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REJECTION BEHAVIOR OF MANGANESE IONS FROM SYNTHETIC WASTEWATER BY NANOFILTRATION AND ESTIMATION OF MEMBRANE TRANSPORT PARAMETERS

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Abstract: The present study is based upon nano-filtration as a novel separation technique using TFC NF-30 membrane for the separation of manganese ions from synthetic waster water containing MnSO₄.H₂O salt. The effects of various operating parameters such as feed concentration (20-60 ppm), applied pressure (5-8 kg/cm²) and pH (4-6) on rejection of heavy metals are studied. The present works conclude that rejection coefficient for manganese ions increase with the increasing pressure. As the feed concentration of manganese ions increases at the constant flow rate the rejection coefficient decreases. The effect of the pH are studied and found that the rejection of the manganese ions increases with the increasing pH. The maximum rejection of the metal is found to be 99.03% for an initial feed concentration at 20 ppm. The experimental data are analyzed using membrane transport models; combined-film theory-solution-diffusion (CFSD). Estimation of the membrane transport parameters namely the solute transfer parameter by CFSD model. *Index Terms - Nano filtration, Manganese Removal, Membrane transport Model, CFSD model*

I. INTRODUCTION

Membrane operations in the past few years have shown their potentialities in the rationalization of production systems [1]. Without water the life on the earth would be non-existent. The pollution of water resources is a common occurrence but particularly portable water has become greatly affected and has lost its original purpose. There are many sources of water pollution but two main general categories exist: direct and indirect contaminant sources. Direct sources are effluent outfalls from industries, refineries and waste treatment plant. Indirect sources are contaminants that enter the water supply from soil/grounds water system and from the atmosphere via rain water [2]. Heavy metals are classified into three main groups: toxic metals (Cr, Pb, Hg, Cu, Ni, Cd, Zn, As, Co, Sn, etc.), precious metals (Au, Pt, Ag, Pd, Ru, etc.) and radionuclides (Ra, Th, U, etc.) [3, 4, 5]. Manganese (Mn) is the twelfth most abundant metal on earth and is not encountered as free metal in the environmental. In nature it occurs combined with other elements such as oxygen, carbon, silicon, sulphur and chlorine in manganese compounds. Even if exist in many oxidation states (from -3 up to +7), the most common one is +2. Manganese has three oxygen states in the solution that are Mn (II), Mn (III), and Mn (IV). Manganese makes up to about 0.1% of the earth crust. Soil contains 7-9000 ppm of manganese, in average 400 ppm [6]. Some references report the allowable recommended levels of manganese in drinking water in the range of 0.01-0.1 mg/l [7].

Nanofiltration process has benefits like ease of operation, reliability and comparatively low energy consumption as well as high efficiency of pollutant removal. Solute rejection in NF membrane happens due to mainly electrostatic interaction of membrane and solutes on the membrane surface and size exclusion. Numerous models were proposed to describe and predict solute rejection/flux by NF based on extended Nernst–Planck equation. Spiegler–Kedem model and solution-diffusion model are capable of modeling highly complex and nonlinear systems for NF membranes [8].

II. MATERIAL AND METHOD

2.1 Chemical and membrane

For the experiment, synthetic samples of wastewater are prepared by adding required amounts of manganese (II) sulfate monohydrate (MnSO₄.H₂O) to distilled water. Several solutions are prepared with different concentrations (20-60ppm) of manganese (II) sulfate monohydrate. In the experiment rectangular flat membrane is used. This membrane has mainly three layers. The first layer that does the actual rejection is a 5–20 μ m polyamide polymer layer. The second layer is made of polysulfone of 50 μ m thickness and the third layer, used to bear resistance and strength, which is made of polyester with a thickness of about 150 μ m. As per manufacturer, these membranes are capable to withstand pH in the range 2–12, pressure up to 30 atm and temperatures up to 50°C [9].

2.2 Experimental Set-up

The experiments are performed on a Perma® pilot scale membrane system (Permionics, Vadodara, India). A rectangular flat membrane cell is used for the experiments. The membrane-housing cell is made of stainless steel with two halves fastened together with high tensile bolts. The top half of cell contained the flow distribution chamber and the bottom half is used as the membrane support system. The membrane required support to prevent rupture at high hydrostatic pressures. The following arrangements of special supports are used: a perforated 1mm thick stainless steel plate is laid over with a stainless steel gauge of 300 mesh size. Experiments are performed with a commercial thin-film composite polyamide membrane Perma-TFCNF300. Before conducting the actual experiments, the NF-300 membrane is stabilized at 20 atm, which is the maximum pressure used in this experiment, for 2 h to avoid possible membrane compaction during the experimentation[10].

2.3 Experimental procedure

Experiments were performed for 2 h. The each set of rejection data was taken in batch circulation mode and the permeate samples was collected from high pressure to low pressure for each and every feed concentration and feed flow rate. Both permeate and concentrate was collected in the feed vessel to keep the feed concentration constant. In given time interval samples of permeate was collected, to measure the observed salt rejection (R_0) and permeate volume flux (J_V). After each set of experiments for a given feed concentration, the set-up is rinsed with distilled water for 30min at 4 atm to clean the system [11]. The experiment was carried out for different feed concentration (20 ppm, 40 ppm & 60 ppm), different feed pressure (5, 6, 7 & 8 Kg/cm²), and different pH (4, 5 & 6) at constant flow-rate.

2.4 Analysis of Manganese ions

The manganese ion concentrations are measured according to standard methods by an atomic absorption spectrophotometer (Model SL-173) [11].

III. RESULT AND DISCUSSION

3.1 Effect of feed concentration on rejection

In fig. 3.1 to 3.4 shows the effect of feed concentration such as 20 ppm, 40 ppm and 60 ppm on rejection of manganese ion for different applied pressure at different pH such as 4, 5 and 6. The experimental runs were carried out for 20 min and samples were tested for every 5 min on AAS. We observed that the manganese ions rejection decrease when the concentration of feed increase at the every point of time during separation. This behavior is common. The increase in the concentration of solutions involves the increase of solute concentration near the membrane surface and forms a layer of concentration polarization. Another phenomenon is observed simultaneously with increase in feed concentration and it is the effect of osmotic pressure. Osmotic pressure is a function of the type and concentration of salts or organics contained in feed water. The increase in solute concentration in the retentate and in particular at the membrane wall with increased feed concentration leads to an increase in osmotic pressure. The increase in osmotic pressure of solution tends to flow more solvent in permeate side and decrease the rejection coefficient. These causes permeate concentration to decrease and hence rejection coefficient decreases with increased feed concentration. Similar results are found by Z.V.P. Murthy et al for Nickel ions and R. R. Bhutale et al for chromium ions [8, 11].







Fig. 3.2 % Rejection Vs feed concentrations (C_f) for different pH at P= 6 kg/cm²



Fig. 3.3 % Rejection Vs feed concentrations (C_f) for different pH at P= 7 kg/cm²



Fig. 3.4 % Rejection Vs feed concentrations (C_f) for different pH at P= 8 kg/cm²

3.2 Effect of applied Pressure on rejection

Fig. 3.5 to 3.7 shows the effect of pressure applied rating from 5 to 8 kg/cm² on rejection of manganese ion for different feed concentration. The results shows that the manganese ions rejection increase when the pressure increase at the every point of time during separation. This result obtained because the ion transport due to convection becomes important compared to diffusion. With increase in pressure maximum solvent passes through the membrane pores due to increased convective flux. This dilutes the concentration of solute in the permeate. A low diffusive transport of manganese ion through the membrane compared to convective transport is cause of low retention at low pressure. With increasing pressure, convective transport of solvent becomes more important. Thus the retention coefficient increases for increased pressure. Same results are observed by Z.V.P. Murthy et al for Nickel ions and R. R. Bhutale et al for chromium ions [8, 11].



Fig. 3.6 Rejection Vs Pressure for different pH at Cf = 40 ppm



Fig. 3.7 Rejection Vs Pressure for different pH at Cf = 60 ppm

3.3 Effect of pH on rejection

Fig. 3.8 to 3.11 shows the effect of pH from 4, 5 and 6 on rejection of manganese ion for different feed concentration at different pressure from 5 to 8 kg/cm². It is observed that the manganese ions rejection increase with the increase in feed solution pH upto pH 6. Higher pH of the feed solution contributed to transformation of soluble divalent Mn^{2+} ions to Mn^{4+} ions which were more stable and easily precipitated on membrane surfaces. The increase of feed solution pH has decreased the solubility of the divalent metallic ions (Mn^{2+}). Therefore, flocculation of metallic ions in the feed solution as the pH increased has resulted to higher rejection of the metal components from the synthetic wastewater. The same results are found by Norherdawati Kasim et al for Iron and Manganese ions [12].



Fig. 3.9 Rejection Vs pH for different feed concentrations at Pressure = 6 kg/cm^2



Fig. 3.10 Rejection Vs pH for different feed concentrations at Pressure = 7 kg/cm^2



Fig. 3.11 Rejection Vs pH for different feed concentrations at Pressure = 8 kg/cm^2

3.4 Effect of Pressure on Permeate flux

Fig. 3.12 to 3.14 shows the effect of applied pressure ranging from 5 to 8 kg/cm² on permeate flux for different time period, different pH 4, 5 & 6 and feed concentration. The permeate flux increased with increasing pressure. As pressure increases, convective transport and concentration polarization become more important. The result found that change in the permeate flux remains linear with increasing pressure, which indicates insignificant concentration polarization. Same results are observed by R. R. Bhutale et al for chromium ions [11].



Fig. 3.14 Permeate Flux Vs Pressure for different feed concentrations at pH = 6

3.5 % Rejection at Different Flux, pH and Feed Concentration

As shown in Fig. 3.15 to 3.17 for manganese as the permeate flux increased the rejection was found to increase with a linear relationship. Similar results are found by B.A.M. Al-Rashdi et al for Cd (II), As (III), Cu (II), Mn (II), Pb (II) ions [13].



IV. MEMBRANE TRANSPORT MODEL

4.1 Combined Film Theory Solution Diffusion Model

The working equations of the Combine Film theory solution-diffusion model [14] are as below:

$$Jv = A \left(\Delta P - \Delta \pi\right) \tag{1}$$

$$\mathbf{J}_{\mathrm{A}} = \left(\frac{\mathrm{DAMK}}{\delta}\right) (\mathbf{C}_{\mathrm{A2}} - \mathbf{C}_{\mathrm{A3}}) \tag{2}$$

$$R = \frac{(C_{A1} - C_{A3})}{C_{A2}}$$
(3)

Where A is the permeability parameter of the solvent and can be estimated from pure water permeability measurements and $(DAMK/\delta)$ is considered as a single parameter, namely the solute transport parameter. Eqn. (1) and (2) may be combined with Eq. (3), as illustrated by Pusch [14], to give

$$\frac{1}{R} = 1 + (\text{DAMK}/\delta) (1/\text{JV}) \tag{4}$$

Eq. (4) predicts that R approaches 1.0 for infinite permeate flux

This is not realistic for many solutes, which do not approach for perfect rejections at high permeate flux rate [15] Eq. (4) can be arranged to

$$\frac{R}{1-R} = \frac{\frac{J}{DAMK}}{\delta}$$
(5)

$$\frac{R_0}{(1-R_0)} = \left[\frac{R}{(1-R)}\right] \left[\exp\left(\frac{-J_v}{k}\right)\right]$$
(6)

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Now, Eq. (5) can be substituted into (6) to give

$$\frac{\text{Ro}}{1-\text{Ro}} = \left[\frac{\frac{Jv}{DAMK}}{\delta}\right] \left[\text{Exp}\left(-\frac{Jv}{k}\right)\right]$$
(7)

Now, taking Ln on both side of Eq. (7)

$$\ln\left(\frac{J_{V}(1-R_{0})}{R_{0}}\right) = \ln\left(\frac{D_{AM}K}{\delta}\right) + \frac{J_{V}}{k}$$
(8)

By plotting graph In [Jv(1-Ro)/Ro] vs. Jv the parameter (DAMK/ δ) and the mass transfer coefficient, k, for different concentration can be estimated graphically shown in Fig. 4.1, 4.2, 4.3 where ln(DAMK/ δ) is an intercept of straight line and k is the slope of line [8]. Calculated values of ln[Jv(1-Ro)/Ro] and Jv are given in below table.



Fig. 4.1 $\ln[Jv(1-Ro)/Ro]$ Vs flux for different feed concentrations at pH = 4



Fig. 4.3 $\ln[Jv(1-Ro)/Ro]$ Vs flux for different feed concentrations at pH = 6

Experimental data were fitted with CFSD model as shown in Fig. 4.1, 4.2, and 4.3 and the value of R^2 were founds to be above 0.90. $D_{AM}K/\delta$ and k is calculated from intercept and slope respectively for different concentration were given in (Table 4.1). These values were comparable with Latesh B. Chaudhari et. al for nickel ion removal by using Nanofiltration [8].

Table 4.1 Parameter estimated using data-fitting method for various models for manganese salt

	East Concentration (name)	CFSD model					
рп	reed Concentration (ppm)	D _{AM} K/δ (m/s)	k (m/s)				
pH 4	20 ppm	7.39 x 10 ⁻⁷	3.18 x 10 ⁻⁵				
	40 ppm	8.40 x 10 ⁻⁷	4.53 x 10 ⁻⁵				
	60 ppm	8.30 x 10 ⁻⁷	3.23 x 10 ⁻⁵				
рН 5	20 ppm	9.64 x 10 ⁻⁷	6.58 x 10 ⁻⁵				
	40 ppm	8.58 x 10 ⁻⁷	3.42 x 10 ⁻⁵				
	60 ppm	9.27 x 10 ⁻⁷	2.58 x 10 ⁻⁵				
рН б	20 ppm	1.41 x 10 ⁻⁷	1.11 x 10 ⁻⁵				
	40 ppm	2.69 x 10 ⁻⁷	2.94 x 10 ⁻⁵				
	60 ppm	4.26 x 10 ⁻⁷	2.57 x 10 ⁻⁵				
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From (table 4.1) observed that the values of $(DAMK/\delta)$ and mass transfer coefficient k can be estimated. Same results are observed by R. R. Bhutale et al for chromium ions [11].

рН	Feed Concentration (ppm)	20 ppm		40 ppm		60 ppm	
	Pressure	Roe	Roм	ROE	Roм	ROE	Roм
pH 4	5	0.9057	0.9271	0.8929	0.9084	0.8775	0.8992
	6	0.9125	0.9376	0.9007	0.9180	0.8860	0.9094
	7	0.9208	0.946	0.9104	0.9297	0.8923	0.9189
	8	0.9329	0.9607	0.9228	0.9407	0.9100	0.9359
рН 5	5	0.9175	0.9325	0.9072	0.9341	0.8893	0.9260
	6	0.9295	0.9432	0.9145	0.9476	0.8903	0.9289
	7	0.9403	0.9545	0.9175	0.9560	0.8997	0.9406
	8	0.9436	0.9605	0.9287	0.9653	0.9029	0.9434
рН б	5	0.9804	0.9814	0.9478	0.9575	0.9177	0.9314
	6	0.9809	0.9824	0.9650	0.9745	0.9243	0.9398
	7	0.9893	0.9906	0.9660	0.9764	0.9301	0.9513
	8	0.9903	0.9916	0.9688	0.9802	0.9514	0.9709

Table 4.2 Observed Rejection from experiment and modeling at different concentration and different pH

From (table 4.2) observed that the values of ROE and ROM were approximately equal. The plot of R_{OE} vs. R_{OM} for a feed concentration of 20 ppm, 40 ppm & 60 ppm at different pH 4 was depicted in Fig. 4.4; which shows the value of R^2 close to 1.



V. CONCLUSION

In the present work we studied that the influence of different operational variables like applied pressure, feed concentration and pH on the removal of manganese ions from the effluent by TFC NF-30 nano-filtration membrane. In the present study, Manganese ions removal was successfully undertaken using the Perma pilot scale membrane system. And the metal analysis was done on the atomic absorption spectrophotometer (model SL-173) according to standard techniques. The present works conclude that rejection coefficient for manganese ions increase with the increasing pressure (5 kg/cm², 6 kg/cm², 7 kg/cm² & 8 kg/cm²). As the feed concentration (20 ppm, 40 ppm & 60 ppm) of manganese ions increases at the constant flow rate the rejection coefficient decreases. The effect of the pH (4, 5 & 6) are studied and found that the rejection of the manganese ions increases with the increasing pH. The maximum rejection of the metal is found to be 99.03% for an initial feed concentration at 20 ppm. In this experiment, evaluation of experimental rejection (R_{OE}) or true rejection and modeling rejection (R_{OM}) or observed rejection for manganese ions estimated by CFSD model. In CFSD model, the experimental rejection and modeling rejection for manganese ions is nearly equal to +/- 0.3.

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