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NAFION 324 MEMBRANE for REMOVAL OF NICKEL (Ni) AND IRON (Fe)

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ABSTRACT

Nafion 324 membrane was investigated for the removal of Ni and Fe metal ions from their synthesized aqueous solutions. The different variables affecting the adsorption capacity of the membrane such as contact time, initial metal ion concentration in the feed solution, pH of the sorption medium and temperature of the solution were investigated on a batch sorption basis. The affinity of Nafion 324 membrane towards metal ions was found to increase in the sequence of Ni and Fe with adsorption equilibrium achieved after 20 min for all metal ions. Among all parameters,pH has the most significant effect on the adsorption capacity, particularly in the range of 2.9–5.5. The variation of temperature in the range of 30–60 °C was found to have no significant effect on the adsorption capacity. Nafion 324 membrane was found to have high stability combined with repeated regeneration ability and can be suggested for effective removal of metal ions such as of Ni and Fe from aqueous solutions.

Keywords: Wastewater, Nafion 324, Heavy Metals

I. INTRODUCTION

Heavy metal ions existing in aqueous waste streams of various industries such as metal plating, mining operations, battery manufacturing and tannery fabrication are posing serious risk to the environment. Leaking of these toxic heavy metals to the soil contaminates groundwater and surface water leading to serious impacts on the health of human and animals. Treatment of high volumes of wastewater containing low concentrations of heavy metals pollutants is becoming increasingly important as the discharge regulations become more stringent.

Various processes have been practiced for treatment of heavy metals contaminated waste streams over the past few decades. These methods include chemical precipitation, ion exchange, membrane filtration, carbon adsorption and co-precipitation/adsorption [1–3]. Among all, ion exchange is highly popular and has been widely practiced in industrial wastewater treatment processes [4, 5].

Most of ion exchange processes use selective chelating resins possess anion functional groups having affinity towards heavy metal ions [6].

Compared to ion chelating resins, ion exchange membranes are very promising alternative materials for metal adsorbence because they are not compressible, and can eliminate the internal diffusion limitations caused by resins used in a flow-by mode [7,8]. Of all ion exchange membranes, Nafion® has been known for its wide use in chemical industries for few decades including being a separator in electrolytic cells, a solid polymer electrolyte in fuel cells and batteries, and a cation exchange membrane in the electrodialytic manufacturing of chlorine and caustic soda [9, 10]. Therefore, Nafion membrane has been subjected to numerous studies ranging from materials characterization and modification to diversified applications. The application of Nafion membrane for the removal of metal ions from solutions has been explored with the removal of alkaline earth metals being reported in literature in various occasions [11–14]. However, there have been scarce investigations on the use of Nafion membranes for the removal of heavy metals from water and waste water [15].

The objective of this study is to investigate the potential use of Nafion 324 membrane for the removal of five toxic heavy metal ions i.e. Ni(II) and Fe(II) from aqueous solutions under various treatment parameters including contact time, initial concentration of the feed solution, pH of the sorption medium, and temperature of the solution.

II. EXPERIMENTAL

The study includes Nafion 324 cation exchange membrane in the heavy metal separation process. The effective area of the membrane is 500 cm^2 and with working electrolyte volume 4500 cm^3. The study will be conducted in batch and as well as in continuous mode. The cathode is stainless steel and anode is DSA (Dimensionally Stable Anode). The 32A/20V DC rectifier, DC tongue tester and Electronic multi meter will be used for the study.Metal salts: Nickel Nitrate (Merck) and Ferrous Nitrate(Merck were reagent grade and used without further purifications. Deionized water was used for dilution (18 MΩ,Millipore).

The metal solutions of Ni(II) and Fe(II), were prepared by dissolving the desired amount of respective metal salt in a deionized water in volumetric flasks followed by dilution to 1000 ml to obtain standard solutions containing concentrations in the range of 0.2–2.0 mg/l of ions for each metal.

The Nafion membrane was cut into strips (5 cm × 5 cm) which, were pretreated by boiling for 1 h in 1 M HNO_3 followed by boiling in a deionized water for 1 h. This process was repeated few times until the membrane brown color was completely removed. The membrane was dried in a vacuum oven at 80 °C for 16 h before it was removed quickly and stored under a desiccator over a fresh silica gel at ambient temperature.

III. RESULTS AND DISCUSSIONS

Nafion 324, a commercial ionomer membrane, was used to remove heavy metal ions from aqueous solutions in this study. Nafion 324 membrane is a tetrafluoroethylene-perfluoro-3,6-dioxa-4-methyl-7-octene sulfonic acid copolymer synthesized by the copolymerization of tetrafluoroethylene (TFE) and a derivative of a perfluoro (alkyl vinyl ether) with sulfonyl acid fluoride through a complex chemistry. Nafion outstanding properties stem from incorporating perfluorovinyl ether groups terminated with sulfonic acid groups onto a tetrafluoroethylene backbone. Such unique molecular architecture of Nafion membrane led to a formation of a hydrophilic/hydrophobic phase separation into the ionic-cluster phases embedded in a perfluorocarbon matrix .

This made its microstructure and transport characteristics to be affected by the water content . In the present study, the physico-chemical properties of Nafion324 membrane samples were determined after activating them with a standard pretreatment procedure and the obtained data is presented in Table 1.

3.1. Effct of contact time and sorption kinetics

The effect of contact time on the metal removal was investigated to determine the optimum contact time for the adsorption of Ni(II) and Fe(II) in Nafion 324 membrane. Fig. 1 shows timecourses of adsorption ofNi(II) and Fe(II) in Nafion 324 membranes. Rapid adsorption kinetics can be obviously seen within the first 15 min and the adsorption equilibria of both metal ions were attained within 20 min. Therefore, the optimum equilibration time for other experiments of other parameters was set at 30 min. The maximum values of metal adsorption capacities in Nafion 324 were found to be 63 and 72 mg/g for Ni (II) and Fe(II) respectively.

Since, kinetics in a chelating polymer are not only relaying on the availability of chelating functional groups but also on their accessibility by counter ions without a steric hindrance, which is greatly determined by the polymeric matrices characteristics, the rapid metal adsorption kinetics in Nafion 324 can be attributed to the strongly acidic and the hydrophilic nature of the membrane caused by the presence of sulfonic acid groups with their hydration spheres, which are responsible for interaction with the metal ions (counterions) by electrostatic attraction. The high capacity of Fe(II) removal is hard to be explained at this stage as adsorption capacity is well known to be controlled by several parameters, such as structural properties of the sorbent (size, surface area, porosity), metal ion properties (e.g. hydrated ionic radius and electronegativity), initial concentration of metal ions, pH, temperature, chelate formation rate or presence of the competing ions .

3.2. Effect of initial feed concentration

The adsorption capacity of ions was investigated in correlation with the variation in the initial metal ion concentrations in the range of 0.3 to 2.0 mg/l and the obtained data was plotted in Fig. 2. The adsorption capacity for both metal ions was found to increase with the increase in metal ion concentration in the feed and level off at a concentration of 1.0 mg/l. For instance, Fe(II) showed the highest metal adsorption (62 mg/g) unlike Ni(II) which recorded the lowest value (59.5 mg/g). This behavior can be attributed to the fact that cation affinity for a Nafion 324 membrane is mainly due to the electrostatic interaction between the hydrophilic negatively charged Nitric acid groups and the counter metal ions in the solution. The higher the valance of the counter ions, the larger is the electrostatic attraction. Therefore, Nafion 324 membrane prefers counter ions of higher valence such as Ni(II) over Fe(II). However, larger counter ions most likely produce ionic clusters of lower water content since the water content of ionic cluster in membrane decreases as the size of the counter ions increases . It may be concluded that the metal ion adsorption in Nafion 324 membrane is highly dependent on the initial concentration within the range of 0.3–1.0 mg/l. Moreover, the order of the affinity of the metal ion towards the membrane is in the sequence of Fe(II)>Ni(II).

Table 2 presents the efficiencies of Ni(II) and Fe(II) ions removal by Nafion 324 membrane. The efficiency of heavy metal removal is defined as the percent of metal uptake was found to increase with the increase in the initial heavy metal concentration in the range of 0.3–1.00 mg/l. All metal ions recorded their highest metal uptake at a concentration of 1.0 mg/l with the maximum recovery obtained for Ni(II) (89 %) and Fe(II)(96.98 %). The decreasing trend in the metal uptake with the increase in initial metal ion concentration in the solution is most likely to be caused by a decrease in the affinity of Nitrate functional groups with increasing the degree of site occupation, which followed the early and easy access of the binding sites at low metal concentration. Such trend also suggests an increase in the equilibrium constant with the decrease in the metal affinity.These results suggest that Nafion 324 is most effective for removal of Ni(II) and Fe(II) at initial feed concentrations in the range of 0.5 to 1.0 mg/l.

3.3. Effect of pH

The effect of pH on the removal capacities of heavy metal ions was examined in the range of 2.9–5.5 by varying the initial pH of the sorption medium at a constant contact time (20 min) and the obtained data is plotted in Fig. 3. As can be seen, the metal adsorption increases with the increase in pH in the range of 2.9-5.5 for both metal ions beyond which it tends to level off. Therefore, the optimum pH of sorption medium for the experimental investigation with other parameters was set at 5.5 for both heavy metals to ensure achieving maximum metal removal. The low removal of all metal ions at low pH can be ascribed to competitive adsorption of hydronium (H_3^+O) ions and metal ions for the same active adsorption sites. As the pH increases, the adsorption surface becomes less positive and therefore electrostatic attraction between the metal ions and the functional groups in membrane surface is likely to be increased. In addition, other parameters taking part in metal uptake process i.e. ion exchange capacity together with the nature of the active sites in the membrane are also pH dependent. From Fig. 3, it can be noticed that Fe(II) recorded the highest adsorption capacity whereas Ni(II) showed the lowest value.

3.4. Effect of temperature

Fig. 6 shows the relationship between the metal adsorption capacity of Nafion 324 membrane and the temperature of the sorption medium. It can be obviously seen that the variation of the temperature in range of 30–60 °C has no significant effect on the metal adsorption as indicated by very minor changes in the adsorption capacity with all tested metal ions. This suggests that temperature has a little role to play in the adsorption of Ni(II) and Fe(II) ions in Nafion 324 membrane.

3.5. Removal of metal ions and reusability

To qualify a membrane for practical use, the utilized membranes have to be chemically stable and reusable. Nafion 324 membrane could be regenerated by treatment with 0.1 M HNO_3 for 15 h. The desorbed Nafion 324 membranes were found to be able to adsorb almost the same amount of all metal ions even after 5 cycles conducted in this work as shown in data presented in Table 3. This clearly shows that Nafion 324 membrane can be effectively and economically used for the removal of heavy metal ions from water solutions.

IV. CONCLUSIONS

Nafion 324 membranes were used to investigate the removal of Ni(II) and Fe(II) metal ions from synthesized aqueous solution on batch process basis. The ion exchange behaviors of these 2 metals under the effect of contact time, initial metal ion concentration in the feed solution, pH of the sorption medium and temperature of the solution were studied. Based on this study, the following conclusion can be drawn:

1. The order of the affinity of the heavy metal ions towards Nafion 324 membrane was found to be in the sequence of Fe(II)>Ni(II).
2. The Nafion 324 membrane was found to have a fast kinetics towards all metal ions as indicated by the equilibration time which was found to be 20 min of contact time.
3. The maximum values of metal adsorption in Nafion 324 were found to be 62, 75 mg/g for Ni(II) and Fe(II) respectively.
4. The metal ion adsorption in Nafion 324 membrane is highly dependent on the initial concentration within the investigated range.
5. The optimum pH of sorption medium to achieve maximum metal adsorption was found to be 5.5 for both investigated metal ions.
6. The removal of Ni(II) and Fe(II) ions in Nafion 324 is independent of temperature of the medium solution.

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Table 1: Physical Properties of Nafion 324 membrane

Properties	Values
Thickness(µm)	175
Water uptakes(%)	40
Ion Exchange Capacity(meq/g)	0.92
Equivalent Weight(g/meq)	1090
Ionc. Conductivity (S/cm)	0.11

Table 2 : The efficiencies of Ni and Fe ions removal by Nafion 324 membrane

Initial Concentration (mg/l)	Metal uptake (%)	
	Ni	Fe
1.0	85.4	95.11
0.8	80.2	90.45
0.6	86.9	96.98
0.4	89.00	95.09
0.2	86.5	95.6

Table 3 : The reusability of Nafion 324 for removal of Ni and Fe heavy metals ions

Cycles	Metal uptake (%)	
	Ni	Fe
1	59.50	62.00
2	57.80	62.00
3	57.50	61.9
4	59.50	61.8
5	55.10	62.00

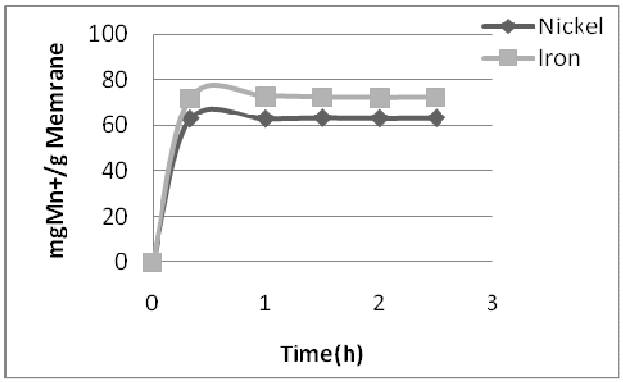

Fig. 1: Time required for the adsorption of Metal Ions in Nafion 324 membrane

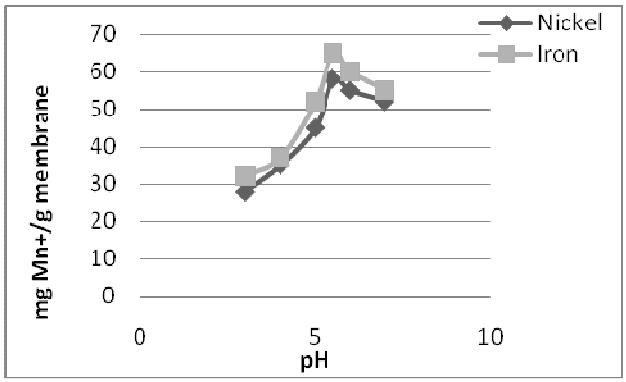

Fig. 3 : The effect of pH on removal capacity of Metal ions in Nafion 324

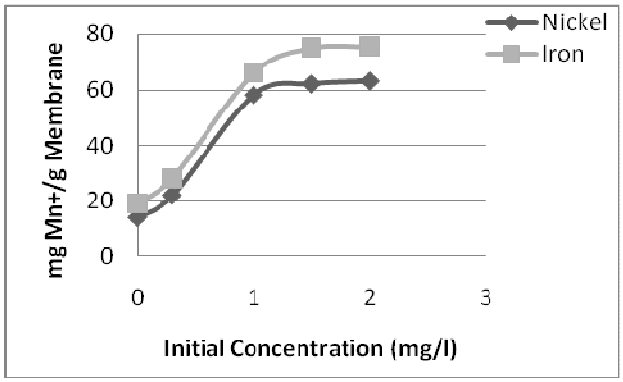

Fig. 2 : The effect of Initial Concentration on removal capacity of Metal ions in Nafion 324

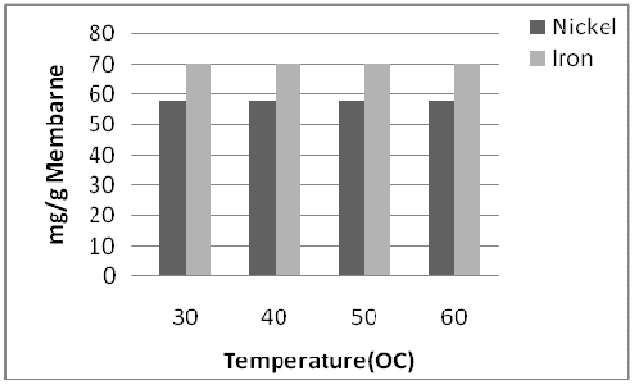

Fig. 4 : The effect of Temperature on removal capacity of Metal ions in Nafion 324