

Removal of Manganese from Solution using Polyamide Membrane

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Abstract. The work demonstrates the performance of polyamide membrane in the removal of manganese ions from single salt aqueous solution simulating real acid mine drainage. The membrane was tested using a dead-end filtration cell with manganese sulphate was used to prepare a feed solution. The membrane flux and metal rejection was evaluated. Effect of operating parameters such as pH, initial feed concentration and pressure on membrane performance was investigated. The pressure was varied between 10 and 15 bar and it was observed that increasing the pressure increases the membrane flux. Acidic pH conditions contributed to the removal of the contaminate as Mn^{2+} ions are freely at low pH. The percentage rejection was found to be 63.5 to 77.6 % as concentration is increased from 290 ppm to 321 ppm for a feed solution. The membrane showed satisfactory results in removing metal ions from solution.

1. Introduction

The mining industry makes use of different type of utilities to extract valuable desired products from ore; minerals such as gold, copper, nickel etc. However, the common problem encountered by most industries is that of acid drainage which contains high concentration of toxic substances such as cyanides and heavy metals which have serious human health and ecological implications [1]. Generally, acid mine drainage is produced, usually but not exclusively, in iron sulphide-aggregated rocks and can be accelerated when naturally-occurring bacteria such as acidithiobacillus assist in the breakdown of sulphide minerals. Acid Mine Drainage (AMD) is wastewater produced when sulphide-bearing material from underground mining is exposed to oxygen and water. It is characterized by low pH and high concentration of heavy metals and other toxic elements that can severely contaminate surface and ground water, as well as soils. Mining operations promote AMD formation during rock exploration which exposes the sulphide bearing rocks and during comminution which increases the surface area [2]. The process begins with pyrite (Fe_2S) oxidation which releases Ferrous iron (Fe^{2+}), Sulphate ions (SO_4^{2-}) and Hydrogen ions (H^+). Fe^{2+} undergoes further oxidation to form Fe^{3+} , which will react with water to form ferric hydroxide $Fe(OH)_3$, an insoluble orange precipitate. Although there are numerous reasons for the toxicity of AMD to receiving water bodies the major impact is because of the proton acidity of the AMD, which will lead to a decrease in pH of the recipient water should it have insufficient neutralization capacity [3].

The need to address acid mine drainage inspired research to explore treatment technologies to treat the effluent before discharging into the environment. Active and passive treatments are traditional technologies which have been practiced for decades to deal with the problem. Active treatment depends on addition of alkaline chemicals which neutralizes the acidity of AMD and passive treatment relies on biological, geochemical and gravitational processes. Adding alkaline materials such as lime



cause the pH to increase and cause the metals present to precipitates. This will result in the production of iron rich sludge that may also contain several metals depending on the chemistry of the mine water treated [4]. Mostly, the sludge produced is collected and disposed of through burial or injection into abandoned mine [5]. However; little effort has been focused on the beneficial use of precipitated metals in these systems, especially in passive systems as oxides, carbonates, or sulphides. Recovery of these minerals will not be as profitable as the mine itself, due to slow reaction kinetics of the process [6]. Passive treatment systems involve using sulphate-reducing bacteria or limestone or both to neutralize acidity and precipitate dissolved metals. The systems are sometimes called wetlands or bioreactors [7]. It relies on sulphate-reducing bacteria (SRB) that can be found in natural environments where anoxic conditions prevail [1]. Passive treatment systems have been shown to be more economical than hydrated lime or similar neutralizing reagent methods [6]. However, the activity of Sulphate reducing bacteria (SRB) is controlled by the reactive mixture composition and this limit the long-term efficiency of the process [1].

The demand for clean water and environmental consciousness has prompted researchers to explore cost effective technologies which could treat acid mine drainage up to drinking standards. Membrane technology has emerged as a promising technology to substitute conventional methods [8] Advantages such as easy operation, inexpensiveness, low energy consumption, high separation efficiency and no need for integrated steps for further treatment, makes membrane technology an effective and attractive technology [9]. Reverse osmosis membranes are preferred during AMD treatment for the removal of heavy metals, salts and even ions through electrostatic repulsion and filtration due to smaller pore sizes [10]. These membranes are known as polymers which enclose repeating amide, -CO-NH-, linkages. They are well-known for their high strength, abrasion resistance, and resilience.

2. Experimental

2.1. Materials and equipment

A non-porous polyamide membrane manufactured by GE healthcare Companies was commercially purchased from Sigma Aldrich. A packet acquired contained 100 pieces with pore sizes of 0.45 μ m and 0.047m diameter. Atomic Absorption Spectrometer (Thermo scientific ICE 3000 series) was used to analysis metal ions. pH and conductivity were measured using Metler Toledo dual meter (Sevenduo pH /conductivity meter with a Metler Toledo inLab Pro ISM pH electrode and inLab 738 ISM conductivity probe).

2.2. Permeation batch tests

Membrane performance (water flux and metal ion rejection) was tested in a dead-end filtration with a capacity of 300 mL and effective filtration area of 14.6 cm². Pure water flux (J , L/m² h) was

determined by $J = \frac{A}{Vt}$ and metal ion rejection by $R = \frac{C_{feed} - C_{permeate}}{C_{feed}}$. Feed solution was prepared

by dissolving MnSO₄.2H₂O in water to make 321mg/L solution and the pH was altered using H₂SO₄ to 3.2. The solution was fed through the dead-end cell using nitrogen gas to push the solution through and filtrated were collected and analysed using AAS for metal content.

3. Results and discussions

3.1. Membrane flux

Figure 1 shows the variation in % removal of Cu²⁺ in different molar ratios with the number of batch reduction.

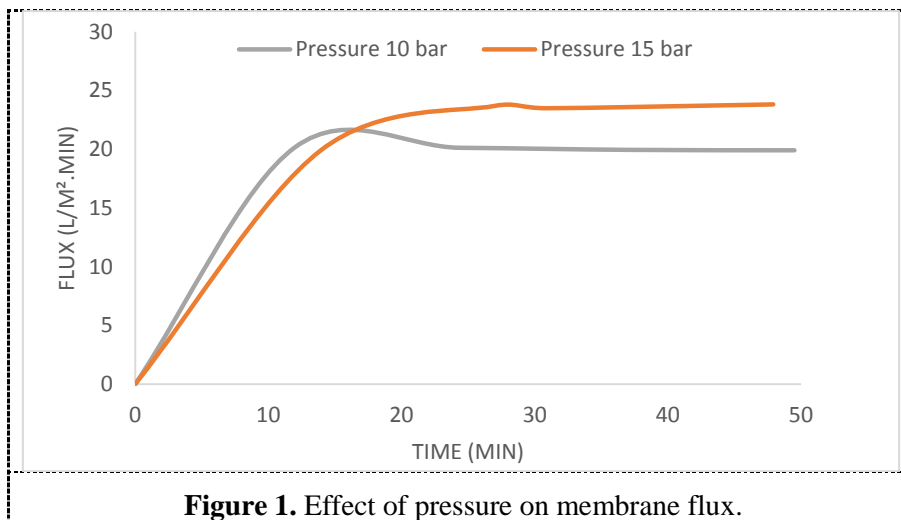
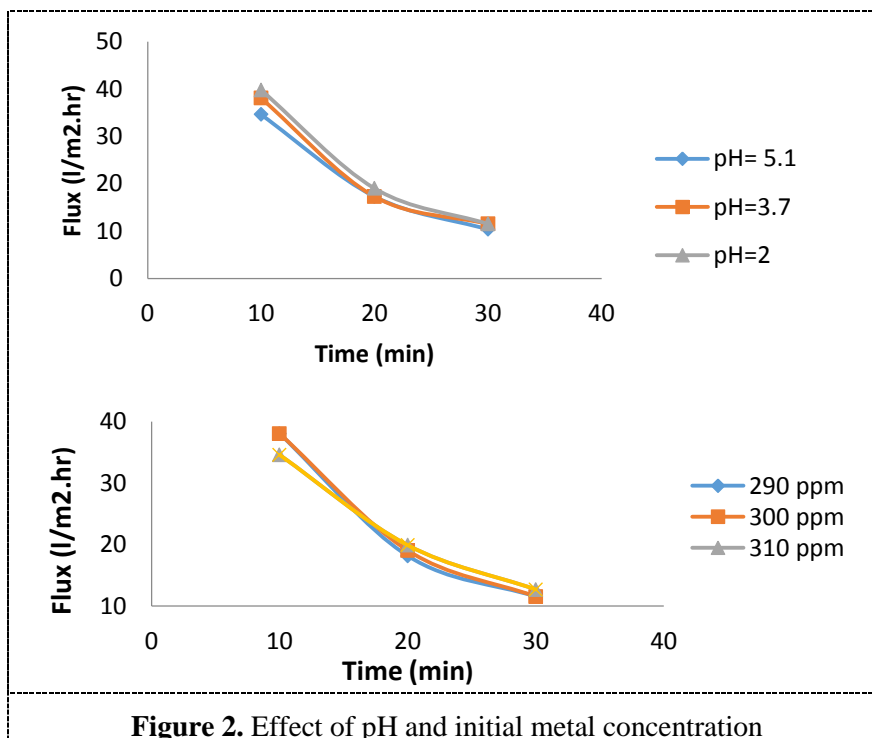


Figure 1 shows the effect of pressure on membrane flux. This was done to calculate the water permeability of the membrane using pure water. The experiments were run for 30 min using 3 replicated samples collected after every 10 min. Pressure of 10 bar and flow rate of 0.034 L/hr resulted in a calculated water flux of 20.17 L/m².hr. In addition, at 15 bar pressure and flow rate of 0.048 l/hr, the flux was found to be 24.78 L/m².hr. This is because operational conditions, such as feed pressure, temperature, and feed flow rate, influence the convective transport of molecules toward the membrane surface. The hydrophilicity of polyamide membranes had great influence as the chemical structure had affinity for water molecules and easily let them pass through the membrane.

3.2. Effect of pH and feed concentration on flux



The influence of solution pH and metal concentration on membrane flux was investigated by manipulating the pH to 2, 3.7 and 5.1 using sulphuric acid. The feed concentration was varied from

290 to 321 ppm. The trend which agrees with what was reported [11], the functional groups of polyamide membrane becomes positive under acidic conditions and this creates an electrostatic repulsion between the membrane and the metal contaminate. Over time, more metal ions are repelled from the membrane surface creating back pressure which pushes solution backwards and reducing membrane flux. Accumulation of metal ions on membrane surface due to filtration causes what is termed concentration polarization. Over time, the membrane effective pore sizes get blocked and this reduces membrane flux.

3.3. Effect of pH and feed concentration on metal rejection.

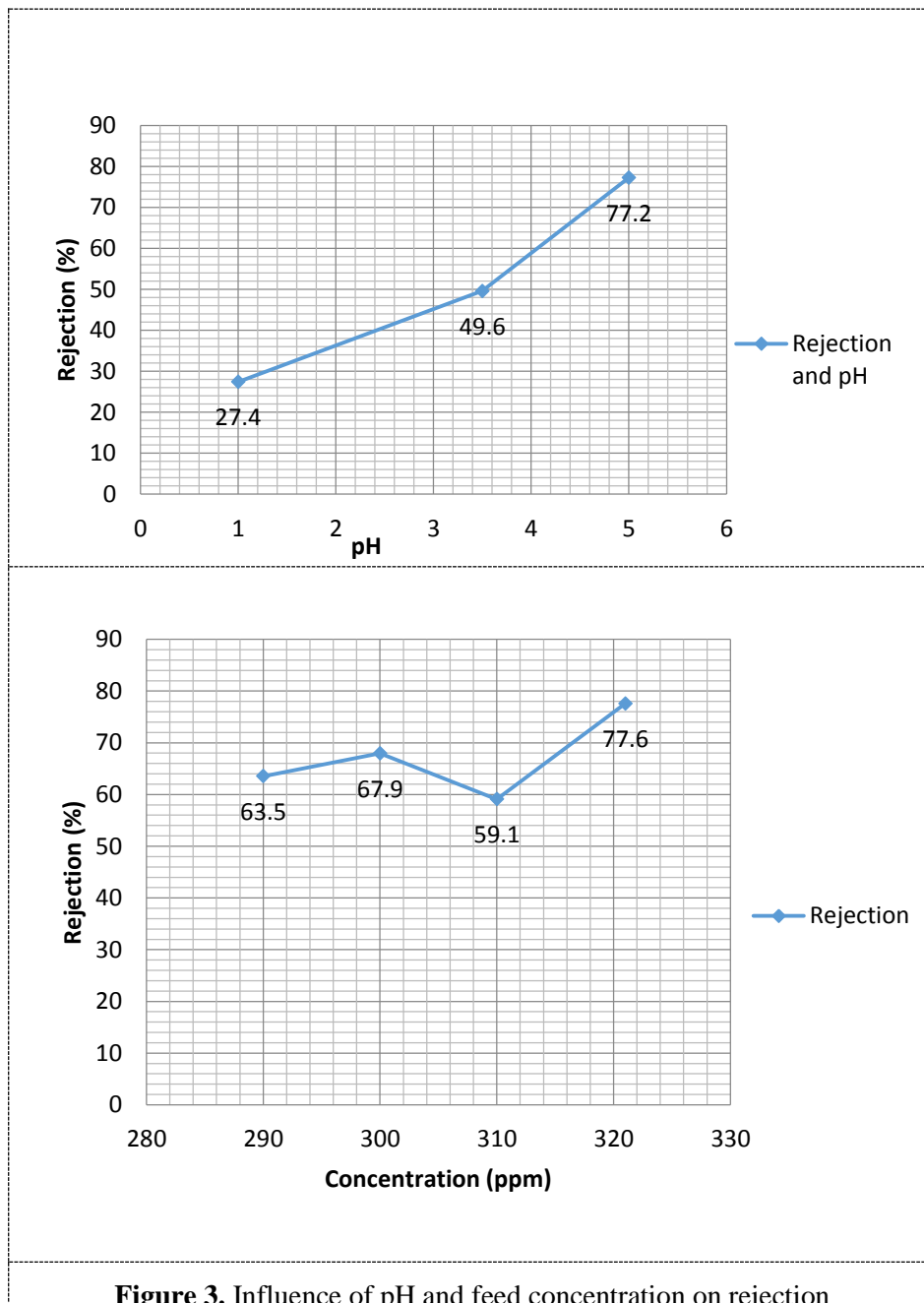


Figure 3. Influence of pH and feed concentration on rejection

Metal ion removal from solution could be due to absorption by the membrane through filtration and/or the attachment of metal ions to functional groups on the membrane surface. Reverse osmosis membrane constructed using polyamide material are known for high metal ion rejection owing to their small effective pore sizes. This trend agrees with Riley et al. [12] in a study on Polyamide reverse osmosis membrane fouling and its prevention. They deduced that when reaction reaches equilibrium at pH level of 7, manganese occurs as $\text{MnO}_2(\text{c})$, an insoluble crystal. As the pH reduces to below 6, it becomes oxidised and remains (at equilibrium) in its most stable form as a $\text{MnSO}_4(\text{aq})$. Reducing the pH further to below 2 (~ 1.7) reduces MnSO_4 to Mn^{2+} ions free to move about in solution. Hence more high rejection was observed towards neutral pH. Polyamide membranes have very small. The percentage rejection was found to be 63.5 to 77.6 % as concentration is increased from 290 ppm to 321 ppm for a feed solution pH of 2. At this pH, it is suggested that manganese crystals (MnO_2) have oxidised to form MnSO_4 which is also oxidizing to form (Mn^{2+}). These large molecules (MnSO_4) may not have found free pathways through the membrane therefore it is suggested that they are remaining sliding on the surface of the membrane. An irregular trend is observed when the concentration of the feed has reached 310ppm when the pH is lowest 1.5. At this level, the rejection is reduced to 59.1 % for a concentration of 310ppm. This trend can suggest that the solution is reaching equilibrium where all the MnSO_4 molecules oxidise to Mn^{2+} at pH below 2 and some ions can pass through the cross-linked membrane structure.

4. Conclusion

The study showed maximum flux of $24.78 \text{ L/m}^2\cdot\text{hr}$ after 30 min at an operation pressure of 15 bar. Polyamide materials which are normally used to fabricate reverse osmosis membranes, are known to have very small effective pore sizes, hence high pressure is needed to push molecules through the membrane. The feed solution pH alters the membrane surface charge in which under acidic conditions, the functional groups become positively charged and this creates an electrostatic repulsion between the membrane surface and cationic metal contaminants which reduces membrane flux but effectively increases membrane rejection. Additionally, the solution pH influences the stability of the manganese metal in which under acidic condition it moves freely as Mn^{2+} and is able to pass through the membrane but increasing the pH towards neutral, it exist as an insoluble oxide which is large enough to get trapped by the membrane. Further studies should investigate the anionic metal rejections by polyamide to see the effect of membrane charge under acidic conditions. Also, checking the anti-fouling behaviour of the membrane could be helpful to understand the long-term sustainability of the membrane.

5. References

- [1] Neculita C-M, and Zagury G.J 2007 Passive treatment of acid mine drainage in bioreactors using sulfate-reducing bacteria *Journal of Environmental Quality* 36(1), 1-16.
- [2] Akcil A and Koldas S 2006 Acid Mine Drainage (AMD): causes, treatment and case studies *Journal of Cleaner Production*, 14, 1139-1145.
- [3] Ford K 2003 Passive treatment systems for acid mine drainage.
- [4] Gusek J and Clarke-Whistler K 2005 Where Does the Recovery of Metal Resources from Passive Treatment Systems Fit in Sustainable Development Initiatives Associated with Large Mining Projects? Annual Meeting of the American Society for Mining and Reclamation Breckenridge, USA.
- [5] Hallberg K 2010 New perspectives in acid mine drainage microbiology *Hydrometallurgy* 104(3), 448-453
- [6] Hedin R.S 2003 Recovery of marketable iron oxide from mine drainage in the USA. *Land Contamination and Reclamation* 11(2), 93-98
- [7] Hilal N, Al-Zoubi H, Mohammad A.W and Darwish N.A 2005 Nanofiltration of highly concentrated salt solutions up to sea water salinity *Desalination*. 184: 315–326.

- [8] Johnson D. B and K B Hallberg 2005 Acid mine drainage remediation options: a review. *Science of the total environment* *338(1)*, 3-14
- [9] Shen M, Kete S and Lueptow R.M 2016 Rejection mechanisms for contaminants in polyamide reverse osmosis membranes *Journal of Membrane Science*, *509*, pp.36-47.
- [10] Zhong C, Xu Z, Fang X and Cheng L 2006 Treatment of Acid Mine Drainage (AMD) by Ultra-Low-Pressure Reverse Osmosis and Nanofiltration *Environmental Engineering Science*. *24 (9)*: 1297-1306.
- [11] Shockravi A, Vatanpour V, Najjar Z, Bahadori S and Javad A 2017 A new high performance polyamide as an effective additive for modification of antifouling properties and morphology of asymmetric PES blend ultrafiltration membranes *Microporous and Mesoporous Materials* *246*, pp.24-36.
- [12] Riley R.L, Ridgway H and Ishida K 2000 Polyamide reverse osmosis membrane fouling and its prevention: oxidation-resistant membrane development, membrane surface smoothing and enhanced membrane hydrophilicity *Separation Systems Technology, Inc., San Diego, CA, Orange County Water District, Fountain, CA*