Adsorption Behavior of Metal Ions by Amidoxime Chelating Resins

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Summary: In this work, the acrylonitrile (AN) – divinylbenzene (DVB) –methylacrylate (MA) resin was synthesized via suspension polymerization in the presence of toluene as diluent, and benzoylperoxide (BPO) as initiator. The effect of MA, toluene and alkaline treatment on the exchange capacity of the resin were investigated. The results showed that the anion exchange capacity decreased with an increase in the amount of MA, while alkaline treatment had no significant effect. Also, the cation exchange capacity increased with an increase in the amount of hydrophilic agent and reached a maximum point. The sorption equilibrium was achieved relatively fast within 40 mins, and the resin exhibited affinity towards lead (II), copper (II) and in particular uranium (VI). The adsorption of uranium was directly depended up on the pH value. Furthermore, the macroreticular chelating resin, containing amidoxime group had higher adsorption of uranium (VI) in comparison to other metal ions studied. Finally, the alkaline treatment enhanced the potential for much faster adsorption characteristics and the highly porous chelating resin provided a more favorable pore structure for the rapid rate of diffusion of metal ions.

Keywords: acrylonitrile (AN) – divinylbenzene (DVB) – methylacrylate (MA) ion exchanger; adsorption; alkaline treatment; hydrophilic agent; ion exchange capacity

Introduction

There is a continuous need for new separation techniques which selectively extract metal ions from dilute waste waters and industrial process streams. Concern over environmental issues and possible re-cycle of extracted metals have enhanced the search for new processes. Ion exchange has been widely studied for the recovery of metal ions from diluted streams.[1–5] Commercially available ion exchange resins show high performances but generally poor selectivity towards different metal ions.[6] A high selectivity can be observed in some cases,[7] but kinetics is slow due to the hydrophobic character of the polymeric backbone.[8] An appealing alternative method is the use of chelating agents grafted on a hydrophilic support in a solid-liquid extraction process.

Many complexing agents which form negatively charged complexes have been employed for the separation of metal ions on anion exchange resins. The separations are based on the different stabilities of the complexes, and their different affinities for the resins.[9–13] It is worth noting that, chelating groups have been introduced into resins via synthetic techniques or by simple loading, and the modified resins have been used for the selective recovery or preconcentration of metal ions.[14–17]

The process using adsorbents is thought to be the most effective method for recovering heavy metals because of its high selectivity, the ease of handling and the environmental issues. Adsorbents containing both amidoxime and hydrophilic groups

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have a much higher uptake potential than those containing amidoxime. This is due to less hydrophilic nature of the amidoxime group.[18,19]

Varraest et al[20] demonstrated that Inuline modified with an amidoxime groups formed stable complexes with Cu (II). Colella et al[21] also demonstrated that poly (acrylamidoxime) can be successfully used for the preconcentration of trace metals from aqueous solutions. Hence, in this study, a new polymeric adsorbent having both hydrophilic and amidoxime groups were synthesized via suspension polymerization and the effects of different parameters such as hydrophilic and diluent agents investigated by using Taguchi experimental design method. Also the adsorption potential of the resin for some metal ions, especially those which have impact on the environment, from aqueous media was considered.

Experimental Part

All the reagent and chemicals used were of analytical grade obtained from Merck.

Preparation of Macroreticular AN-DVB-MA Copolymer

Macroreticular acrylonitrile (AN, $CH_2=CHCN$) - divinyl benzene- methacrylic acid (MA, $CH_2=CCH_3COOH$), AN-DVB-MA, (DVB, 10 mol %) copolymer bead were synthesized via suspension and polymerization in the presence of toluene as diluent, and benzoyl peroxide (BPO) as polymerization initiator. Polymerization was carried out at 80 °C for 11 h. Amidoxime groups were introduced by means of a reaction of these polymeric beads with 3 vol % of hydroxylamine in methanol/water in 1:1 molar mixture for 2h at 80 °C.

Alkali and Acid Treatment

The resin (0.5 g) was treated with 50 cm^3 of 0.1 M sodium hydroxide solution at 30 °C for 5 h (alkali treatment) or with 50 cm^3 of 1 M hydrochloric acid solution at 30 °C for 15 h (acid treatment).

Measurement of Anion and Cation Exchange Capacity

0.5 g sample of the resin and 50 mL of 0.1 M hydrochloric acid solution were shaken at 30 °C for 15 h. The anion exchange capacity of the adsorbent was measured by determining the amount of chloride in the supernatant by titrating with 0.1 M silver nitrate solution in the presence of fluorescein as an indicator.

In order to determine the cation exchange capacity, the adsorbent used for the measurement of anion exchange capacity was washed with deionised water until it was free of acid, then air dried and finally dried at 40 °C under vacuum. 0.5 g of the sample and 50 mL of 0.1 M sodium hydroxide solution were shaken at 30 °C for 15 h. 5 mL portion of the supernatant was titrated with 0.1 M solution of HNO_3 solution using methyl orange as an indicator. After methyl orange end point was reached, the chloride released was titrated with 0.05 M solution of $AgNO_3$ using 0.5 mL of 0.05 M K_2CrO_4 solution for the detection of the end point. The cation exchange capacity was determined by subtracting the amount of chloride released from the amount of sodium hydroxide exhausted.

Effect of Reaction Conditions

The effects of five variables, including the amounts of initiator, suspending, hydrophilic and diluent agent, and the speed of stirrer, at four levels on the ion exchange capacity of AN-DVB-MA resins were investigated by using a factional (Taguchi) experimental design method. An M_{16} orthogonal array of experiments was chosen in order to examine the effects of variables on each target variables, in only 16 experiments.

Adsorption of Cu^{2+} and Pb^{2+} by Batch Method

The adsorbent was mixed with a 2.5% KOH solution and heated at 80 °C for 1 h. 0.1 g of the sample prior to alkaline treatment was placed in a 500 mL solution containing 0.01 M of Cu^{2+} (Pb^{2+}) as its

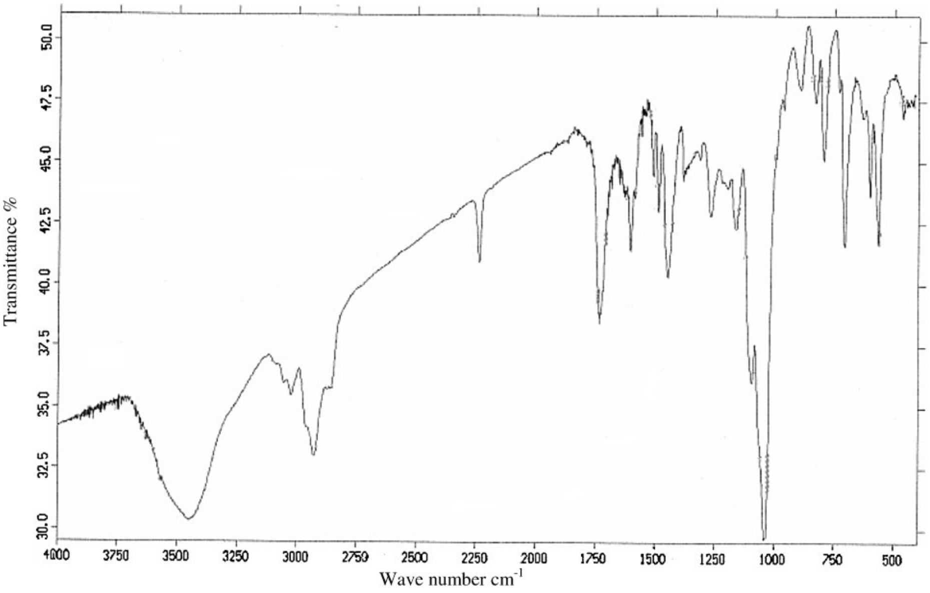

Figure 1.
Infrared spectrum of the amidoximated resin.

nitrate at pH 5 with continuous stirring at 30 °C for 48 h. Samples were collected at various time intervals in order to monitor the adsorption of Cu^{2+} (Pb^{2+}). The samples loaded from a solution of Cu^{2+} (Pb^{2+}) were stripped by using 10 mL of 1M HCl at 25 °C and analysed by ICP. The instrument was calibrated using appropriate standard solutions of Cu^{2+} (Pb^{2+}), and all solutions were diluted down to between 0.5 and 5.0 ppm prior to analysis.

Adsorption of UO_2^{2+}

0.1 g of the adsorbent was equilibrated in a batch process with 50 mL solution of 0.01 M UO_2^{2+} as its nitrate in a thermostated shaker at 30 °C for 24 h. The amount of UO_2^{2+} adsorbed was measured by gamma spectrometry.

Chemical and Instrumental Analysis

A GFL model 1086 thermostated shaker was used for shaking solutions at a desired temperature. The pH measurement were made with a Schott CG841 pH-meter; the infrared spectra were recorded using a Perkin-Elmer spectrometer by KBr disk method; thermogravimetric analysis were carried out using a Dupont model 951, approximately 5 mg of the dry sample was heated at a 10 °C/min heating rate under nitrogen atmosphere.

Table 1.
The statistical analysis of the ion exchange capacity experimental results.

Variable Factors	DOF		Sum of Squares		Variance		Percent %	
	Anion Ex. Ca	Cation Ex. Ca	Anion Ex. Ca	Cation Ex. Ca	Anion Ex. Ca	Cation Ex. Ca	Anion Ex. Ca	Cation Ex. Ca
RPM	3	3	0.93	0.13	0.31	0.04	0.46	0.40
TCP	3	3	0.31	0.11	0.10	0.04	0.15	0.35
MA	3	3	195.73	28.84	65.24	9.61	95.60	89.67
Toluene	3	3	7.37	2.54	2.46	0.85	3.60	7.89
BPO	3	3	0.39	0.54	0.13	0.18	0.19	1.69

The elemental analysis was obtained using Inductively Coupled Plasma spectrometer model 5500 Perkin-Elmer; X-ray powder diffractometry was carried using a 1800 PW Philips diffractometer with CuK_α beam in order to determine the structure of the adsorber. The finely powdered sample of the adsorber was packed in a flat aluminium sample holder, where the X-ray source was a rotating anode operating at 40 kV and 30 mA with a copper target. Data were collected between 4 and 60 degrees in 2θ.

The solubility of the adsorber was determined at room temperature by equilibrating 0.1g of the sieved material in various solutions for 24 h. The supernatant was analysed by ICP. Macroreticular structures (Macropores) was characterised by the specific surface areas which were measured on a Quantocrom model Chem BET 3000 surface area apparatus (BET method).

Elemental analysis (C, H, N, O) were performed on an Elementar-Vario ELIII; and finally the radioactivity was counted using an ultra low level liquid scintillation spectrometer Quantuluse TM 1220/gamma spectrometer Ortec model GMX-15185-5.

Results and Discussion

An Infrared spectrum of the amidoximated resin is shown in Figure 1. The characteristic stretching band of nitrile groups (–CN) appears at 2240 cm^{-1}, and a predominant peak at 1450 cm^{-1}. The band at 3450 cm^{-1} is assigned to symmetric and asymmetric stretching mode of NH_2 groups. The bands at 1660 and 920 cm^{-1} are assigned

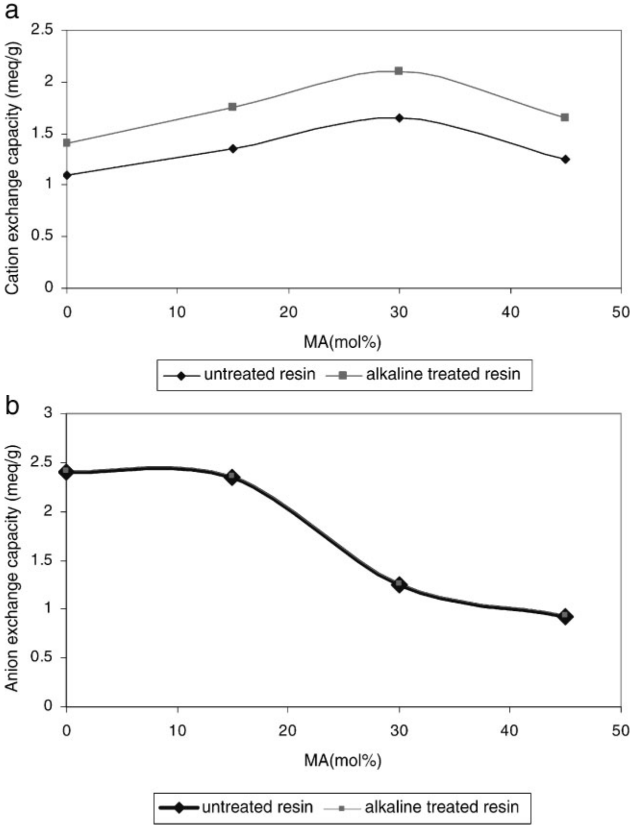

Figure 2.
a The effect of MA on the cation exchange capacity b The effect of MA on the anion exchange capacity.

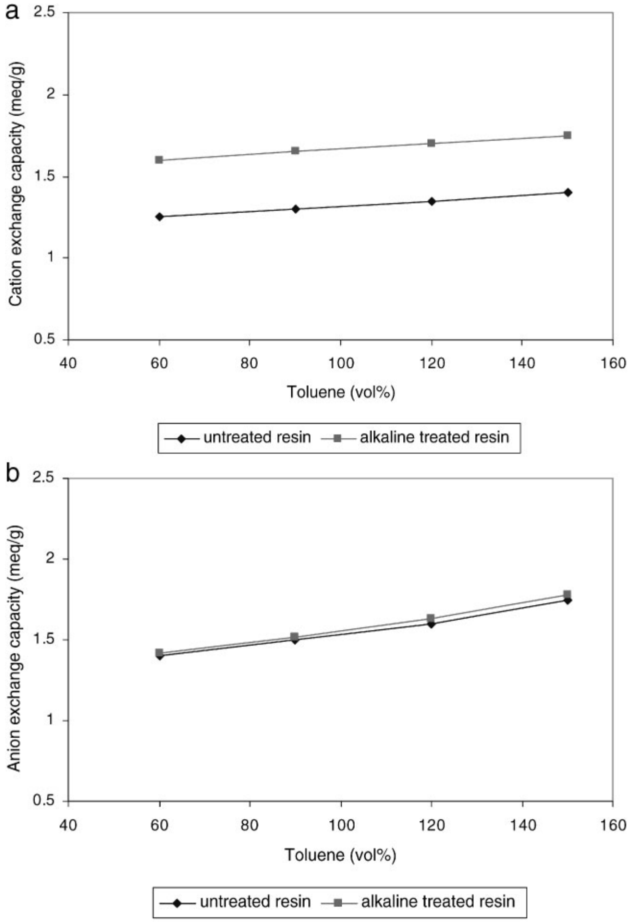

Figure 3.
a The effect of toluene on cation exchange capacity b The effect of toluene on anion exchange capacity.

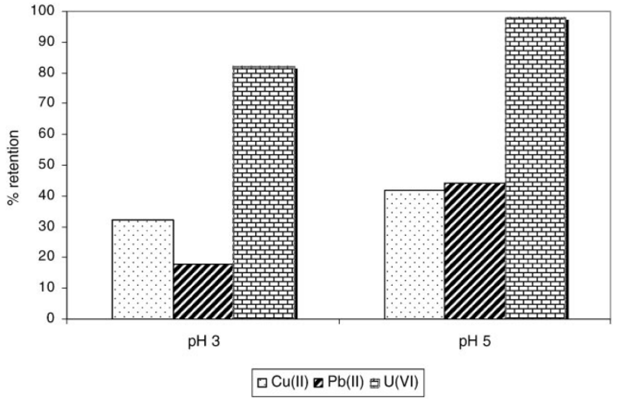

Figure 4.
The effect of the pH on the adsorption of Cu(II), Pb(II) and U(VI) metal ions by 0.1 g resin and 1 gL^{-1} metal ions for 1 h at 25 °C.

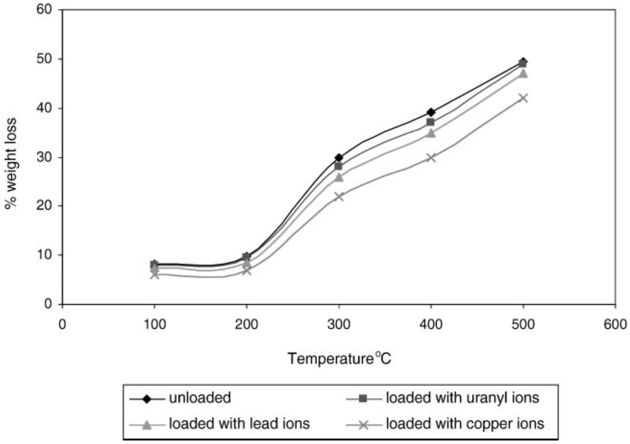

Figure 5.
Thermograms of the unloaded and loaded resin with uranyl, lead and copper ions. The heating rate was 10 °C/min under nitrogen.

to a C=N stretching mode and an N–O stretching mode of oxime groups, respectively.[22,23]

Table 1 shows the statistical analysis, where the analysis of variance (ANOVA) revealed that only the effects of MA and toluene variables on the mentioned target variables are highly significant. Furthermore, the effect of hydrophilic agent (MA) is more significant than the rest of variables considered.

Figure 2a shows that the cation exchange capacity increased with an increase in the amount of MA to reach a maximum. Further increasing of MA content resulted in a decrease in the cation exchange capacity of the synthesized amidoxime resin. These changes can be explained by the decrease of acrylonitrile content and the increase of hydrophilicity in copolymer beads by the formation of the hydroximic and carboxylic acid groups based on the increase of methylacrylate.

Figure 2b shows that with increasing the amount of MA, the anion exchange capacity decreases. This behavior could be due to a significant decrease of amidoxime groups, when hydrophilic agent was increased. Furthermore, since the anion exchange capacity was not changed by alkaline treatment, the amidoxime groups were hardly hydrolyzed by a weak alkaline solution. Also, due to increase in porosity, anion and cation exchange capacity of

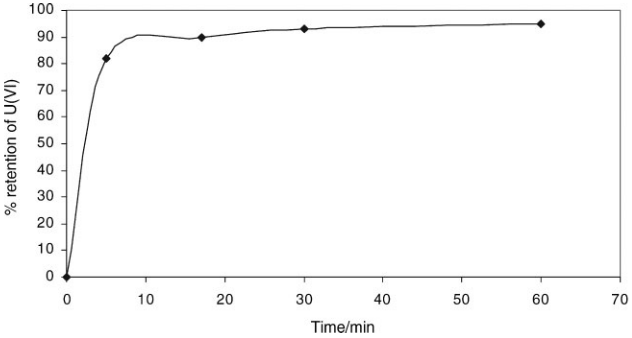

Figure 6.
The adsorption rate behavior of uranyl ions on resin at pH 5.

synthesized resins increased with an increase of toluene content, as shown in Figures 3a and 3b.

Egawa et al[21] reported that anion exchange capacity decreased with the alkaline treatment due to the hydrolysis of amidoxime group. Here, the enhanced hydrophilicity by the alkaline treatment hastened the diffusion of hydrochloric acid in to the fibrous adsorbent. Therefore, it was supposed that the anion exchange capacity did not show a significant decrease after the alkaline treatment. On the other hand, the increase in cation exchange capacity by the alkaline treatment is consistent with results reported in the literature.[21]

Figure 4 shows the retention behaviour of the resin for Cu(II), Pb(II) and U(VI) metal ions at various pH values. The retention increases as the pH increases and the higher retention was observed for all metal ions at pH 5. An increase in pH decreases the competition of H^+ ions for the resin sites and the complexation of the metal ion is favoured.

Thermogravimetric analyses were carried out to determine the effect of UO_2^{2+}, Pb^{2+} and Cu^{2+} adsorbed on the thermal stability of the resin. The resin was loaded with UO_2^{2+}, Pb^{2+} and Cu^{2+} at pH 5 according to the maximum load capacity. The metal ions had no significant effect on the thermal stability. In all compounds, a weight loss of less than 10% was observed at 200 °C. It increased to approximately 40% at 400 °C, but it was lower than 50% at 500 °C (see Figure 5).

Figure 6 shows the adsorption rate behavior of uranyl ions on to the resin from 1 gL^{-1} of aqueous solution at pH of 5. A rapid adsorption rates are achieved within 5 mins and adsorption equilibrium is achieved after 40 mins. It is worth noting that several factors namely agitation rate in the aqueous phase, the amount of sorbent, the sorbent structural properties as well as the metal ions properties such as hydrated ionic radius and initial concentration of metal ions are parameters that determine the adsorption rate.

Figure 7 shows the effect of the initial concentration of uranyl ions on the adsorption capacity of the resin. The amount of uranyl ions adsorbed by the resin increased with respect to the increase of initial concentration of metal ion.

The resin exhibited affinity towards lead (II), copper (II) and in particular U (VI). The adsorption of uranium increased with increasing the pH and reached its maximum of 2.7 meq/g. This shows that the macroreticular chelating resins which contain amidoxime groups are more useful for the recovery of uranium (VI). Furthermore, the maximum load capacity for U (VI) was

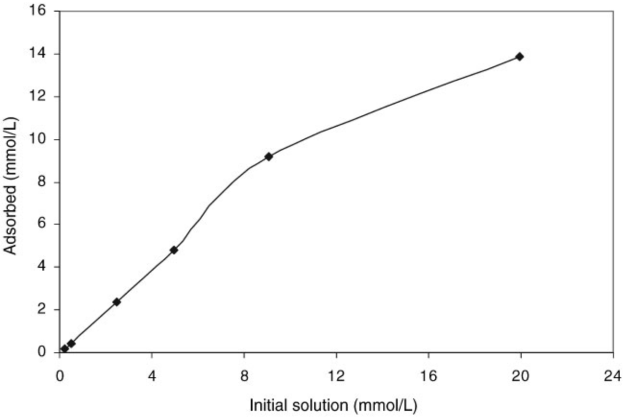

Figure 7.
Uranium (VI) ion adsorption capacity of resin at pH 5.

found at pH 5, which illustrates that the amidoxime sites were practically saturated since the retention was about 98.9%.

Conclusion

The effect of hydrophilic agent, diluent and alkaline treatment on the exchange capacity of AN-DVB-MA showed that the anion exchange capacity decreased with an increase in the amount of hydrophilic agent, while alkaline treatment had no significant effect. It is worth nothing that in the amidoxime resins, the anion exchange capacity determines the content of amidoxime groups. Furthermore, the cation exchange capacity increased with an increase in the amount of hydrophilic agent to reach a maximum.

Further increasing of MA content resulted in a decrease in the cation exchange capacity of the synthesized amidoxime resin. A similar behavior was observed for the resins before and after alkaline treatment, but cation exchange capacity of the alkaline treated resins was higher. Increasing of cation exchange capacity after alkaline treatment was due to the alkaline hydrolysis of esters. Due to pore forming role of diluent agents in the synthesis of polymeric resins, anion and cation exchange capacity increased with an increase of toluene content before and after alkaline treatment.

The sorption equilibrium was achieved relatively fast within 40 mins, and the resin exhibited affinity towards lead (II), copper (II) and in particular uranium (VI). The adsorption of uranium increased with increasing the pH and reached its maximum of 2.7 meq/g. This shows that the macroreticular chelating resins which contain amidoxime groups are more useful for the recovery of uranium (VI).

Finally, the studies of pore structure in the swollen state showed that the alkaline treatment greatly enhanced the formation of micropores due to the increased hydrophilicity based on the high swelling. The highly porous chelating resin provided a more favorable pore structure for the rapid rate of diffusion of metal ions. Also, the alkaline treatment enhanced the potential for much faster adsorption characteristics. Thus it can be concluded that both pore structure in the swollen state and chemical structure contribute to the overall performance achieved.

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