COMPARATIVE ADSORPTION OF MAJOR CATIONS FROM BRINES BYION EXCHANGE PROCESSING USING AMBERLITE 252-RFH RESINS AND AMIDOXIME FIBRES

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ABSTRACT

The Amberlite 252 RFH resin and poly(amidoxime) fibre containing the amidoxime group were used to investigate the adsorption of Na(I) in brine waste water as a function of contact time, metal ion concentration, and initial solution pH. Brines are problematic effluents created by water desalination processes, oil and gas production, coal and gold mine drainage and evaporative cooling in power stations and process industries. The poly(amidoxime) was synthesized by conversion of the nitrile groups of polyacrylonitrile (PAN) copolymers into amidoxime groups by a reaction with hydroxylamine under alkaline conditions. Characterization was carried out in terms of elemental composition, surface functionality, FT-IR, exchange capacity, and the effects of pH. Amberlite resin showed a higher metal ion adsorption capacity for the Na(I) ion (25.03 mg/g) than poly(amidoxime) fibre (16.40 mg/g) due to its higher exchange capacity. The adsorption capacity of Ca(II), Mg(II), and Na(I) in the adsorbent increased with an increase in poly(amidoxime) alkali treatment reaction time. The uptake of the alkali or alkaline earth metals was shown to be independent of pH, hence the amidoxime functionalized fibres do not exhibit any pH dependent selectivity for Na(I) ions and Amberlite being a strong acid cation exchange resin is not affected by pH. The kinetics of the fibrecation ion interaction, however, was found to be sufficiently rapid reaching equilibrium in 10-20 mins as compared to the resin which reaches equilibrium in 30-40 min. The advantage of a faster rate of equilibrium is achieved because of the fibrous configuration of the polymer backbone which allows for more rapid kinetics than resin bead type backbones.

Keywords: Acrylonitrile; Adsorption; Amberlite; Amidoxime; Fibre adsorbent; Brine; Ion exchange capacity;

1. INTRODUCTION

Brines are problematic effluents created by water desalination processes, oil and gas production, coal and gold mine drainage and evaporative cooling in power stations and process industries. Such brines are usually mixtures of many salts and disposal is environmentally problematic and costly (Mohamed et al., 2005).

There are many different methods for treating industrial wastewaters and current methods include precipitation, coagulation/flotation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, ion exchange, biological processes and chemical reactions (Leinonen and Lehto, 2000). Amongst these, ion exchange process has been developed as a major option for separation and purification of metals from different dilute aqueous solutions (<0.5g/L) (Kentish, 2001) where precipitation is not efficient. The reversible nature of ion exchange and sorption processes make them particularly suited for treating industrial wastewaters. Commercially available ion exchange resins show high performances but generally poor selectivity towards different metal ions and slow kinetics due to the hydrophobic character of the polymeric backbone (Sahni, S.K., 1984). An appealing alternative method is the use of fibres or modified fibres, including activated polyethylene terephthalate, carbon fibre, cotton fibre and polymer fibre (polyester, polypropylene, and polyacrylonitrile, polystyrene), that have been used to adsorb metal ions and/or separation of metal from aqueous solutions (Liu R., Li Y., Tang, H., 2002).

Fibres, which have larger specific surface areas and high adsorption rates have attracted great attention in metals ion removal from waste water in recent years. Among them, poly(acrylonitrile) (PAN) based fibrous adsorbents containing amidoxime groups have been demonstrated in the separation or adsorption of metals from aqueous solutions due to their higher adsorption capacity, and rapid adsorption rate (Katoh et al., 1982b). The chelate-type adsorbent with amidoxime group was prepared by free radical polymerization of acrylonitrile (AN=99.5%) and methacrylic acid (MA=0.5%) monomers and the cyano groups of acrylonitrile on resulting poly(acrylonitrile) were converted to the amidoxime groups (-C(=NOH)NH_2). They have a high tendency to form strong complexes with a wide variety of heavy metal ions such as As(III), Al(III), Cu(II), Fe(III), Co (II), Ca(II), Zn (II) and radioactive metals such as Uranium (Hirotsu et al. 1986). Kabay and Egawa (1994) demonstrated that polymeric amidoxime-resins rapidly take up uranium from seawater and that such resins have a stronger preference for uranium and several other metal ions than for alkali and alkaline-earth metal ions. The adsorption ability is greatly influenced by alkaline treatment of the resin; it increases the cation exchange capacity and enhances the uptake of uranyl ions and the formation of the uranium complexes (Nilchi et al., 2008). A similar resin with amidoxime functional group was used by Egawa and Harada (1979) for recovery of uranium from seawater and recovery of 80% uranium in seawater was achieved. The resin has been used for the separation and simultaneous concentration of Fe^{3+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} from sea water and pond water (Colella et al., 1980). The adsorption performance of the amidoxime resins is affected by pH thus being selective for particular metals at particular pHs levels (Shiraishi et al., 2003; Lutfor et al., 2000).

In this study, PAN fibres were functionalized in a 3% hydroxylamine solution under alkaline conditions and the performance comparison between Amberlite 252 RFH resin and poly(amidoxime) fibres in sodium ion adsorption was studied. The poly(amidoxime) fibres were characterized by FT-IR and its surface morphology before and after adsorption were examined through SEM images. Contact time, pH of the initial solution, adsorbent dosage, equilibrium isotherms were studied to understand the adsorption phenomena, loading capacity and adsorption kinetics of sodium from aqueous solution.

2. EXPERIMENTAL

Material

The cationic resin, Amberlite 252 RFH (styrene divinylbenzene copolymer with an active group -SO_3H) supplied by Rohm & Haas Co. was employed without any further purification. As per the standard procedure, the resin was activated by immersing it in 1mol/L HCl for 24 hrs. The resin was then washed several times by de-ionised water to remove all chloride content. Then the resin was dried at a temperature of 45°C. On the other hand, the poly(amidoxime) fibres were obtained from the commercially available synthetic polyacrylonitrile fibre (99.9 % acrylonitrile and 0.1 % vinyl acetate) PAN by the one step reaction with 3 % hydroxylamine in methanol at 70 °C.

All synthetic solutions were prepared from analytical grade chemicals and ultra pure water was used as a solvent. Stock solutions of 1000 mg/L of sodium chloride (NaCl) solution were prepared by dissolving 58.44g of NaCl in 1 litre of ultra pure water. The working solutions containing 100, 200 and 230 mg/L sodium ions were prepared by appropriate dilution of the stock solution immediately prior to their use.

Instrumentation

FT-IR spectra were recorded using a Perkin-Elmer spectrometer with a specially designed compartment to cater for solid samples. A scanning electron microscope (Hitachi X650, Scanning Electron Micro analyzer) at 10-20 kV was used to examine the surface morphology of PAN and poly(amidoxime) surfaces before and after functionalization. The amounts of sodium ions were determined using an Atomic Absorption Spectrophotometer (AAS). A GFL model thermostated water bath shaker was used for shaking the solutions at desired temperatures. The pH was measured using a glass electrode (micro ohm pH meter). Its calibration was carried out using standardized Merck buffer solutions (pH 4 and pH 7).

Preparation of Amidoxime Fibres

The amidoxime fibres were obtained by treatment of nitrile groups with hydroxylamine under reflux, at 70°C, giving rise to a selective functional group (Egawa *et al.*, 1992as shown in the figure 1.

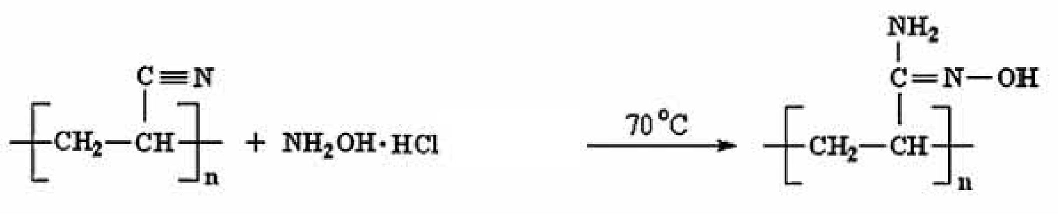


Figure 1.Reaction of hydroxylamine hydrochloride with PAN nitrile group.

About 10 ± 1 g of Polyacrylonitrile (PAN) fibre was placed into in the flask and 3 % hydroxylamine solution was added to the flask and the reaction was carried out at 70ºC for 2 hrs shaking gradually. After completion of the reaction, the fibre was separated from the solution by filtration and washed several times with deionized water until no further NH2OH remained in the solution. The fibre was characterized by the following techniques: FT-IR infrared spectrum, anion and cation capacity measurements, surface functionality, and the effects of pH.

Treatment of Functionalized Fibres with NaOH Solution

Dried, functionalized fibres were treated with NaOH solution prior to using them for adsorption experiments to determine their performance in alkaline conditions. For this, 3 ± 0.1 g of fibre was treated with 200 mL of 1.0 mol / L NaOH solution at 30^{o}C in a water bath, shaking for 24 hr. The treated fibres were washed with deionized water until no alkalinity remained in the washings (checked with phenolphthalein). Thus treated fibres were washed and dried prior to use in adsorption experiments.

Adsorption Kinetics and Equilibrium Isotherms of Metals Ions onto Aopan Fibre

The batch experiments for the adsorption of calcium, magnesium and sodium were carried out in a conical flask using a thermostated water bath shaker at 30°C for 24 hrs. Dried samples of both resins and fibres (0.1g) were stirred in a 50mL synthetic metal ion solution (100 ppm) by batch technique and equilibrium isotherms were also studied as a function of the concentration of synthetic metal ion solution at equilibrium time (24 hrs) and at 20°C. The concentration of the metal ions in solution was determined by AA spectrometer and the amount adsorbed (mg/g) was calculated as follows:

$$q(mg/g) = \frac{(C_o - C_e)V}{M}$$

$$Adsorption\ (\%) = \frac{(C_o - C_e)\times 100}{C_o}$$

where q is the amount adsorbed (mg/g), Co is the initial metal ion concentration, Ce is the final metal ion concentration (mg/L), V is the solution volume (L) and M is the amount of adsorbent used (g) (Sang et al., 2008).

3. RESULTS AND DISCUSSION

FT-IR Study

Fig. 2, shows the FT-IR spectra of the PAN, poly(amidoxime) and alkali-treated poly(amidoxime) fibres. The key absorption lines in the FT-IR measurements are those due to C≡N oscillation at wavenumber of 2242cm^{-1} in the cyano groups, N-H oscillation at 3100 - 3400cm^{-1}, in the polyacrylonitrile fibre. The absorptions due to C=N oscillation at 1657cm^{-1} and N-O oscillation at 909cm^{-1} were observed in the FT-IR spectra of poly(amidoxime) fibre. The relative decrease in the intensity of the characteristic C≡N bonds in PAN is a function of functionalization reaction time. Accordingly, the C≡N groups are expected to be replaced with H_2N-C=NOH at the end of the reaction, hence the nitrile group in the amidoxime functionality was indicated by the reduction in absorption of the C≡N groups at 2242cm^{-1}, appearance of C=N stretching at 1657cm^{-1} and amide band of N-H at 1450cm^{-1}, respectively. These results were in agreement with that in the literature (Egawa et al., 1992).

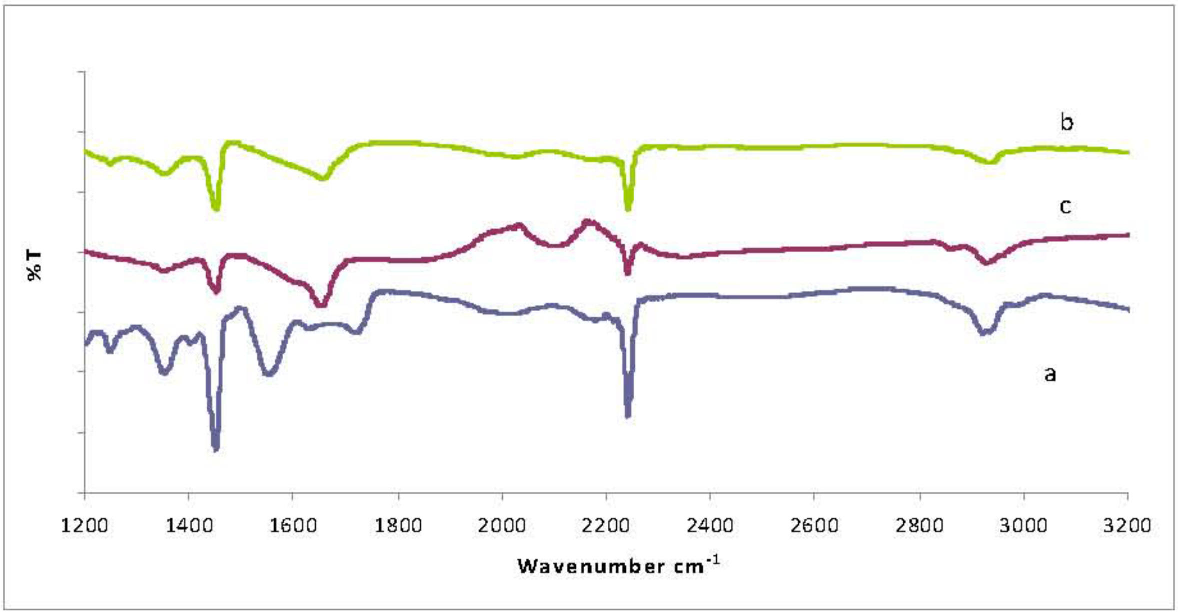
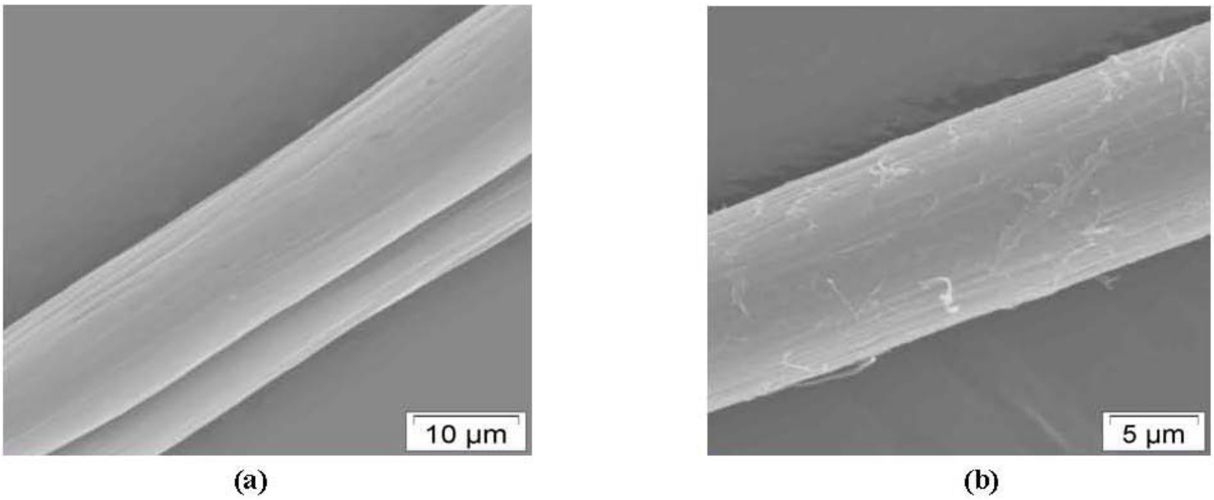


Figure 2. The FT-IR spectra of (a) polyacrylonitrile and (b) poly(amidoxime) and (c) alkali treated poly(amidoxime).

Morphologies of Pan and Aopan Fibres

A scanning electron microscope (Hitachi X650, Scanning Electron Micro analyzer) at 10-20 kV was used to examine the surface morphology of PAN and poly(amidoxime) fibre surfaces before and after functionalization and it showed that the surfaces of the PAN before the functionalization was relatively smooth and uniform, as shown in Fig. 3. After functionalization, the fibre surface was composed of etched strips and stops, became rough and corroded, indicating that the functionalization reaction occurred on the surface of the PAN fibre.



(a) (b)

Figure 3. SEM images showing the surface morphologies of (a) Polyacrylonitrile, PAN and (b) Functionalized Polyacrylonitrile, poly(amidoxime) before and after functionalization.

Exchange Capacity

Table 1 shows the exchange capacities with standard deviations of poly(amidoxime) fibres and the Amberlite resin. The capacity of the adsorbent is one of the factors which determine how large a quantity of adsorbent will be needed for quantitative removal of a specific metal ion from solution. Here, the anion exchange capacity corresponds to the amount of amidoxime groups introduced and the cation exchange capacity represents the amounts of acidic sites (mainly carboxylic groups) formed by hydrolysis of nitrile and/or amidoxime group during the functionalization and/or alkali-treatment process. The alkali-treatment of RNH partly converts amidoxime groups into more hydrophilic carboxylic groups, enhancing the swelling of RNH greatly and the anion exchange capacity decreased observed by Egawa et al. (1992. The increased adsorption ability of the resulting fibre after alkaline treating was attributed to changes in the physical and chemical structures of the fibre in alkaline medium, which is consistent with the results reported in the literature (Kabay et al., 1993

Table 1: Cationic and anionic exchange capacities of poly(amidoxime) fibre and cationic exchange capacity of amberlite 252 RFH resin

	EXCHANGE CAPACITY	
	Anionic (meq/g)	**Cationic (meq/g)**
Amidoxime Fibres	1.96 (± 0.039)	1.36 (± 0.062)
PAN fibres	1.82 (± 0.129)	1.27 (± 0.153)
Amberlite® 252 RFH		3.94 (± 0.046)

Effect of Adsorbent Dosage

The effect of resin dosage on adsorption of sodium from aqueous feed containing 230 mg/L metal ion concentration was studied keeping retention time for mixing at 24 hrs. Resin dose was varied from 0.1 to 1.0g (2.0-20.0g resin/L of aqueous solution) in 50mL solution. The results presented in Fig. 4 indicate the increase in adsorption of metal ions with increase in resin dose as available sites or surface area increases with higher quantity of resin. An increase in surface of resin automatically enhances the rate of adsorption reaction. The total adsorption of metal ions was found with resin dose of 8.0g resin/L. Further increase in resin has shown negligible effect towards increase in percentage adsorption of metal ions from the solution.

In Fig. 5 the results show total adsorption of sodium was found with fibre dose of 2.0g fibre/L. The fibre dose was varied from 0.1 to 0.5g in 50 mL solution.

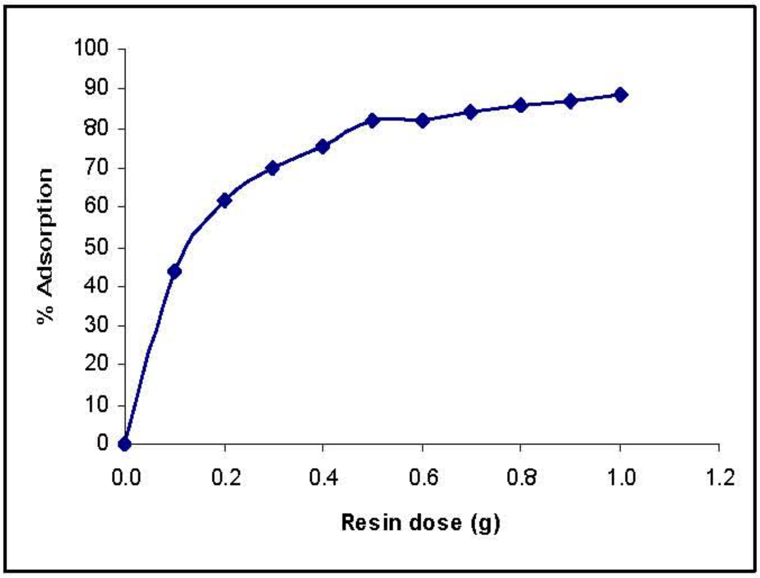


Figure 4. % Adsorption of sodium ions with Amberlite resins as a function of resin mass.
(Metal ion concentration, 230 mg/L; temperature, 30°C; volume, 50mL; contact time, 24 hrs).

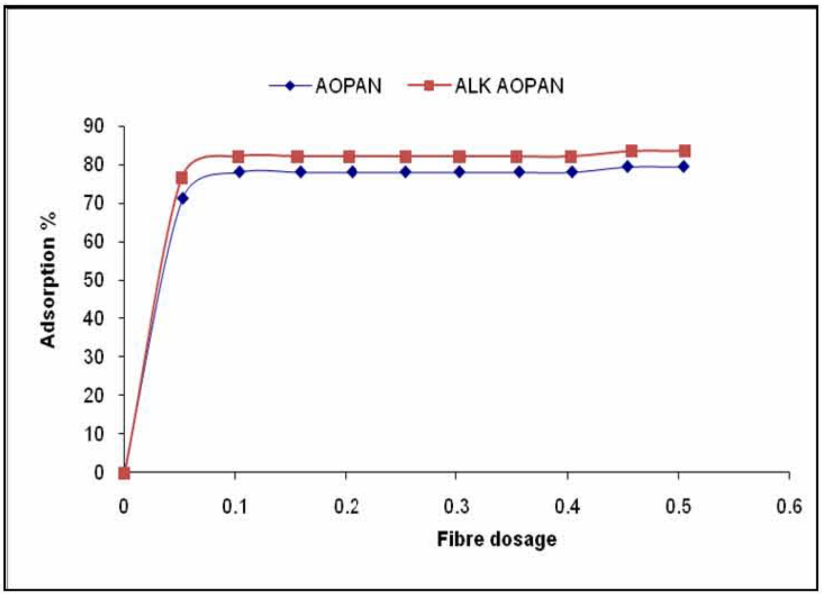


Figure 5. % Effect of fibre dose on the adsorption of sodium ions by poly(amidoxime) and alkali treated poly(amidoxime) fibres. (Metal ion concentration, 200 mg/L; temperature, 30°C; volume, 50 mL; contact time, 24 hrs).

Effect of Ph

The studies were made to see the effect of pH on the adsorption of sodium from the aqueous feed solutions containing sodium 200 ppm with a fixed quantity of poly(amidoxime) fibres. The pH of the solutions was adjusted by the addition of phosphate buffer solutions. The results presented in Fig. 6 shows that the adsorption of both sodium increases very slightly with the increase in equilibrium pH of the solution. The sorption of sodium ions on the poly(amidoxime) fibre was studied at seven different pH values (pH 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0). The maximum adsorption (about 38 mg/g fibre) for Na(I) were found at pH 5. The sorption of Na(I) ions was very slightly dependent upon pH and the data indicates that there is a 14 mg/g fibre difference in adsorption, between the low and high pH values, in the metal ion adsorption capacities. This indicates that the fibre does not form strong complexes with sodium ions hence the adsorption reaction is ion exchange based reaction rather than chelating. The ability of a metal ion to compete favourably over another metal for an available complexation site at various pH levels can be used as a measure of the apparent selectivity of the fibre for that specific metal ion.

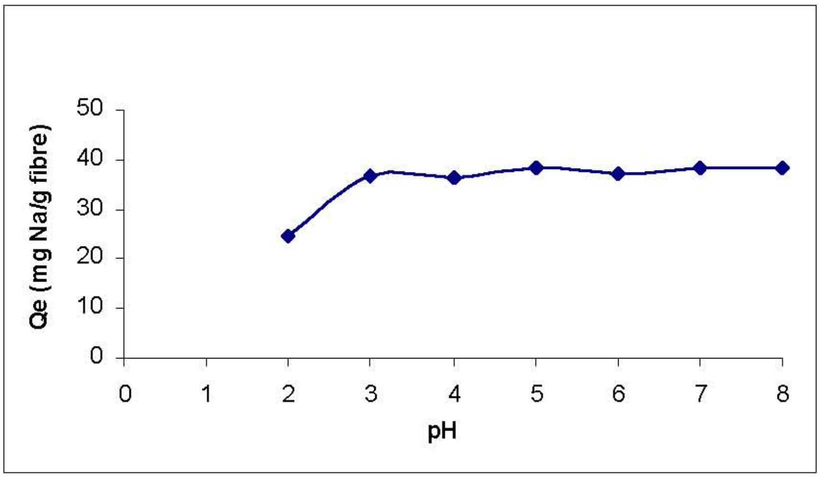


Figure 6. % Effect of pH on the adsorption of sodium ions by poly(amidoxime) fibres.
(Metal ion concentration, 200 ppm; temperature, 30°C; volume, 50mL; contact time, 24 hrs).

Effect of NA+ Concentration

The equilibrium data obtained from the experiment for sodium adsorption on poly(amidoxime) fibre was analyzed using the Langmuir and Freundlich equation (Deng, S. 2003). The Langmuir equation which is valid for monolayer sorption onto a surface with a finite number of identical sites is given by the following equation:

$$q_{eq} = \frac{Q_o b C_{eq}}{1 + b C_{eq}}$$

$$\left[\frac{1}{q_{eq}} = \frac{1}{Q_o} + \frac{1}{b Q_o C_{eq}} \right]$$

where q_{eq} is the amount adsorbed (mg/g), C_{eq} is the equilibrium concentration of the adsorbate (mg/L), and parameters Q_o and b are Langmuir constants related to maximum adsorption capacity (mg/g) (monolayer capacity) and bonding energy of adsorption (L/mg), respectively, which are functions of the characteristics of the system as well as time.

The Freundlich model assumes neither homogeneous site energies nor limited levels of sorption instead it assumes that the uptake or adsorption of metal ions occurs on a heterogeneous surface by monolayer adsorption. The model is described by the following equation:

$$q_{eq} = K_F C_{eq}^{1/n}$$

$$\left[\ln q_{eq} = \ln K_F + \frac{1}{n} \ln C_{eq} \right]$$

Fig. 7 illustrates the equilibrium adsorption amounts at 24 hrs under various equilibrium concentrations. It was found that the adsorption of Na(I) increased initially with increase in concentration and then levelled off.

The initial increase in metal adsorption might be due to many available exchange site on the poly(amidoxime) fibres. The plots '$1/q_{eq}$ versus $1/C_{eq}$' and '$\ln q_{eq}$ versus $\ln C_{eq}$' to validate the Langmuir and Freundlich isotherms respectively for the aqueous feed containing sodium were evaluated and data presented in Table 2.

As shown in Fig. 7, the amount of sodium adsorbed at adsorption equilibrium on the resin was more than that on the amidoxime fibres. When the sodium ion concentration was 100 mg/L, the sodium amount adsorbed by resin reached 22.80 mg/L, as compared to 15.43 mg/L by the amidoxime fibres. The plots for the Langmuir isotherm are presented in Fig. 8. The least square values of correlation coefficient (R^2) were obtained to compare the suitability of the adsorption process. The constants for each isotherms were also calculated. Data presented in Table 2 showed that the Langmuir equilibrium isotherm was found to fit the experimental data better than the Freundlich isotherm equation.

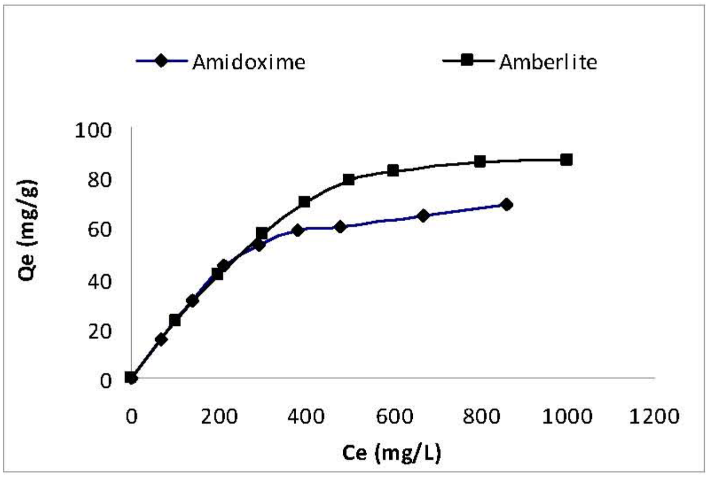


Figure 7. Adsorption isotherm plot of sodium on the poly(amidoxime) fibres and Amberlite 252 resin.

Table 2. Constants and correlation coefficients of Langmuir and Freundlich isotherms for adsorption of sodium

	Concentration	Freundlich Isotherm			Langmuir Isotherm		
	ppm	n	K_f	R^2	q_m	K_1	R^2
Amberlite	100 – 1000	1.4575	1.5203	0.9931	142.8571	0.003516	0.9991
Amidoxime	100 - 1000	1.3344	1.7452	0.9725	227.2727	0.001065	0.9932

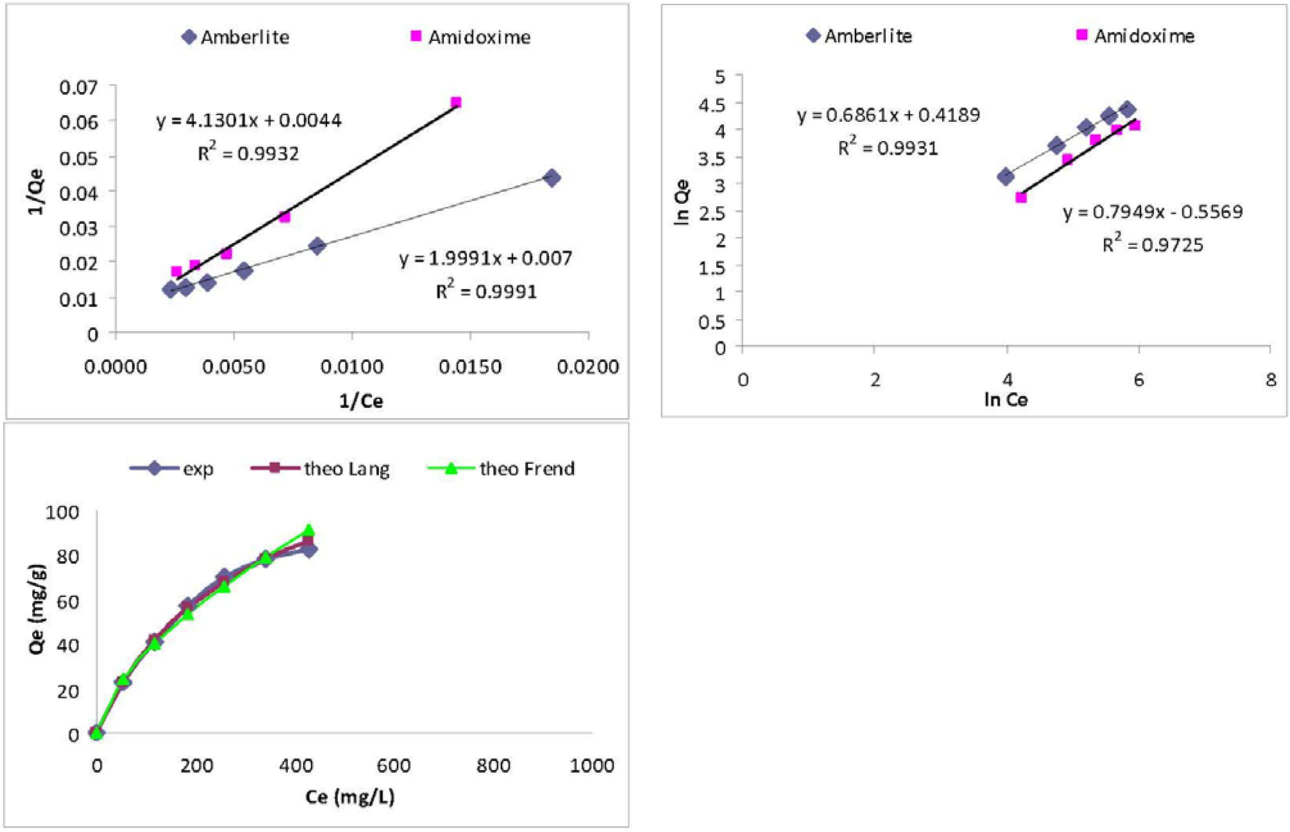


Figure 8. (a) Langmuir isotherm, (b) Freundlich isotherm and (c) theoretical & experimental plots for the adsorption of sodium by poly(amidoxime) fibres and Amberlite 252 resin.

Adsorption Kinetics

Adsorption kinetics was studied by adding 0.1 g of the Amberlite 252 resin and Amidoxime fibres to 50 mL of sodium chloride solution with a sodium concentration of 100 mg/L into separate flasks. As shown in Fig. 9, the adsorption of sodium ions onto the Amidoxime fibres was very fast and the adsorption equilibrium could be reached in about 10-20 minutes as compared to the Amberlite resins with equilibrium being reached in 30-40 mins. This phenomenon can be attributed to the large surface area of and possibly the high density of adsorption site on the fibres. Therefore sodium adsorption can be controlled mainly by the diffusion of sodium ions from the bulk solution onto the surface of the fibres. Adsorption of metal ion from aqueous solution onto many conventional granular adsorbents, such as activated carbon and resin, has been reported to be a long process (adsorption equilibrium reached in several hours or more) because the kinetics of metal ion adsorption onto those porous adsorbents is mainly controlled by an inner surface diffusion process which is generally much slower than the bulk diffusion of metal ions in solution (Sánchez, J. M. 2001)

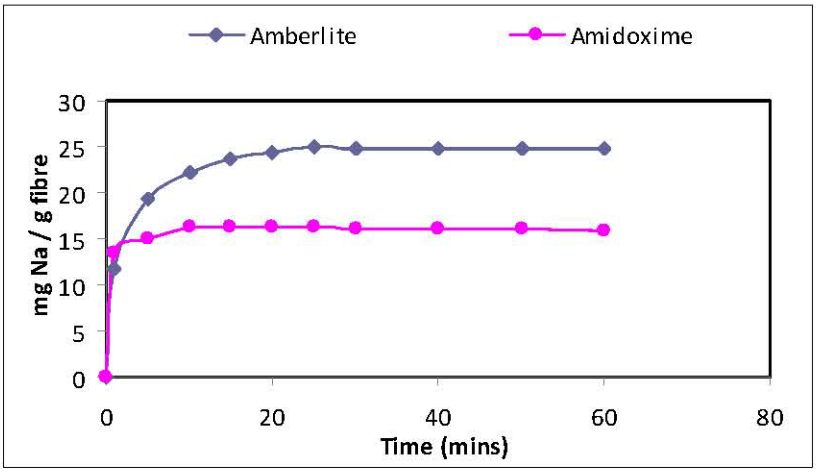


Figure 9. Kinetics of sodium ion adsorption onto Amberlite 252 resin and poly(amidoxime) fibres.

4. CONCLUSIONS

The surface of polyacrylonitrile fibre was modified through a simple functionalization process in a 3% hydroxylamine solution under alkaline conditions. The poly(amidoxime) fibre possessed, $-H_2NC=NOH-$, on the surface, which is responsible for the increase in the exchange capacity of the poly(amidoxime) fibre was confirmed by the FT-IR and the exchange capacity results. The pH of the initial solution does not play a major role in the amount of sodium ion adsorption onto the poly(amidoxime) fibre, instead this shows that the sodium ion fibre interaction is an ion exchange phenomenon based on the concentration effect and the charge on the metal ions. Bench scale studies carried out in shake out flask showed that poly(amidoxime) fibres reach equilibrium in 15 mins. Adsorption capacities of 25.03 mg Na/g fibre (51.5% adsorption) and 16.40 mg Na/g fibre (33.76% adsorption) were achieved for Amberlite resin and poly(amidoxime) fibre respectively. The data for adsorption of sodium was found to be conforming to the Langmuir isotherm equation for both Amberlite resin and poly(amidoxime) fibres indicating that adsorption took place at specific homogeneous sites within the adsorbent and once the metal-ion occupied it, then no further adsorption occurred at that location (monolayer adsorption).

5. REFERENCES

Colella, M. B.; Siggia, S.; Barnes, R. M. Analytical Chemistry, 1980, 52, 967-972.

Colella, M. B.; Siggia, S.; Barnes, R. M. Poly(acrylamidoxime) resin for the determination of trace metals in natural waters, Analytical Chemistry, 1980, 52, 2347-2350.

Egawa, H., Kabay, N., T. Shuto, T., and Jyo, A., Recovery of Uranium from Seawater. XII. Preparation and Characterization of lightly Crosslinked Highly Porous Chelating Resins Containing amidoxime Groups, Journal of Applied Polymer Science, 1992, 46, 129.

Egawa, H., Nakayama, M., Recovery of Uranium From Seawater. X. Pore Structure And Uranium Adsorption Of Macroreticular Chelating Resin Containing Amidoxime Groups, Journal of Applied Polymer Science, 1994, 45, 837-841.

Hirotsu, T., Katoh, S., Sugaska, K., Seno, M., Itagaki, T., Binding Properties of a Polymer Having Amidoxime Groups with Protons and Metal Ions, Separation Science technology, 1986, 21, 1101.

Kabay, N., and Egawa, H., Kinetic Behaviour of Lightly Crosslinked Chelating Resins Containing Amidoxime Groups for Batchwise Adsorption of UO2 2+,Separation Science and Technology, 1993, 28, 1985.

Katoh, S., Sugasaka, K., Sakane, K., Takai, N., Takahashi, H., Umezawa, Y., Itagaki, K., Enhancement Of The Adsorptive Property Of Amidoxime-Group Containing Fiber By Alkaline Treatment, Nippo Kagaki Kaishi, 1982b, 1455.

Kentish S.E., and Stevens G.W., Innovations in Separation Technology For The Recycling And Re-Use Of Liquid Waste Streams, Chem. Eng. J., 2001, 84, 149-159.

Kobuke Y., Tanaka, H., and Ogoshi, H., Polymer Journal, 1990, 22, 179.

Leinonen, H and Lehto, J., Ion-exchange of nickel by iminodiacetic acid chelating resin Chelex 100, Reactive & Functional Polymers, 2000, 43, 1-6.

Liu R., Li Y., and Tang, H., Synthesis And Characteristics Of Chelating Fibers Containing Imidazoline Group Or Thioamide Group, Journal of Applied Polymer Science, 2002, 83, 1608-1616.

Liu, R. X., Zhang, B. W., Tang, H. X., Synthesis And Characterization Of Poly(Acryaminophosphoric-Carboxyl-Hydrazide) Chelating Fiber, Reactive & Functional Polymers, 1999, 39, 71-81.

Lutfor, M. R., Silong, S., Md Zin, W., Ab Rahman, M. Z., Ahmad, M., and Haron J., Preparation And Characterization Of Poly(Amidoxime) Cheleting Resin From Polyacrylonitrile Grafted Sago Starch, European Polymer Journal, 2000, 36 2105-2113.

Mohamed, A. M. O., Maraqa, M., and Al Handhaly, J., Impact Of Land Disposal Of Reject Brine From Desalination Plants On Soil And Groundwater, Desalination, 2005, 182, 411-433.

Nilchi, A., Babalou, A. A., Rafiee, R., Sid Kalal, H., Adsorption Properties Of Amidoxime Resins For Separation Of Metal İons From Aqueous Systems, Reactive and Functional Polymers, 2008, 68, 1665-1670.

Sang, Y., Li, F., Gu, Q., Liang, C., and Chen, J., Heavy metal-contaminated groundwater treatment by a novel nanofibre membrane, Desalination, 2008, 223, 349-360.

Sahni, S. K., Reedijk, J., Coordinate Chemistry Reviews, 1984, 59, 1.

Shiraishi, T., Tamado, M., Saito, K., and Sugo, T., Recovery Of Cadmium From Waste Of Scallop Processing With Amidoxime Adsorbent Synthesized By Graft-Polymerization, Radiation Physics and Chemistry, 2003, 66, 43-47.