtually all of the polymeric membrane separations which incorporate, ultrafiltration, microfiltration, gas separation and gas absorption, and also reverse osmosis (Chung et al., 2000).

A schematic view of the experimental setup is shown in Figure 3.1.

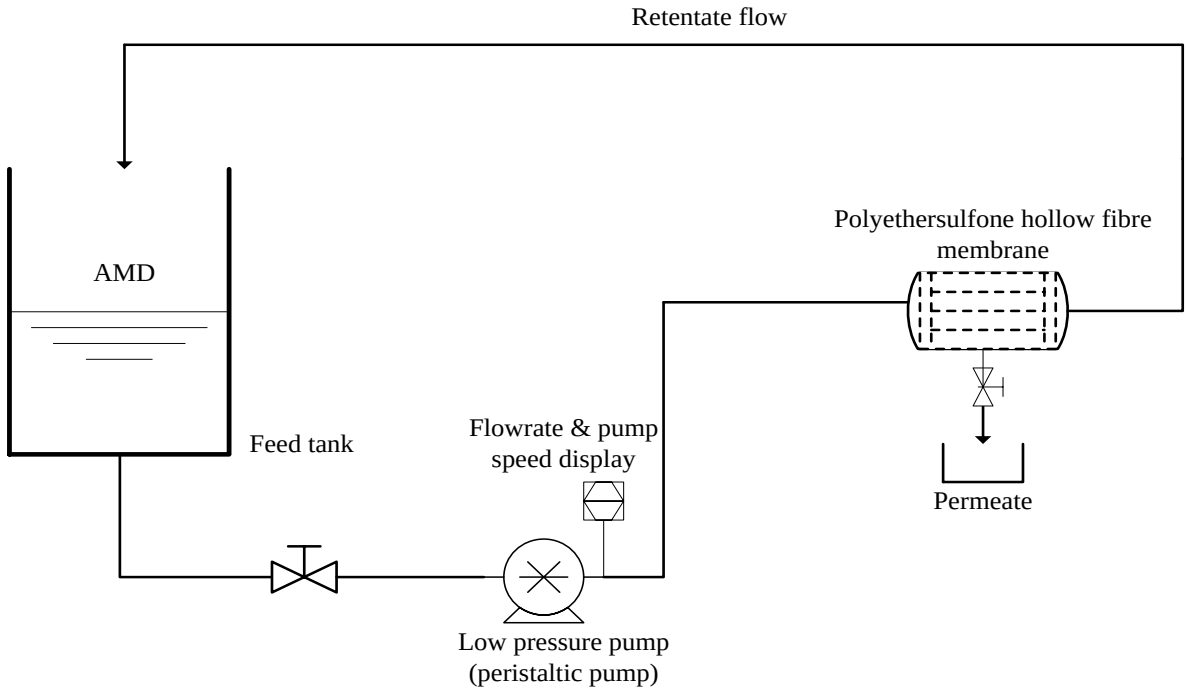


Figure 3.1: Experimental Set up

The feed tank was charged with AMD and a low pressure pump with variable flowrate was used to pump the acid water into the membrane. The permeate was collected for analysis while the retentate was recycled back to the feed tank in all experimental runs (flux and rejection efficiency investigations).

3.2 Sampling

Sampling was carried out with adherence to recommended sampling procedures (USEPA, 2007b; Quevauviller, 2001). AMD samples were collected directly from a small stream at the foot of the Rand mine dumps in Dobsonville (between Extension 1 and Extension 2) using polypropylene bottles. The bottles were rinsed with the site AMD immediately before sampling to ensure equilibrium between the sampling equipment and sample environment. Furthermore, care was taken when sampling from the stream not to disturb the bottom sediments within its bed. The water in the stream is characterized by a very brown water colour insinuating the presence of a high concentration of dissolved ferric iron (Fig 3.2, (a)). Efflorescent crusts of

metal sulphates due to evaporation were visible at the sampling point (Figure 3.2 (b) and 3.2 (c)). The colors of these crusts ranged from pale pink to various shades of yellow.



(a) (b)



(c)

Figure 3.2. Photographic plates taken at sampling point: (a) polluted water in a small stream; (b) efflorescent crust on the bank of the stream; (c) efflorescent crusts of different colours.

In the laboratory, a portion of the AMD samples were filtered under vacuum with 0.45 μm filter papers and used for the anions determination. Samples were stored at 4 ^{o}C until analysis.

3.3 Analysis

3.3.1 Elemental analysis (total concentrations)

Total metals concentrations were determined with an inductively coupled plasma optimized emission spectrometry (ICP-OES, Spectro Genesis, Germany), under the following standard optimum conditions:

Table 3.2: ICP-OES Optimized Parameters

Parameter	Value
Plasma power	1400 W
Coolant flow	14 ml min^{-1}
Auxiliary flow	1 ml min^{-1}
Nebulizer flow	1 ml min^{-1}
Total pre-flush time	45 s
Measure time	45 s

Commercial multi-elemental standards of 10 mgL^{-1} in 1% HNO_3 were diluted to make working standards of 0.1 to 1 mgL^{-1} for the instrument calibration from which the limit of detection (LOD) was calculated. Metals analysed were zinc, lead, cadmium, copper, magnesium, manganese, sodium and iron.

3.3.2 Major anion analysis

Anions in AMD and leachate samples were analysed by ion chromatography (Metrohm, Switzerland) equipped with a separation centre (733 IC), a detector (732 IC), an interface (762 IC), a suppressor module (753 IC) and a pump (709 IC). Samples were first filtered through a 0.45 μm filter paper to avoid the clogging of the working column and diluted before analysis in order to fit them into the calibration curve. The eluent used was a solution of 1.0 mM $NaHCO_3$

and 3.2 mM Na_2CO_3. A 50 mM solution of H_2SO_4 was used as a conductivity suppressor solution (USEPA, 2007c), and samples were injected using a 5ml syringe. The sulphate and chloride ions were analysed.

3.3.3 Field measurements

pH and electrical conductivity (Ec) measurements were carried out with a calibrated and pre-tested portable kit (WTW multi-parameter instrument pH/Cond 340i and ORP, Germany) equipped with a pH electrode, an integrated temperature probe, a standard conductivity cell and an oxidation-reduction potential probe. Measurements were taken mainly by inserting the respective probe into sample.

3.3.4 Acid mine drainage characteristics from site

The properties of the AMD analyses from site are summarized in Table 3.3. The pH and conductivity were 2.63 and 6.25 mS/cm respectively.

Table 3.3: AMD of original sample analysis from site and the DWAF (Department of Water Affairs) standard concentrations for potable water.

Constituent	AMD concentration (mg/L)	Standard Deviation (Std.dev)	DWAF standard concentration for potable water (mg/L)
Iron (Fe^{2+})	1.055	0.021	0.100
Zinc (Zn^{2+})	0.005	0.000	3.000
Copper (Cu^{2+})	0.051	0.013	2.000
Lead (Pb^{2+})	0.005	0.000	0.010
Cadmium (Cd^{2+})	0.001	0.000	0.003
Sulphate (SO_4^{2-})	3639.301	2.631	200.000
Manganese (Mn^{2+})	35.003	0.203	0.500
Magnesium (Mg^{2+})	523.011	0.629	30.000
Sodium (Na^{+})	861.004	1.037	200.000
Chloride (Cl^{-})	508.200	0.921	100.000

As per the analysis, the AMD contains very high concentrations of Iron and sulphate and trace amounts of heavy metals (Zn, Cu, Pb and Cd). Furthermore, it also contains high amounts of magnesium, manganese, sodium and also chloride ions (Cl^-). With the high concentration of Magnesium above 120 mg/L, the AMD is considered as hard water (Al-Zoubi et al., 2010). At pH less than 3, Stumm and Morgan (1996) reported that Fe (III) become unstable and continues to oxidize pyrite to give Fe (II) and SO_4^{2-} and this is consistent with the expatiation of the high concentration of both ions in the AMD due to the favourable pH of 2.63.

Effects of pH (2.63, 3.33, 4.37, 5.04, 5.94, 6.55) and feed flowrate (277, 337, 476, 595, 713 and 872 ml/min) were investigated both for rejection efficiency and flux. The feed flowrate was varied using the pump speed while dilution with deionised water altered the pH. The temperature of the solution in the system remained at 21.2 ^oC.

Experiments on the effect of time on flux were investigated by taking one of the membranes and run deionised water (DIW) first, followed by the AMD solution. From the deionised water flux, the behaviour of the membrane's pure water flux with varying flowrate could be ascertained and these were compared with that of AMD flux. The flux was measured at 15 minutes interval for a period of 135 minutes while the retentate was recycled into the feed tank.

The procedure for investigating the effect of pH on rejection and flux is summarised in Table 3.4. This procedure tacitly includes verification of fouling and the effect of backwashing as described in the subsequent subsection (subsection 3.4).

Table 3.4: Experimental protocol for the effect of pH on rejection and flux

Step	Description	Samples	Operation
1	Pure water flux determination	Samples taken	Recycle mode and permeate samples
2	Flux measurements at a specific pH (e.g pH 2.63)	Several samples (three samples taken so to obtain average flux values and also for rejection analysis).	Recycle mode and permeate samples
3	Pure water flux	Samples taken	Recycle mode and permeate samples
4	Backwash	-	-
5	Pure water flux	Samples taken	Recycle mode and permeate samples
5	Change of pH interval and repeat step 1 to 4.	-	-

3.3.5 Principal equations

Both the percentage conductivity and metals rejection efficiency were computed using the expression given hereunder:

$$R(\%) = \frac{C_{feed} - C_{permeate}}{C_{feed}} \times 100\% \qquad (3.1)$$

where, C_{feed} is either the metal concentrations or conductivity of the feed and likewise, $C_{permeate}$ is same as the aforementioned but for the permeate liquid.

For both nanofiltration and reverse osmosis, the rejection can also be expressed in terms of mass transfer coefficients using the equation below (Blau et al., 1992):

$$R = 1 - \frac{L_s}{L_p(\Delta P - \Delta\pi)(2-2RC) \div (2-2RC) + L_s} \quad (3.2)$$

where, $RC = Q_f / Q_c$, RC is water recovery efficiency (Q_p is the permeate quantity (L/h) and Q_f is feed quantity (L/h)); L_s is solute mass transfer coefficients (L/h); L_p is water permeability parameter; ΔP is the transmembrane pressure; and $\Delta\pi$ is the osmostic pressure.

The governing mass transfer equation is solute permeation flux which is computed using the equation below:

$$J_{solute} = L_{solute}(C_{membrane} - C_{permeate}) \quad (3.3)$$

where, J_{solute} is the solute flux (mol/m^2 hr^{-1}); L_{solute} is solute mass transfer coefficients; $C_{membrane}$ is the solute concentration on the membrane surface (mol/L); and $C_{permeate}$ is the permeate concentration (mol/L). In this study, the flux was calculated by dividing the amount of permeate by the product time taken and membrane area. Initialisation by running deionised water until stabilisation of permeate flux was done for the membrane.

3.4 Fouling prevention measures

In this study, short term fouling was circumvented by hydraulic cleaning (backwashing). This is a reversed filtration process whereby backflow from permeate to the feed side is induced. The backflow expands the fouling layer and hence fluidises it for ease of removal. Studies by Arnal et al. (2012) attest that the backwash method is advantageous to other conventional methods such as chemical cleaning for short term fouling deterrence. Figure 3.3 depicts a full factorial concept of backwashing with regard to the PES hollow fibre membrane.

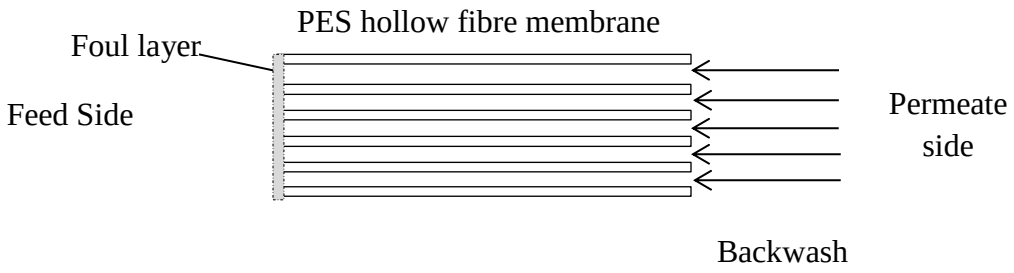


Figure3.3: Backwash to prevent fouling in hollow fibre membrane

To substantiate the effect of fouling and backwashing; the following schematic procedure was followed. The procedure involves the use of both deionised water (DIW) and AMD solution.

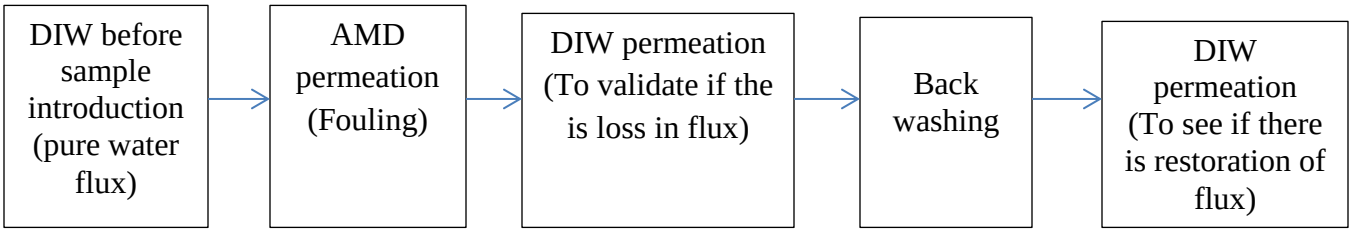


Figure 3.4: Fouling experimental procedure

From Figure 3.4, using one of the PES membranes, the flux of DIW was first measured. Then the AMD (fouling solution) flux measurements followed. After that, DIW followed again to determine if there was a loss of flux. Furthermore, back washing was introduced to remove foulants, and lastly, DIW flux measurements were done to substantiate the effect of backwashing through restoration of flux. All the flux measurements in this case were taken after almost steady state is reached. Steady state was assumed when the flux didn't fluctuate that much for a period of 15 minutes. At each permeation experiment, several results would be taken to ensure that at least a quasi-steady state juncture has been reached and the average value of flux was calculated.

The pure water flux before fouling with AMD was used as a basis and the flux loss in the subsequent permeation experiments was computed as follows:

$$\%F_i = {DIW_1 - Y_i}/{DIW_1} \times 100 \qquad (3.4)$$

where, F_i is the percentage loss in flux of permeation experiment *i*; *DIW* is the pure water flux before fouling of membrane; and Y_i is the flux of permeation experiment *i*.

CHAPTER 4

4 RESULTS AND DISCUSSION

4.1 Effect of feed flowrate

Figure 4.1 shows the effect of feed flowrate on flux (left axis) and rejection efficiency (right axis) of the membrane *(see Appendices, Table A 1 for data)*. The elimination of the AMD constituents was taken as the total rejections based on the electrical conductivity of feed and permeate solutions. This encompasses the sum total of all the cations and anions in the AMD solution. The feed flowrate spanned from 277ml/min to 872ml/min at a pH of 2.63, conductivity of 6.25 mS/cm and temperature of 21.2 ^{0}C.

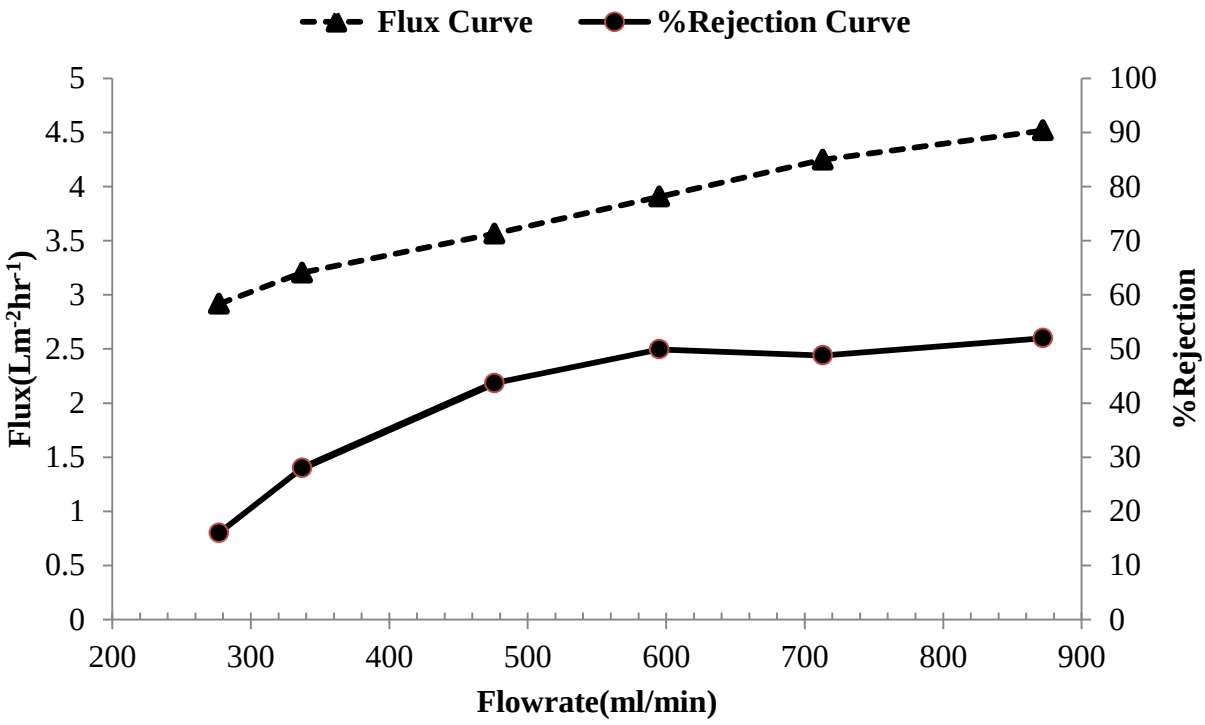


Figure 4.1: Effect of flowrate on flux and rejection efficiency of the membrane

From Figure 4.1, with regard to the flux, an increase feed flowrate shows an increase in flux. This is congruent with studies by Kuo and Cheryn (2007) who inferred that high flow rates are associated with large shear stress forces at membrane wall surface which prevents the accumulation of foulant materials and thus, improved flux. Furthermore, as discussed in literature, high feed flowrate will eliminate the chances of any polarised gel layer forming at membrane surface and this has been regarded as one of the effective and most simplest ways to circumvent the effects of concentration polarisation (Cheng and Lin, 2004; Strathmann, 1990). Conversely, at low feed flow rates, the flux is lower which could be necessitated by laminar flow conditions that may allow for accumulation of particles on membrane wall and thus, low flux. On the other hand from Figure 4.1, considering rejection, it can be gathered that an increase in feed flowrate from 277 ml/min to 595ml/min shows an increase in rejection and likewise, a further increase to 872 ml/min depicts the same behaviour but it is less pronounced as compared to the former. This implies that the possible maximum rejection efficiency may not be attained if the feed flow rate is not high enough. It can be deduced that the higher the feed flow rate the better the rejection and vice versa. Predictably, it would be expected that when the feed flowrate is high (implication being reduced fouling and increased flux in this case), more materials will permeate membrane and hence rejection will not increase as seen in studies by Shahtalebi et al (2011). However, such puzzling behaviour on rejection can be expounded by taking into account the variable flowrate in relation to transmembrane pressure (ΔP). When flowrate is increased, ΔP increases regardless of the flow regime (lamina or turbulent) of a fluid within a conduit. Such behaviour of high rejection at high flowrates can be implicitly explained through work done by Sourirajan (1970) and Zhong et al (2007). They found that as the transmembrane pressure increases, there is preferential sorption of water as compared to solutes in various nanofiltration and reverse osmosis membranes; hence, high rejection. Furthermore, from equation 3.2 as explained by Zhong et al (2007), it can be deduced that as ΔP increases (hence increase in flowrate), the term $L_p(\Delta P - \Delta\pi)$ and RC (water recovery efficiency) increase. Again, the value of $(2 - 2RC)/(2 - RC)$ decreases with an increase of RC. Since the value of RC is in a small range as attested by Blau et al (1992), this surmises that the decrease of $(2 - 2RC)/(2 - RC)$ is negligible compared to the increase of L_p. It follows that in order to increase the rejection, a high feed flowrate which implies higher ΔP should be applied. From this, it can be construed that the

results of Figure 4.1 are harmonious with theory and also it's best for the membrane to be operated at a higher feed flowrate.

Following from the indication that the possible rejection efficiency may not be attained if the feed flow rate is not high enough: Table 4.1 shows the rejection of selected individual constituents of the AMD at the pH of 2.63, temperature of 21.2 ^{0}C and maximum flowrate of 872ml/min. Rejection of heavy metals and other elements that were available in trace amounts are shown in the Appendices (*Table A 2*). These metals have been appended since they are in trace concentrations relative to the stipulated standard water concentrations (DWAF standards). It is worth mentioning that the temperature of permeate, feed and retentate streams did not change with time and so the effects of temperature on membrane performance were negligible. This is due to the use of a low pressure pump (peristaltic pump) which cannot dissipate significant amounts of heat within the system so to alter temperature.

Table 4.1: Rejection of selected Ions in original AMD sample at maximum flowrate

	pH	Conductivity (mS/cm)	Fe^{2+} (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	Cl^- (mg/L)	Mn^{2+} (mg/L)	Mg^{2+} (mg/L)
Feed	2.63	6.05	1.055	3639.301	861.004	508.200	35.003	523.011
Std.dev			0.021	2.631	1.037	0.921	0.203	0.829
Permeate	3.69	3.01	0.411	2403.100	442.010	389.100	16.300	253.100
Std.dev			0.004	0.960	0.623	0.769	0.003	0.009
%Rejection			61.04	33.97	48.66	23.44	53.40	51.61

From Table 4.1, the rejection of cations is higher than the rejection of anions at the original pH of the AMD (pH 2.63). Regarding the cations (Fe^{2+}, Mg^{2+}, Mn^{2+} and Na^+), the rejection of iron, magnesium and manganese is more than that of sodium. An analogous trend of results were obtained by Al-Zoubi et al (2010) using a different nanofiltration membrane (NF) and such behaviour is ascribed to the small size of sodium ion relative to the aforementioned cations;

henceforth, less sodium being rejected as it permeates through the relative small pores of NF membranes (Hilal et al.,2005) . Further, the rejection of anions (SO_4^{2-} and Cl^-) is generally lower as compared to cations and this can be attributed to zeta potential effects on the membrane surface. As expounded in the theory section, not only the sieving effects exhibit a part in nanofiltration; however, membrane charge has a very dynamic role in ions separation. A plausible explanation for more removal of cations than anions could be that the membrane is more positive at lower pH, thus, electrostatic repulsions are more dominant for cations relative to anions which leads to more Fe^{2+}, Mg^{2+}, Na^+ and Mn^{2+} being rejected than SO_4^{2-} and Cl^-. Although the rejection of anions is less than cations at this pH, SO_4^{2-} has a higher rejection than Cl^{-1} and this is agreement with theory (that is, nanofiltration removes divalent ions more than monovalent). This is due to the greater size of SO_4^{2-} as compared to Cl^- (Maryam et al., 2011); hence, higher rejection of the former with respect to particle size exclusion.

Also adsorption of ions on membrane surface might play a role in rejection. However, there was hindrance in acquiring electron microscope images (SEM) so to authenticate ion adsorption. Since the module was a commercial one, taking SEM images was held up by the modules casing because it had to be dismantled and that would have interfered with the membrane surface (surface damage). For further studies concerning characterisation when making the membrane: SEM images would be necessary. At this juncture, SEM images are not of crucial significance. Furthermore, from Table 4.2, the conductivity of the permeate is lower as compared to that of the feed since the ionic content in the former is reduced as a result of rejection by the membrane. Since conductivity is a function of temperature, the temperature of the feed solution was the same as permeate; hence, no temperature effects can be ascribed. On the other hand, permeate pH is a bit higher than the feed pH. This might be explained in concurrence with the sorption of water at increased transmembrane pressure (high flowrate, section 4.1). It follows that if the is a degree of preferential sorption of water molecules through the membrane from an acid solution, the pH will slightly surge in the direction towards neutrality within the pH scale; hence, increase in pH. The effect of pH change on ion speciation cannot be determined retrospectively and is beyond the scope of this study.

4.2 Effect of time on permeate flux

The permeate flux as a function of time for the original AMD solution was investigated (sample of pH 2.63, temperature of 21.2^{o}C, conductivity of 6.25mS/cm and flowrate of 872 ml/min). Likewise, flux with deionized water (DIW) was also observed with time. Figure 4.2 shows the relationship. Data for this is presented in the Appendices section (*Table A 3*).

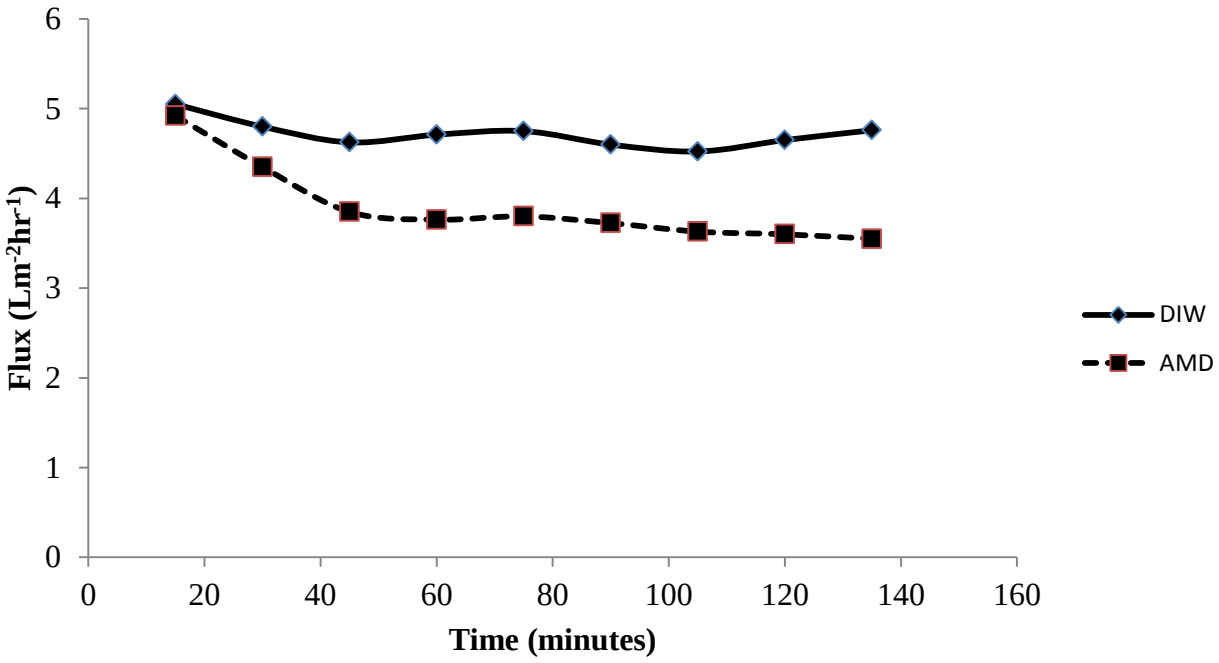


Figure 4.2: Permeate flux as a function of time at maximum flowrate

It can be observed that the permeate flux with pure water (DIW) is more or less constant and this is due to the privation of organic matter and dissolved ions in the water. On the other hand, with regard to the AMD sample, it can be observed that in the initial stages (first 45 minutes) of nanofiltration process, there is a fairly accentuated decrease in the permeate flow, that is, a sharp decrease in flux. Furthermore, with time, it can be seen that the flux continues to decrease but not as pronounced as in the first forty five minutes. It has been acknowledged through several studies that the initial sharp decline in flux is caused by concentration polarisation and to some extent the formation of a gel layer (Zuo et al.,2008; Wang et al., 2006; Kim and Lee , 2006). Likewise, the subsequent flux decline after concentration polarisation is due to fouling (Rieger et al., 2009). To substantiate the effects of fouling and backwashing, Figure 4.3 shows the results

of: DIW (pure water flux); AMD solution flux; flux before backwashing (BBW) which is the flux of DIW after fouling by AMD; and the flux after backwashing (ABW) which is the flux of DIW after membrane has been cleaned. The percentage on top of each bar indicates the loss of flux. The pure water flux was used as a basis.

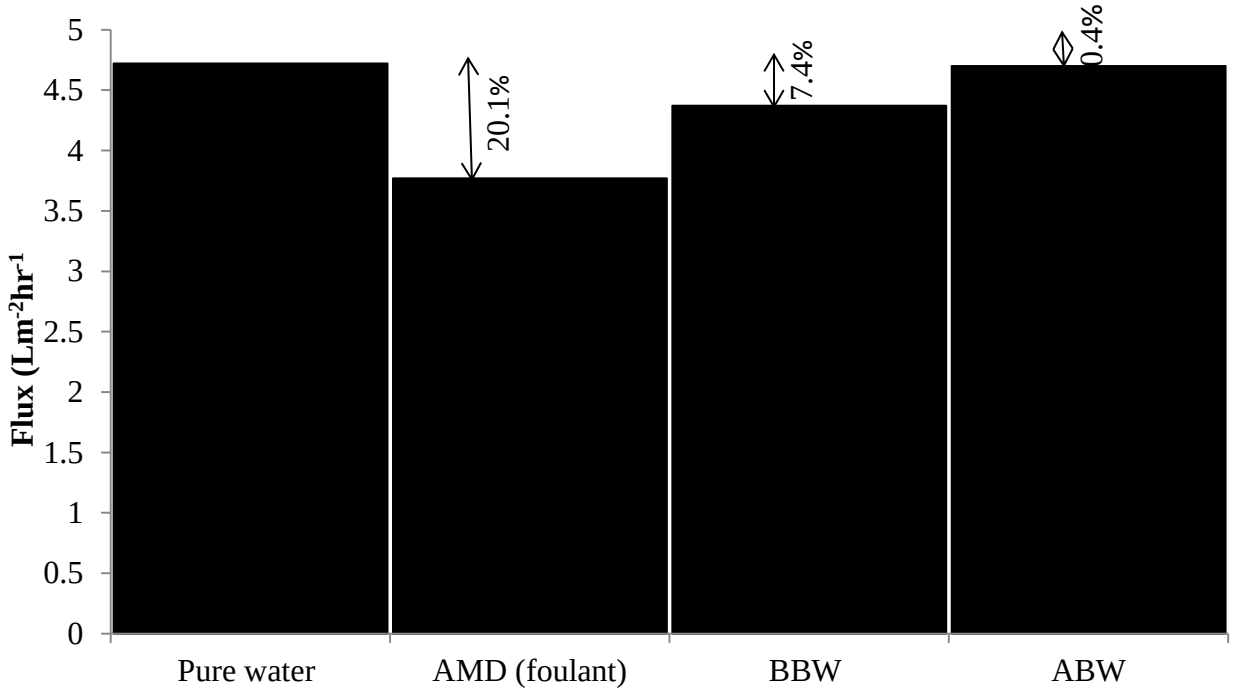


Figure 4.3: Fouling experimental results

Figure 4.3 shows the existence of membrane fouling and also the effect of backwashing in restoring flux. It can be seen that the AMD solution induced a membrane flux decline of 20.1% relative to the pure water flux. In addition, a 7.4% pure water flux decline was obtained after membrane has been fouled but before backwashing. After backwashing the flux was almost restored, that is, it was 0.4% less compared to the original flux and such a small discrepancy can be ascribed to parallax error when taking volumetric readings for flux computation (Kadis,2004). Since the mean flux losses were 0.4%: the membrane virtually experienced reversible fouling as the flux losses were less than a percent (Tang and Chen, 2002). This implicitly supposes that if the effect of backwashing on rejection was investigated (that is, measuring rejection after backwashing): the same rejection would be attained as in Figure 4.1 since flux is restored.

4.3 Effect of pH on rejection

The effect of pH on rejection was studied on the major constituents of the AMD (at a temperature of 21.2^{o}C and maximum feed flowrate of 872ml/min). As expounded in literature, both anions and cations were considered as they are affected differently in terms of rejection. Figure 4.4 illustrates the effect of pH on the rejection efficiency of Fe^{2+}, Mg^{2+}, SO_4^{2-} and Cl^{-}.

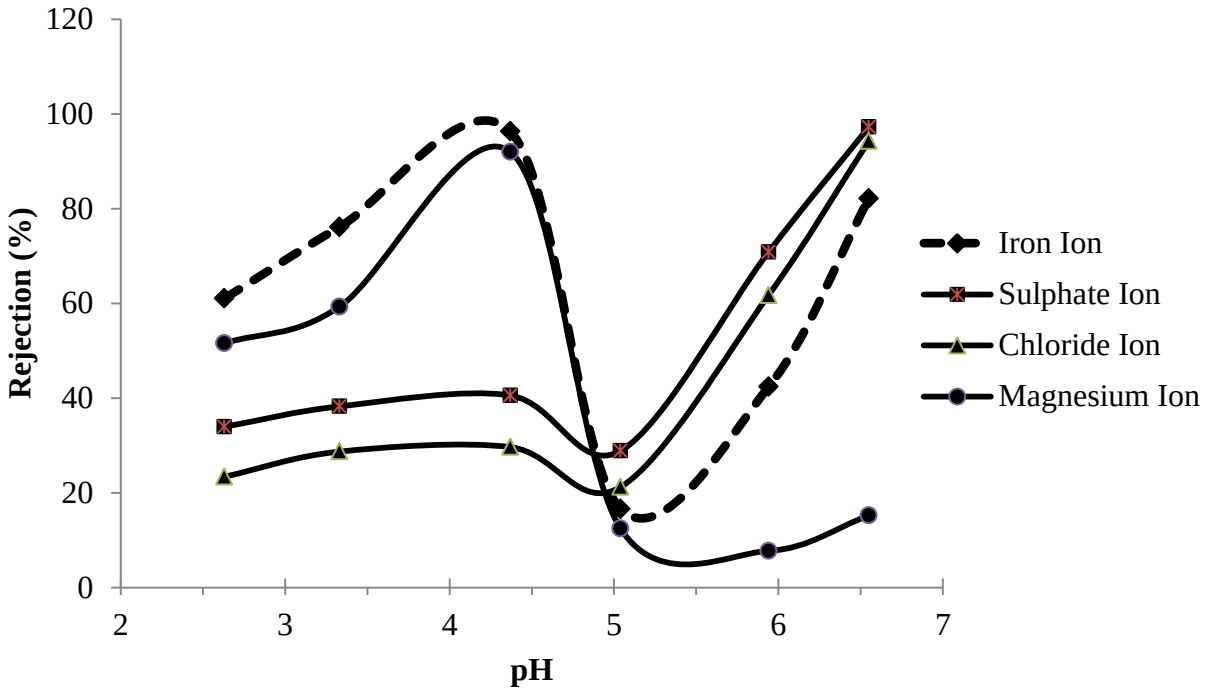


Figure 4.4: Effect of pH on rejection efficiency

Figure 4.4 shows a confounding observation on the effect of pH on the rejection efficiency of major ions by the PES membrane. The rejection increases, decreases and then increase again with increase in pH. An explanation to this behaviour can be acknowledged to isoelectric or zero potential charge effect within a certain pH range of the membrane. Without measuring the zero potential of the membrane, studies have shown that the pH with the lowest percent rejection of ions corresponding to a peak in flux (as can be observed in Figure 4.6) indicates the isoelectric point of a membrane (Huisman et al., 1997; Childress and Elimelech, 2000; Hagmeyer and Gimbel, 1998). It follows that the isoelectric point for the PES membrane is around pH 5.04. In addition, studies have also shown that polymeric membranes are usually positively and

negatively charged at lower and higher pH values respectively (Tanninen et al., 2004; Artug 2007). This surmises that the surface charge of the membrane above pH 5.04 becomes more negative and at lower than pH 5.04 it is less negative. Consequently, the higher rejection of cations (Fe^{2+} and Mg^{2+}) at pH<5 as compared to anions (SO_4^{2-} and Cl^-) could be attributed to mutual repulsion of the positively charged membrane and the metal ions. Likewise, the high rejection of anions at pH>5.04 could be ascribed to the aforementioned concept, that is, repulsive forces between the negative charged ions and membrane. Furthermore, the maximum rejection for cations was experienced at pH 4.37 for Fe^{2+} and Mg^{2+} with a rejection of 96.28% and 91.99 % respectively. Accordingly, the permeate concentrations of both ions were within the water standards, 0.034 mg/L for the former and 27.02 mg/L for the latter (*see Table A 4 for data*). In addition, the high removal of Iron at this pH could be witnessed as the permeate was devoid of the brown colour of ferric iron (Figure 4.5). Rejection of other metals at the pH of 4.37 is shown in the Appendices (*Table A 4*).

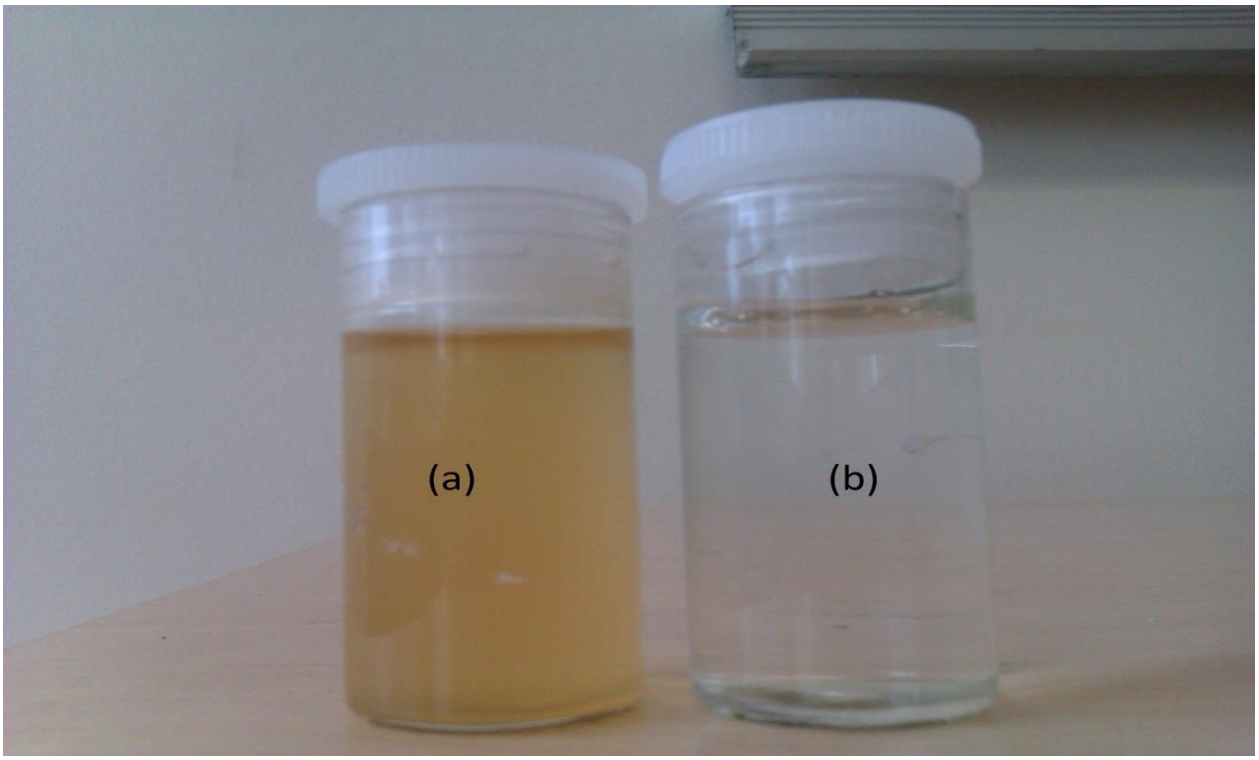


Figure 4.5: (a) AMD sample before nanofiltration; (b) permeate due to nanofiltration

On the other hand, from Figure 4.4, the maximum rejection of anions was at pH 6.55 with a rejection of 97.25% and 94.30% for SO_4^{2-} and Cl^- respectively *(see Appendices, Table A 5 for data)*. A minimum rejection of Fe^{2+}, SO_4^{2-}, Mg^{2+} and Cl^- was attained at a pH of 5.04, suggesting an isoelectric point (IEP) at the vicinity of pH 5. With regard to IEP, at the pH of 5.04, the membrane is neither positive nor negative and the mode of separation is more or less due to sieving, hence reduced rejection efficiency of ions regardless of their charge. Furthermore, from Figure 4.4, when comparing the rejection of Iron and Magnesium at higher pH (pH>5.04), iron is rejected more than magnesium. This can be explained from the behaviour of metal ions at higher pH, that is, their capability to form complexes with OH^- ions. Al-Zoubi et al (2010) states that nanofiltration membranes have a higher rejection of metal complexes as compared to metal ions (accordingly, even though the pore size and its distribution were not mentioned by the manufacturer, by virtue of being a nanofilter, the same applies to the PES membrane). Ferric hydroxide precipitates at a pH between 5.5 and 8.5 (Hansel et al., 2003; Biederman and Schindler, 1957) while magnesium hydroxide precipitates at pH above 9 (Stratful et al., 2001). In view of that, this affirms the high rejection of iron as compared to magnesium which means the former forms a hydroxide hence solute become a larger molecule thus high rejection.

When comparing Figure 4.3 and Figure 2.2 (literature section) with respect to cations, there is a difference in the shape of the graphs: however, they show a general trend of a local minimum in rejection of each ion. With respect to the latter, at lower pH, before the local minimum is reached in rejection of each ion, the rejection decreases whereas in the former it increases then decreases forming a crest. This dissimilarity may be due to the differences in surface charge characteristics of the membrane and also on the pH range used (that is, if the initial pH in Figure 4.3 was 4.37, the same trend will have been observed in both graphs).

4.4 Effect of pH on flux

The effect of pH on the membrane flux was investigated. This was done under identical conditions as in the previous section (that is, samples were replicated; one for rejection studies and other for flux studies) for ease of inference and drawing sound judgement on pH effects. Figure 4.6 shows the effect of pH on flux. Data is available in the Appendices (*Table A 6*).

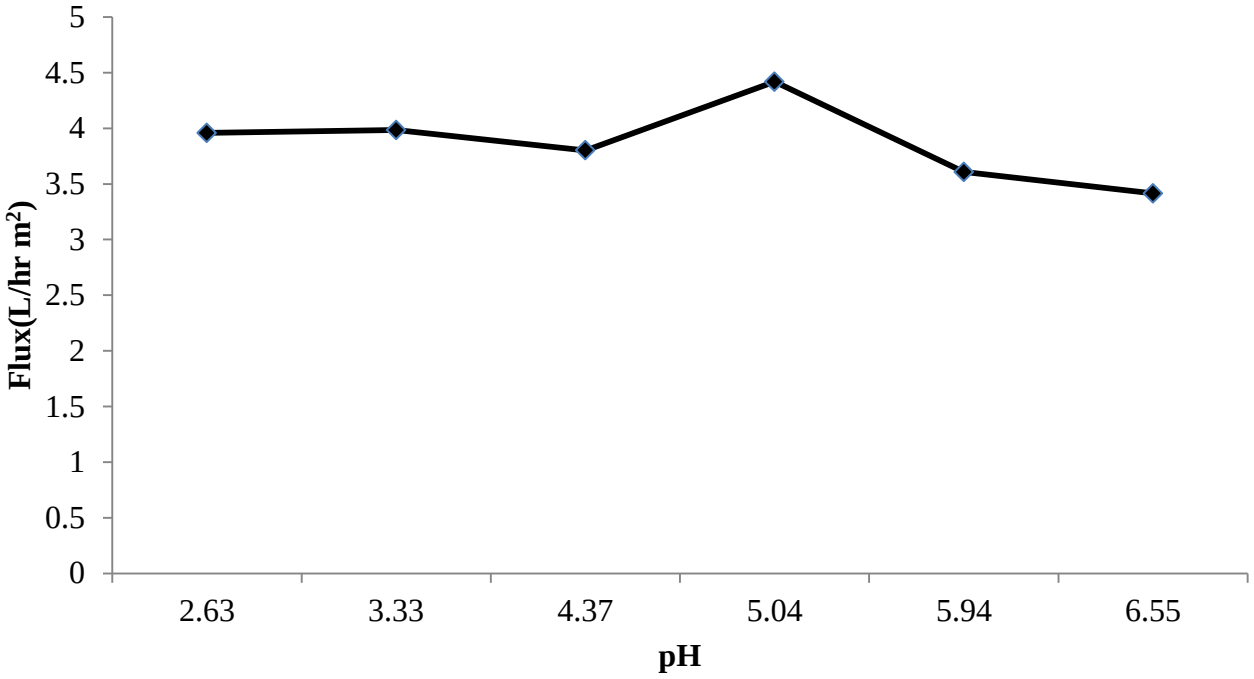


Figure 4.6: Flux as a function of pH

It can be observed that at the pH of 5.04, the flux is the highest and then it decreases with increase in pH. The reason for this behaviour can be explained in conjunction with the observations in Figure 4.4. In Figure 4.4, the lowest rejection was at pH 5.04 which holds good explanation for the flux behaviour in Figure 4.6 since when there is the lowest rejection, high flux is ascertained because it infers that most of the material permeates the membrane. Likewise, when rejection is the highest, low flux is observed and this is consistent with conclusions drawn by Ozaki et al., 2002.

In order to ensure a degree of credibility in comparing data between different runs or parameter variations, the flux with DIW was adapted as an ancillary approach to construe whether the membrane was due for change or not. Flux with deionized water was measured between experiments after backwash to know if the module has to be replaced since membrane separation could be an irreversible process. In all parameter variations, the membrane was not replaced since the flux with deionized water between runs didn't vary appreciable as compared to pure water flux of the membrane (Figure 4.7 shows the results). Thus, this affirms that the membrane

is suitable over a wide pH range as reported in various studies (Rahimpour and Madaeni, 2007; Betrand *et al*., 1997; Arkhagelsky *et al*., 2007).

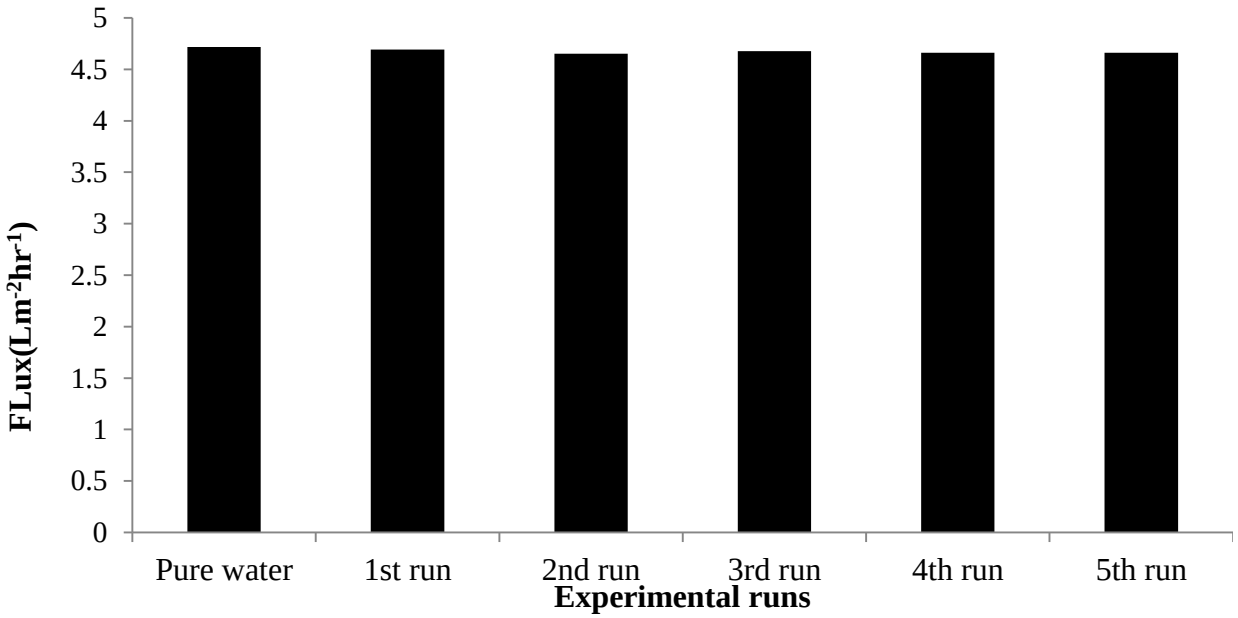


Figure 4.7: Flux of DIW in between experimental runs

CHAPTER 5

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Experimental results showed that the acid mine drainage had a very high concentration of Iron and sulphate ions. The pH was found to influence the rejection of both metals ions and sulphate ions. The maximum rejection of iron and magnesium was 96.28 % and 91.99 % respectively at a pH of 4.37, maximum feed flowrate of 872ml/min and the permeate concentrations were within the potable water standards (0.034 mg/L for the former and 27.02 mg/L for the latter). Accordingly, with the lower concentrations of magnesium implies that the PES membrane is able to remove the AMD hardness. On the other hand, maximum rejection of sulphate ions was 97.30% at a pH of 6.55 and maximum feed flowrate. The pH seemed to have a major effect on the membrane surface charge which in turn affects the rejection of the polyethersulfone membrane. At lower pH<5.04, the membrane showed plausible characteristic of being positively charged as rejection of cations were higher than anions due to repulsive like charges. Likewise at a pH> 5.04, it displayed the contrary (negatively charged) as rejection of anions were higher. Again on pH, its effect on flux was found to vary, this is explained in amalgamation with the effect of pH on rejection. That is, when there is the lowest rejection, high flux is ascertained because it infers that most of the material permeates the membrane and this was observed at the pH of 5.04. Furthermore, the effect of feed flowrate on flux and rejection of the membrane showed that an increase in flow rate results in higher flux and rejection. The reasonable explanation for this is that: high flow rates are associated with large shear stress forces at membrane wall surface which prevents the accumulation of foulant materials and thus improved flux; high rejection because of preferential sorption of water at increasing feed flowrates which results in increase of transmembrane pressure. The permeate flux declined with time and it is attributed to the different forms of fouling.

5.2 Recommendations

Although the membrane had a larger surface area ($2m^2$), the flux was not that higher (ranged from 3 - 4.5 L/m^2hr) and this can be attributed not only to various forms of fouling but also to the hydrophobic nature of the membrane polymers. Further studies are required in addressing the augmentation of flux and antifouling by modification of the PES polymer matrix. Future studies need to strike conciliation between hydrophobicity and hydrophilicity, and specifically localize the latter within membrane pores, so to effect a surge in flux and also reduction in fouling without compromising the mechanical stability of the PES membrane. Such enhancement processes can be introduction of hydrophilic nanoparticles, for example, introducing carbon nanotubes. As per the objectives, the study did not dwell on the characterisation of the membrane: however, it is of significance in future studies (for example, determination of the surface charge density, pore size and pore size distribution). Also, the extent of fouling need to be further studied, that is, over a lengthy period.

REFERENCES

Adam, K., Gazea, B., Kontopoulos, A. 2012. A review of passive systems for the treatment of acid mine drainage. *Minerals Engineering*. 9(1): 23-92

Akcil, A., Koldas, S. 2006. Acid Mine Drainage (AMD): causes, treatment and case studies. *Cleaner Production*. 14: 1139-1145.

Al-Amoudi, A.,Lovitt, W.L. 2007. Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency. *Membrane Science*. 303(2): 4-28.

Ali, N., Mohammad, A.W., Jusoh, A., Hasan, M.R., Ghazali, N., Kamaruzaman, K. 2005. Treatment of aquaculture wastewater using ultra low pressure asymmetric polyethersulfone (PES) membrane. *Desalination*. 185: 317-326.

Al-Rashdi, B. A. M., Johnson, D. J., Hilal, N. (2013). Removal of heavy metal ions by nanofiltration. *Desalination*. 315: 2-17.

Al-Zoubi, H., Rieger, A., Steinberger, P., Pelz, W., Haseneder, R., Hartel, G. 2010. Optimisation study for treatment of Acid Mine Drainage using Membrane Technology. *Separation and Technology*. 14 (14): 2004-2016.

Al-Zoubi, H., Omar, W. 2009. Rejection of salt mixtures from high saline by nanofiltration membranes. *Chemical Engineering*. 26 (3): 799–805.

Arkhangelsky, E., Kuzmenko, D., Gitis, V. 2007. Impact of chemical cleaning on properties and functioning of polyethersulfone membranes. *Membrane Science*. 305: 176-184.

Arthanareeswaran, G., Thanikaivelan, P., Srinivasn, K., Mohan, D., Rajendran, M. 2004. Synthesis, characterisation and thermal studies on cellulose acetate membranes with additive. *European Polymer*. 40: 2153-2159.

Artug,G. 2007. Modelling and simulation of nanofiltration membranes. Gottingen: Cullivier Verlag

Azapagic, A. 2004. Developing a framework for sustainable development indicators for the mining and minerals industry. *Cleaner Production*. 12(6): 639-662.

Baker, W. R. 2004. Membrane Technology and Applications. John Wiley and Sons: Chichester

Bertrand, S., LemaRre, I., and Wittmann, E. 1997. Performance of a nanofiltration plant on hard and highly sulphated water during two years of operation. *Desalination*. 113:277–281.

Bian, R., Yamamoto, K., and Watanabe, Y. 2000. The effect of shear rate on controlling the concentration polarization and membrane fouling. *Desalination*. 131(1): 225-236.

Biederman, G., and Schindler, P. 1957. On the solubility product of precipitated iron hydroxide. *Acta Chemica Scandanivia*. 11(4): 9-15.

Birley A.W., Martyn, J. 1982. Plastic materials: properties and applications. Glasgow: Leonard Hill

Blau, T. J., Taylor, J. S., Morris, K. E., Mulford, L. A. 1992. Dayton Beach Plant (DBP) control by nanofiltration: cost and performance. *American Water Works Association*. 84(12): 104-116.

Blodau, C. 2006. A review of acidity generation and consumption in acidic coal mine lakes and their watersheds. *Science of the Total Environment*. 369(1–3): 307–332.

Celik, E., Park, H., Choi, H. 2011. Carbon nanotube polyethersulfone membrane for fouling control in water treatment. *Water research*. 45 (1): 274-282.

Chen, J. C., Li, Q., Elimelech, M. 2004. In situ monitoring techniques for concentration polarization and fouling phenomena in membrane filtration. *Advances in Colloid and Interface Science*. 107(2): 83-108.

Chen, V., Fane, A. G., Madaeni, S., Wenten, I. G. 1997. Particle deposition during membrane filtration of colloids: transition between concentration polarization and cake formation. *Membrane Science*. 125(1): 109-122.

Cheng, T., Lin, C. T. 2004. A study on cross flow ultrafiltration with various membrane orientations. *Separation Purification Technology*. 39: 13–22.

Cheryan, M. 1998. Ultrafiltration and microfiltration handbook. Chicago: Technomic Publishers

Childress, A. E., Elimelech, M. 2000. Relating nanofiltration membrane performance to membrane charge (electrokinetic) characteristics. *Environmental science and technology*. 34(17): 3710-3716.

Childress, A. E., Elimelech, M. 1996. Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes. *Membrane Science*. 119(2): 253-268.

Chung, T., Qin, J., Gu, J. 2000. Effect of shear rate within the spinneret on morphology, separation performance and mechanical properties of ultrafiltration polyethersulfone hollow fibre membranes. *Chemical Engineering Science*. 55 (6): 1077-1091.

Daufin, G., Marshall, A. D. 1995. Physico-chemical aspects of membrane fouling by dairy fluids. Fouling and Cleaning in Pressure Driven Membrane Processes. Brussels: Dairy Federation

Enrico, D., Giorno, L. 2010. Comprehensive membrane science and engineering. UK: Elsevier.

Eriksson, P., Kyburz, M., Pergande, W. 2005. Nanofiltration membrane characteristics and evaluation for sea water processing applications. *Desalination*. 184: 281-294.

Ernst, M., Bismarck, A., Springer, J., Jekel, M. 2000. Zeta-potential and rejection rates of a polyethersulfone nanofiltration membrane in single salt solutions. *Membrane Science*. 165(2): 251-259.

Evangelou, V. P., Zhang, Y. L. 1995. A review: pyrite oxidation mechanisms and acid mine drainage prevention. *Critical Reviews in Environmental Science and Technology*. 25(2): 141-199.

Feather, C. E., Koen, G. M. 1975. The mineralogy of the Witwatersrand reefs. *Mineral Science Engineering*. 7: 189–224.

Feng, D., Deventer, J., Aldrich, C. 2004. Removal of pollutants from acid mine wastewater using metallurgical by product slags. *Separation and Purification Technology*. 40: 61-73.

Johnson, J. S. 2002. A new polyethersulfone microporous membrane for critical filtrations and diagnostics. *Membrane Science*. 48(5): 18-21.

Johnson, D. B., Hallberg, K. B. 2005. Acid mine drainage remediation options: a review. *Science of the total environment*. 338(1): 3-14.

Hagmeyer, G., Gimbel, R. 1999. Modelling the rejection of nanofiltration membranes using zeta potential measurements. *Separation and purification technology*. 15(1), 19-30.

Hansel, C. M., Benner, S. G., Neiss, J., Dohnalkova, A., Kukkadapu R. K., Fendorf, S. 2003. Secondary mineralization pathways induced by dissimilatory iron reduction of ferrihydrite under advective flow. *Geochimica et Cosmochimica Acta*. 67(16): 2977–2992

Hedin, R. S., Hyman, D. M. 1989. Treatment of coal mine drainage with constructed wetlands. Scheiner: Colorado

Hilal, N., Al-Zoubi, H., Mohammad, A. W., Darwish, N. A. 2005. Nanofiltration of highly concentrated salt solutions up to sea water salinity. *Desalination*. 184: 315–326.

Huisman, I. H., Dutre, B., Persson, K. M., Tragardh, G. 1997. Water permeability in ultrafiltration and microfiltration: Viscous and electroviscous effects. *Desalination*. 113(1): 95-103.

Johnson, D. B., Hallberg, K. B. 2005. Acid Drainage remediation options: a review. *Science of the Total Environment*. 338: 3-14.

Kadis, R. 2004. Evaluation of measurement uncertainty in volumetric operations: the tolerance-based approach and the actual performance-based approach. *Talanta*. 64(1): 167-173.

Kim, I., Lee, K. 2006. Dyeing process wastewater treatment using fouling resistant nanofiltration and reverse osmosis membranes. *Desalination*, 192: 246-251.

Koros, W., Ma, Y., Shimidzu, T. 1996. Terminology of membrane and membrane processes. *Membrane Science*. 120(2): 149-159.

Kuo, K. P., Cheryan, M. 1983. Ultrafitration of Acid Whey in a Spiral Wound Unit: Effect of Operating Parameters on Membrane Fouling. *Food Science*. 48: 1113- 1118.

Lee, S., Aurelle, Y., Roques, H. 1984. Concentration polarization, membrane fouling and cleaning in ultrafiltration of soluble oil. *Membrane Science*. 19(1): 23-38.

Ma, H., Bowman, C. N., Davis, R. H. 2000. Membrane fouling reduction by backpulsing and surface modification. *Membrane Science*. 173(2): 191-200.

Maphutha, S., Moothi, K., Meyyappan, M., Iyuke, S.E. 2013. A carbon nanotube-infused polysulfone membrane with polyvinyl alcohol layer for treating oil-containing waste water. London: Nature publishing group.
Available: http://www.nature.com/srep/2013/130321/srep01509/full/srep01509.html
Accessed 21 July 2013

Manttari, M., Pihlajamaki, A., Nystrom, M. (2006). Effect of pH on hydrophilicity and charge and their effect on the filtration efficiency of NF membranes at different pH. *Membrane Science*. *280*(1): 311-320.

Maryam, A., Gholam., N. B., Behnam, H. 2011. Nanofiltration efficiency in nitrate removal from groundwater: A semi-industrial case study. *Environmental*. 17: 232-236.

Matsuura, T. 1994. Synthetic membranes and membrane separation process. Boca Raton: CRC Press.

Matthiasson, E., Sivik, B. 1980. Concentration polarization and fouling. *Desalination*. *35*:59-103.

McCarthy, T.S., Humphries, M.S. 2013. Contamination of water supply to the town of Carolina, Mpumalanga. *Science*. 109(9): 1-10.

Mulder, M. 1996. Basic Principles of Membrane Technology. Second Edition. Netherlands: Kluwer Academic Publishers.

Munoz, M. G., Rodriquez, M., Luque, S., Ivarez, J. A. 2006. Recovery of heavy metals from metal industry waste waters by chemical precipitation and nanofiltration. *Desalination*. 200: 742–744.

Nakatsuka, S., Nakate, I., Miyano, T. 1996. Drinking water treatment by using ultrafiltration hollow fiber membranes. *Desalination*. 106(1):55-61.

Nepfumbada, M., Keet, M. 2011. Acid Drainage in South Africa with a focus on mine water management in the Witwatersrand gold mining area. DWAF Presentation.

Ozaki, H., Sharma, K., Saktaywin, W. 2002. Performance of an ultra-low-pressure reverse osmosis membrane for separating heavy metal: effects of interference parameters. *Desalination*. 144(1): 287-294.

Praneeth, K., Kalyani, S., Ravikumar, Y. V. L., Tardio, J., Sridhar, S. 2012. Development of polyethersulfone and polyacrylonitrile hollow fiber membranes for clarification of surface water and fungal enzyme broth. *Water Science & Technology: Water Supply*. 13(1): 44-55.

Peppas,A., Komnitsas, K., Halikia, I. 2000. Use of organic covers for acid mine drainage control. *Minerals Engineering*.13(5): 563-574.

Petrik, L., White, R., Klink, M., Somerset, V., Burgers, C., Frey, M. 2003. Utilisation of South African fly ash to treat acid mine drainage and production of high quality zeolites from the residual solids. *Proceedings of the 2003 International Ash Utilisation Symposium*. University of Kentucky: USA

Pretorius, D.A. 1964. The geology of some ore deposits in Southern Africa. *Geological Society of South Africa.*1: 63–108.

Qin, J. J., Oo, M. H., Lee, H., Coniglio, B. 2004. Effect of feed pH on permeate pH and ion rejection under acidic conditions in nanofiltration process. *Membrane Science*. 232(1): 153-159.

Rahimpour, A., Madaeni, S. S. 2007. Polyethersulfone (PES)/cellulose acetate phthalate (CAP) blend ultrafiltration membranes: preparation, morphology, performance and antifouling properties. *Membrane Science.* 305(1): 299-312.

Rautenbach, R., Groeschl, A. 1990. Separation potential of nanofiltration membranes. *Desalination*. 77(1-3): 73-84.

Rieger, A., Steinberger, P., Pelz, W., Haseneder, R., Härtel, G. 2009. Mine water treatment by membrane filtration processes-Experimental investigations on applicability. *Desalination and Water Treatment*. 6(1-3): 54-60.

Riveros, P. 2004. The extraction of Fe(III) using cation-exchange carboxylic resins. *Hydrometallurgy*. 72: 279-290.

Schafer, A. I. 2001. Natural Organic Matter Removal using Membranes: Principles, Performance and Cost. CRC Press: Boca Raton

Schafer, A. I., Andritsos, N., Karabelas, A.J., Hoek, E. M. V., Schneider, R., Nyström, M. 2004. Fouling in Nanofiltration. USA: Elsevier

Scott, K. (2003). Handbook of industrial membranes. Oxford: Elsevier.

Shahtalebi, A., Sarrafzadeh, M., Montazer, R. 2011. Application of nanofiltration membrane in the separation of amoxicillin from pharmaceutical wastewater. *Environmental Health Science and Engineering*. 8(2):109-116.

Singer, P. C., Stumm, W. 1970. Acid mine drainage: rate-determining step. *Science*. 167: 1121-1123.

Stratful, I., Scrimshaw, M. D., Lester, J. N. 2001. Conditions influencing the precipitation of magnesium ammonium phosphate. *Water Research*. *35*(17): 4191-4199.

Strathmann, H. 1990. Synthetic membranes and their preparation. Handbook of industrial membrane technology. New Jersey: Noyes Publications.

Stumm, W., Morgan, J. J. 1996. Aquatic chemistry: chemical equilibria and rates in natural water. New York: John Wiley and Sons

Sourirajan, S. 1970. Reverse Osmosis. London: Logos Press.

Tang, C., & Chen, V. (2002). Nanofiltration of textile wastewater for water reuse. *Desalination*. *143*(1): 11-20.

Tanninen, J., Platt, S., Weis, A., Nyström, M. 2004. Long-term acid resistance and selectivity of NF membranes in very acidic conditions. *Membrane science*. 240(1): 11-18.

Tanninen, J., Nyström, M. 2002. Separation of ions in acidic conditions using Nanofiltration. *Desalination*. 147(1): 295-299.

Thominette F., Farnault, O., Gaudichet-Maurin, E., Machinal, C., Schrotter, J. C. 2006. Ageing of polyethersulfone ultrafiltration membranes in hypochlorite treatment. *Desalination*. 200: 7–8.

Tuttle, J., Dugan, P., Macmillan, C., Randle, C. 1969. Microbia dissimilatory sulphur cycle in acid mine water. *Bacteriology*. 97: 594.

Ulbricht, M., Schuster, O., Ansorge, W., Ruetering, M., Steiger, P. 2007. Influence of the strongly anisotropic cross section morphology of a novel polyethersulfone microfiltration membrane on filtration performance. *Separation and Purification Technology*. 57: 63-73.

United States Environmental Protection Agency. 2008. Membranes: Nanofiltration and Affinity. *Available : www.epa.gov/radiation/docs/cleanup/.../chapter-2-membranes.* Accessed 13 August 2013.

Visser, T. J. K., Modise, S. J., Krieg, H. M, Keizer, K. 2001. The removal of acid sulphate pollution by nanofiltration. *Desalination*. 140: 79-86.

Wakao, N., Takahashi, T., Sakurai, Y., Shiota, H. 1979. A treatment of acid mine water using sulfate- reducing bacteria. *FermentationTechnology*. 57 (5): 445.

Wang, S., Chu, L., Chen, W. 2006. Fouling-resistant composite membranes for separation of oil-in-water microemulsions. *Chemical Engineering*, 14(1): 37-45.

Yadav, K., Morison, K., Staiger, M. P. 2009. Effects of hypochlorite treatment on the surface morphology and mechanical properties of polyethersulfone ultrafiltration membranes. *Polymer Degradation and Stability*. 94: 1955-1961.

Yu, S., Gao, C., Su, H., Liu, M. 2001. Nanofiltration used for desalination and concentration in dye production. *Desalination*. 140(1):97-100.

Zeman, L. J., Zydney, A. L. 1996. Microfiltration and Ultrafiltration: Principles and Applications, Marcel Dekker: New York.

Zhong, C., Xu, Z., Fang, X., Cheng, L. 2006. Treatment of Acid Mine Drainage (AMD) by Ultra- Low-Pressure Reverse Osmosis and Nanofiltration. *Environmental Engineering Science*. 24 (9): 1297-1306.

Zondervan, E., Zwijnenburg, A., Roffel, B. 2007. Statistical analysis of data from accelerated ageing tests of PES UF membranes. *Membrane Science*. 300: 111-116.

Zuo, W., Zhang, G., Meng, Q., Zhang, H. 2008. Characteristics and application of multiple membrane process in plating wastewater reutilization. *Desalination*. 222: 187-196.

APPENDICES

Table A 1 shows the rejection of the original AMD solution in terms of conductivity. The conductivity of the sample was 6.25 mS/Cm. Equation 1 was also used to calculate the rejection but with regard to conductivity.

For example at 277 ml/min; $Rejection = \frac{6.25-5.25}{6.05} \times 100 = 16\%$

Table A 1: Conductivity and rejection at different flowrate

Flowrate	Flux($Lm^{-2}hr^{-1}$)	Conductivity(mS/cm)	Rejection (%)
277	2.916	5.25	16.00
337	3.240	4.50	28.00
476	3.492	3.52	43.68
595	3.906	3.13	49.92
713	4.248	3.20	48.80
872	4.50	3.00	52.00

Equation 3.1 was used in calculating the rejection of metals;

For example Cobalt $R(\%) = \frac{C_{feed}-C_{permeate}}{C_{feed}} \times 100\% = \frac{0.94-0.25}{0.94} \times 100 = 73.40\%$

Table A2 shows the rejection of metals together with concentration in sample and permeate at a pH of 2.63, temperature of 21.2 ^{0}C and maximum flowrate of 872ml/min.

Table A 2: Concentration of metals in sample and permeate at pH of 2.63

Metal	**Sample concentration mgL^{-1}**	**Permeate concentration mgL^{-1}**	**Rejection (%)**
Lead (Pb)	0.006 ± 0.000	0.005 ± 0.000	16.67
Copper (Cu)	0.051 ± 0.013	0.016 ± 0.000	68.63
Zinc (Zn)	0.022 ± 0.000	0.003 ± 0.000	86.30
Cadmium (Cd)	not detected	not detected	-
Potassium (K)	17.710 ± 1.080	10.640 ± 0.820	39.92
Cobalt (Co)	0.941 ± 0.491	0.251 ± 0.060	73.40
Aluminium (Al)	14.510 ± 0.536	5.880 ± 0.713	59.48
Gold(Au)	0.422 ± 0.034	0.341 ± 0.059	19.05
Calcium (Ca)	374.133 ± 3.120	103.592 ± 1.571	72.31
Nickel (Ni)	0.024 ± 0.000	0.012 ± 0.000	50.00
Chromium	not detected	not detected	-

Table A3 presents a summary of the AMD and deionised water flux at different time intervals. The AMD used was the original sample (not diluted) at a pH of 2.63. The feed flowrate was the maximum (872ml/min).

Table A 3: AMD and Deionised water flux at different time intervals

Time minutes	**De- ionised water flux**	**AMD flux**
15	5.05	4.92
30	4.80	4.35
45	4.63	3.85
60	4.71	3.76
75	4.75	3.80
90	4.60	3.73
105	4.523	3.63
120	4.65	3.60
135	4.76	3.55

Table A 4 contains values of rejection of metals together with sample and permeate concentrations at pH 4.37, maximum feed flowrate (872 ml/min) and temperature of 21.2 ^{o}C.

Table A 4: Concentration of metals in sample and permeate at pH of 4.37

Metal	**Sample concentration mgL^{-1}**	**Permeate concentration mgL^{-1}**	**Rejection (%)**
Iron	0.915±0.003	0.034±0.001	96.28
Nickel	0.019±0.000	0.002±0.000	89.47
Magnesium	337.322±3.127	27.020±0.750	91.99
Manganese	31.001±1.000	0.376±0.000	98.79
Cobalt	0.488±0.101	0.028±0.000	94.26
Zinc	0.005±0.001	0.0001±0.000	98.00
Gold	0.407±0.009	0.009±0.001	97.79
Copper	0.012±0.000	not detected	-
Calcium	291.020±3.000	43.208	85.15
Lead	0.030±0.000	not detected	-
Aluminium	1.051±0.000	not detected	-
Cadmium	not detected	not detected	-

Table A 5 shows the rejection of selected element at a pH of 6.55.

Table A 5: Concentration of selected elements in sample and permeate at pH of 6.55

Element	**Sample concentration mgL^{-1}**	**Permeate concentration mgL^{-1}**	**Rejection (%)**
Sulphate	2936.401±1.040	80.751±1.016	97.25
Chloride	460.002±1.008	26.221±0.639	94.30
Iron	0.712±0.004	0.127±0.001	82.16
Magnesium	319.020±1.570	270.460±1.000	15.22

Table A 6 shows the flux at different pH readings while Table A5 shows the rejection of metals at a pH of 4.37.

Table A 6: Flux at different pH readings

pH	**Flux ($Lhr^{-1}m^{-2}$)**
2.63	3.96
3.33	3.98
4.37	3.80
5.04	4.42
5.94	3.61
6.55	3.42