Preparation, characterization and applications of novel iminodiacetic polyurethane foam (IDA-PUF) for determination and removal of some alkali metal ions from water

M.F. El-Shahat[a], E.A. Moawed[b,*], N. Burham[c]

[a] Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt
[b] Chemistry Department, Faculty of Science, Mansoura University, Damietta, Egypt
[c] Chemistry Department, Faculty of Science, Fayoum University, Egypt

ABSTRACT

The new type of ion chelating resin (IDA-PUF) has iminodiacetic group that was prepared from polyurethane foam (PUF) by the reaction between primary amine of PUF and monochloro-acetic acid. The IDA-PUF was characterized using infrared spectra, elemental and thermal analysis. The exchange properties and chromatographic behaviour of the new chelating resin were investigated for removal of some alkali metal ions (lithium, sodium and potassium) using batch and column processes. The maximum distribution coefficient (K_D) of trace alkali metal ions was in the pH range of 8–10. The kinetics of sorption of the alkali metal ions was found to be fast with average values of half-life of sorption ($t_{1/2}$) of 4.93 min. The values of ΔG, ΔS and ΔH were -3.86 kJ mol^{-1}, 57.73 J mol^{-1} K^{-1} and 14.41 kJ mol^{-1}, respectively, which reflects the spontaneous and endothermic nature of ion exchanger process. The average sorption capacity of IDA-PUF is 4.8 mmol/g for alkali metal ions, enrichment factors $\approx$40 and the recovery 95–100% were also achieved with average value of RSD% = 1.67. The proposed method has been successfully applied to preconcentrate, determinate and remove the alkali metal ions from different samples of water.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Chelating resins are ion exchangers in which various chelating materials have been incorporated into the matrix. These substances were commerciated over ten years ago, to combine two analytical processes; ion exchange and complexation reactions. The combination of the two processes in one single system is an innovation which greatly enlarges the scope of fundamental knowledge about ion exchangers and their applications. Chelating ion exchangers are distinguished from the ordinary type of ion exchanger materials by main properties, selectivity, bond strength, sorption capacity and kinetics. The chelating resins, e.g., Amberlite IRC-718, Chelite-C, Chelex-100 and Muromac A-1, which contain iminodiacetic acid functional groups [$-CH_2$-N(CH_2-COOH)$_2$] were used as amplifiable for a wide range of metals [1–16]. The applications of these chelating resins to metal speciation measurements were used in both batch and column modes.

The importance of polyurethane foam has been increased as collector materials due to their efficiency, low cost, easily handling and storage, which is convenient for field studies. Recently, many reports have studied the chemical reaction of the primary amine functional group in the polyurethane foam. It was found that the amine groups are highly reactive towards diazotization by sodium nitrite, and azo coupling with α-naphthol, β-naphthol, resorcinol, 8-hydroxyquinoline, alizarin reds and 4-nitrophenyldiazonium tetrafluoroborate [17–26]. On this basis, an analytical methodology in this study was developed for the synthesis of stable chelating resin which contains iminodiacetic acid functional groups. The IDA-PUF was synthesized using white-polyurethane foam after hydrolysis process and then reacted with monochloro-acetic acid. Also, we investigated the adsorption characteristics of some alkali metal ions onto the IDA-PUF chelating resins.

2. Material and methods

2.1. Reagents and materials

All used reagents were prepared from analytical reagent grade chemicals and bidistilled water. A 1 mg/mL stock solution of Li$^+$ was

---

* Corresponding author. Tel.: +002 023 542 5833.
  E-mail address: emoawed@hotmail.com (E.A. Moawed).

prepared by dissolving 0.9934 g of $LiNO_3$ (Merck) in water containing 1 mL of conc. HNO_3 and dilution of the solution to 100 mL in a measuring flask. A stock solution containing 1 mg/mL of Na^+ was prepared by dissolving 0.3696 of $NaNO_3$ (Fisher) in water containing 1 mL of conc. HNO_3 and dilution of the solution to 100 mL in a measuring flask. A stock solution containing 1 mg/mL of K^+ was prepared by dissolving 0.1908 of KCl (Winlab) in water containing 1 mL of conc. HCl and dilution of the solution to 100 mL in a measuring flask. The pH values were adjusted in the range 1–10 with 0.1–1 M HCl/NH_3.

2.2. Synthesis of PUFIC M-1

A 5 g portion of commercial white-PUF ($d \approx 20\,kg/m^3$) cubes was washed using distilled water followed by acetone, and dried at room temperature. The foam cubes were soaked in 50 mL of 6 M HCl stirred for 2 h and washed with distilled water. Into a 250 mL round-bottomed flask equipped with a reflux condenser, 10 g of monochloro-acetic acid and 150 mL of ethanol were added to the foam cubes and the mixture was gently boiled for 3 h. IDA-PUF material was washed with 0.1 M HCl followed by distilled water, then acetone, and dried at room temperature.

2.3. Apparatus

Flame photometer spectrophotometer (Flame photometer PFP7, Jenway Limited, Dunmow, UK) was used for determining lithium, sodium and potassium ions. The pH measurements were carried out using a pH meter (HANNA Instruments). A mechanical shaker (SL 350, Nuve, Akyurt, Ankara, Turkey) with speed control was used for batch experiments. Glass columns of about 15 cm × 1.5 cm were used for the chromatographic separations.

2.4. General procedures

Extraction of lithium, sodium and potassium ions with IDA-PUF was examined using batch technique; 0.1 g portion of the IDA-PUF was mixed with a 25 mL aliquot of metal ions solution (2 μg/mL) in a shaker thermostated to the desired temperature and adjusted to a desired shaking speed. After 1 h, the solution was separated and the concentration of remaining metal ions was determined by flame photometer.

In the dynamic experiments, a 100 mL aliquot of water sample was passed through column containing 1 g of IDA-PUF at flow rate 3 mL/min then eluted with 25 mL of 3 M HCl. The eluted alkali metal ions were measured by flam photometer.

Table 1
Characterization of white-PUF and IDA-PUF

| Property	White-PUF	IDA-PUF
Colour	White	Dark yellow
Density (kg/m^3)	20	66
IR spectra		
Broadband of –NH and –OH (cm^{-1})	3600–3000	3700–3200
–NCO	2409.5	Disappear
–C=O	1710.4	1710.4, 1718.3
–OH	–	3422.6
Element analysis		
C, H, N and O %	62.53, 5.81, 9.75, 21.91	61.81, 7.03, 10.45, 20.72
Empirical formula	$C_7H_8NO_2$	$C_7H_{10}NO_2$
Thermal analysis		
Weight losses (%)	1.68, 38.39, 52.88, 7.05	3.93, 61.58, 16.73, 17.76
At temperature (°C)	233, 337, 400, >400	113, 290, 400, >400
Endothermic peak (°C)	322.6, 374.7	113.3, 277.2
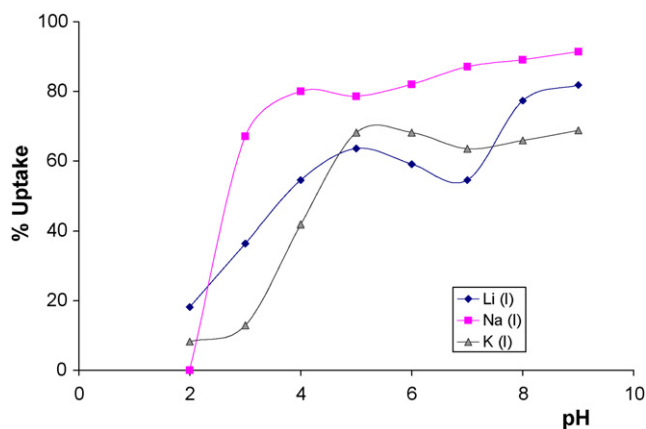
Fig. 2. Effect of pH on the exchange of Li^+, Na^+ and K^+ using IDA-PUF.

3. Results and discussion

3.1. Characterization of PUFIC M-1

The infrared spectra of white-PUF and IDA-PUF were tested using thin film technique. The results obtained showed that the white-PUF has broadband at 3600–3000 cm^{-1} (maximum peak at 3393.1 cm^{-1}) characteristic of the NH and OH groups and
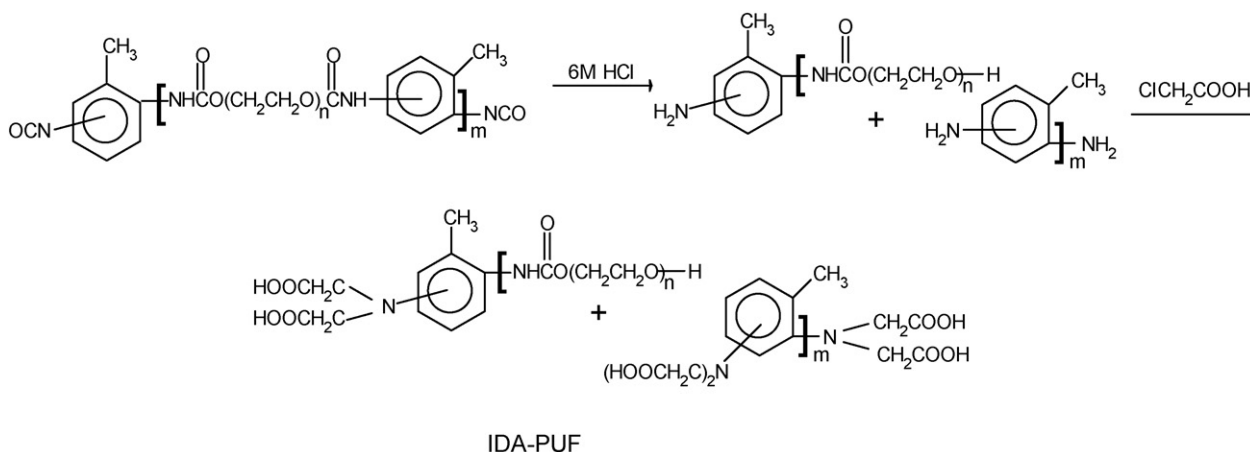
IDA-PUF

Fig. 1. The expected scheme for the preparation of IDA-PUF.

band at 2409.5 cm^{-1} characteristic of isocyanate (–NCO) group. While the bands of –NH and –OH groups of IDA-PUF appeared at 3700–3200 cm^{-1} (maximum peak at 3422.6 cm^{-1}), the band of isocyanate (–NCO) group of the white-PUF disappeared. Also, two new bands at 3422.6 and 1718.3 cm^{-1} characteristic of the OH and C=O groups were appeared, respectively, after reaction with monochloro-acetic acid. These results indicate that the shifted bands of NH groups and the two new bands, the –OH and –C=O groups, are due to the formation iminodiacetic acid groups of IDA-PUF (Table 1).

Thermogravimetric analysis (TGA) of IDA-PUF showed that the weight losses were 3.93, 61.58, 16.73 and 17.76% at 113, 290, 400 and >400 °C, respectively, and two endothermic peak at 113.29 and 277.23 °C have appeared. TGA curves of IDA-PUF showed that the loss of weight (3.93%) at 113 °C is due to losing of a water molecule of iminodiacetic acid group while forming anhydride of six membered rings, which were stable until 277 °C. Also, the endothermic peaks at temperature of 277 °C corresponding to the thermal decomposition of IDA-PUF beginning from 277 °C were observed Table 1). The percentage of iminodiacetic group is 3.93% (39.3 mg/g of IDA-PUF) corresponding to the loss of water molecule. These results indicate that the amount of iminodiacetic group on the IDA-PUF matrix is 2.18 and 4.37 mmol/g of acetic acid groups.

This result was confirmed through the elemental analysis of the white-PUF and IDA-PUF. The percentage of hydrogen and nitrogen in the IDA-PUF was increased (1.216 and 0.695%, respectively) while the percentage of carbon and oxygen was decreased (0.720 and 1.191%, respectively). The percentage of carbon and oxygen was decreased due the partial hydrolysis of some urethane groups (release CO_2). The percentage of hydrogen was increased due to the addition of six atoms of hydrogen in the iminodiacetic acid group while the increasing percentage of nitrogen could be due to the decreasing of carbon and oxygen percentage (Table 1). The expected scheme of the preparation of IDA-PUF is represented in Fig. 1.

The densities of the white-PUF and IDA-PUF were measured. The values obtained were 20 and 66 kg/m^3, respectively. These results show that the IDA-PUF is denser than the white-PUF due to the formation of iminodiacetic acid groups of the PUF (Table 1).

3.2. Chromatographic behaviour for separation and determination of Li$^+$, Na$^+$ and K$^+$

The effect of pH on the extraction of lithium, sodium and potassium ions with IDA-PUF was examined using batch technique. The percentage uptake of Li$^+$, Na$^+$ and K$^+$ was plotted vs. pH values shown in Fig. 2. The optimum pH ranges to extract the alkali metal ions from aqueous solution onto IDA-PUF were 8–10. From Fig. 2 it is clear that the percentage uptake of lithium and potassium ions was increased with increase of pH values (maximum uptake between pH 4 and 5), then it was decreased at pH 6–7 and increased again between pH 7 and 10. The similarity of the curves of sorption of Li$^+$
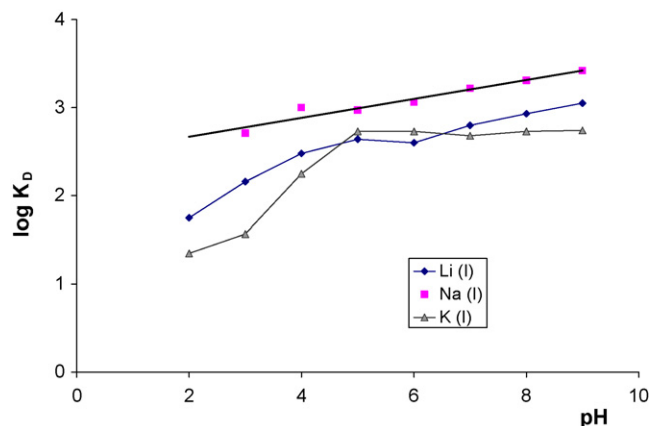

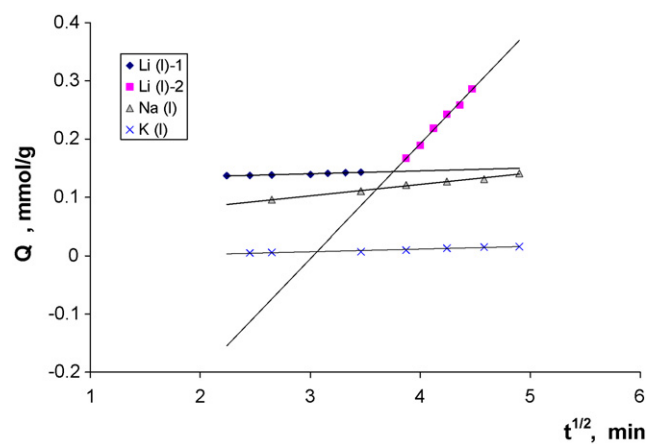**Fig. 3.** The plot of pH vs. log K_D for the sorption of alkali metal ions onto IDA-PUF.

Fig. 4. The plot of Q_t vs. $t^{1/2}$ for the sorption of alkali metal ions onto IDA-PUF.

and K$^+$ could reasonably suggest that the sorption of these metal ions onto IDA-PUF is the same mechanism. The percentage uptake of sodium ion was large increased with the increase of pH values up to 4, then it was slightly increased with pH > 5. The plots of log K_D vs. pH values (Fig. 3), it is clear that the log K_D values of sorption of the lithium, sodium and potassium ions were increased with the increase of pH values. These results indicate that the sorption of alkali metal ions onto IDA-PUF is ion exchanger process. Also, the linear relationship for the sorption of sodium ion onto IDA-PUF indicates that the ion exchange of sodium is an ideal process. Generally the selectivity sequence was in the order Na$^+$ > Li$^+$ ≈ K$^+$, this sequence may be due to the increase of electrostatic interaction.

Kinetic measurements were carried out using IDA-PUF, which has diameter 0.5 cm with V/m 250 mL g^{-1} and in pH 8. The rate of exchange of Li$^+$, Na$^+$ and K$^+$ onto the IDA-PUF has been measured

Table 2
Kinetic parameters for the removal of alkali metal ions from water onto IDA-PUF at different temperature

Metal ions	Rate constant of interparticle transport, k_M (µmol g^{-1} min$^{-1/2}$)	Temperature (K)	Rate constant of sorption, k_1 (min^{-1})	Rate constant of desorption, k_{-1} (min^{-1})	Overall rate constant, k' (min^{-1})	Half-life of sorption, $t_{1/2}$ (min)
Li$^+$	0.086	298	0.189	0.074	0.263	3.67
		333	0.303	0.088	0.391	2.29
Na$^+$	0.020	298	0.158	0.035	0.193	4.39
		333	0.276	0.038	0.314	2.51
K$^+$	0.005	298	0.103	0.020	0.123	6.73
		333	0.293	0.022	0.315	2.37
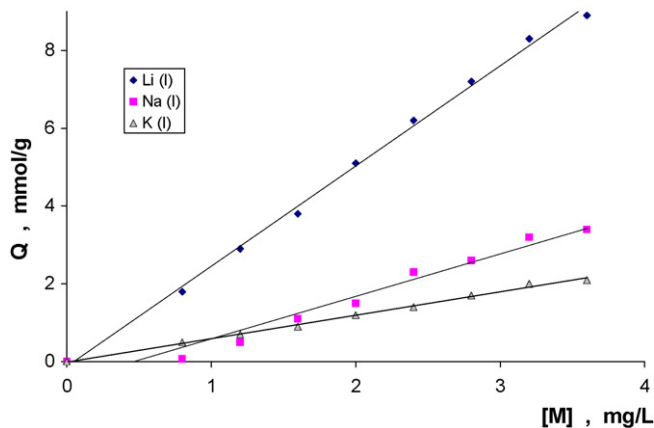
Fig. 5. Isotherm curve of the sorption of alkali metal ions onto IDA-PUF.

Table 3
Thermodynamic parameters of the sorption Li⁺, Na⁺ and K⁺ onto IDA-PUF

Metal ions	Gibbs free energy, ΔG (kJ mol⁻¹)	Enthalpy, ΔH (kJ mol⁻¹)	Entropy, ΔS (J K⁻¹ mol)
Li⁺	−2.61	11.54	46.20
Na⁺	−2.50	27.41	92.70
K⁺	−6.46	4.28	34.30

Table 4
Determination of alkali metal ions using IDA-PUF column (preconcentration factor = 40)

Metal ions	Amount added (µg)	Amount found (µg)	Recovery (%)
Li⁺	0.10	0.095	95
Na⁺	0.20	0.198	98.8
K⁺	0.1	0.110	110

Table 5
Determination of alkali metal ions in tap water from Fayoum city using IDA-PUF column

Metal ions	Direct method (µg mL⁻¹)	Proposed method (µg mL⁻¹)
Li⁺	0.24	0.24
Na⁺	28.8	24.0
K⁺	6.1	5.7

by batch extraction mode at different time intervals, i.e., 1–60 min. From the results obtained, the average time required for exchange equilibrium was found to be 15 and 20 min, respectively.

In order to study the particle diffusion mechanism, the Morris–Weber equation ($q_t = k_M \sqrt{t}$), was applied where q_t is the amount of metal ions sorbed at time t, and k_M is the rate constant of interparticle transport (μmol g⁻¹ min⁻¹/²). The obtained data showed that the diffusion rate is rapid and the values of k_M are 0.086, 0.020 and 0.005 μmol g⁻¹ min⁻¹/² for the exchange of Li⁺, Na⁺ and K⁺, respectively (Fig. 4). The values of diffusion rate of alkali metal ions onto IDA-PUF in the order Li⁺ > Na⁺ > K⁺ shows that the diffusion rate depends on the size of metal ions (Table 2). The exchange process of lithium ion is more or less constant at the beginning then an increase in the capacity (Q, mmol/g) by increasing $t^{1/2}$ is observed (Fig. 4). The difference in the kinetic behaviour of lithium ion exchange from sodium and potassium ion exchange onto IDA-PUF is due to the small size of lithium ion and the lithium metal resembles magnesium more than it resembles other alkali metals.

The kinetic parameters for the sorption of the Li⁺, Na⁺ and K⁺ onto the IDA-PUF according to the first order reaction and the time dependence process were given by the Lagergren equation

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}.$$

A straight-line plot of $\log(q_e - q_t)$ vs. t indicates that the process is a first order reaction. The rate constants of the exchange process calculated from the slope are 0.189, 0.158 and 0.103 min⁻¹ for Li⁺, Na⁺ and K⁺, respectively. The values of half-life of sorption alkali metal ions ($t_{1/2}$) calculated from the slope are 3.67, 4.39 and 6.73 min, for the Li⁺, Na⁺ and K⁺, respectively, are shown in Table 1. These results show that the rate of exchange of alkali metal ions is more fast as compared to the other resins, also it is depends on the size of metal ions. The rate of exchange at different temperatures is calculated

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_2 T_1} \right).$$

It shows that the rate constant of sorption and rate constant of desorption of alkali metal ions increase with increasing temperature while the half-life of exchange decreases (Table 2).

The uptake of the Li⁺, Na⁺ and K⁺ on the IDA-PUF was determined as a function of metal ion concentrations in the aqueous solution (Fig. 5). The resultant isotherms show a good linear relationship over relatively wide range of metal ion concentrations with good correlation (average values of $R^2 = 0.996$).

The results of the alkali metal ion concentrations on IDA-PUF were analyzed in terms of Freundlich and Langmuir models. The Langmuir model was not applicable; this model suggested that the sorption of metal ion from solution to the solid is monolayer coverage. The average values of Freundlich constants ($1/n$) were 0.72 for exchange of Li⁺, Na⁺ and K⁺, which may be attributed to the heterogeneous surface structure of the IDA-PUF. The sorption capacities of the IDA-PUF for Li⁺, Na⁺ and K⁺ are estimated to be 8.9, 3.4 and 2.1 mmol/g, respectively. The capacity sequence is in the order Li⁺ > Na⁺ > K⁺, the difference in exchange capacities of metal ions may be attributed to their different ionic sizes.

Finally, the IDA-PUF has been recycled many times after regeneration using 1 M NaOH, then 1 M HCl without decreasing their capacities significantly.

The dependence of alkali metal ions exchange onto IDA-PUF with temperature has been evaluated using the equations:

$$\log K_c = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R},$$

and

$$\Delta G = \Delta H - T\,\Delta S.$$

The values of ΔG, ΔH, and ΔS at different temperatures (20, 40 and 60 °C) for the exchange of Li⁺, Na⁺ and K⁺ are given in Table 3. The average value of (ΔG) is −3.86 kJ mol⁻¹, the negative values of ΔG are attributed to the spontaneous nature of sorption process. The positive values of ΔH (14.41 kJ mol⁻¹) may be interpreted as the endothermic chemisorptions process. Similarly the positive values

Table 6
Optimum conditions for sorption and desorption of alkali metal ions onto IDA-PUF

Property	Li⁺	Na⁺	K⁺
pH	9–12	8–10	6–10
Loading half-time, $t_{1/2}$ (min)	3.7	4.4	6.7
Capacities (mmol/g)	8.9	3.4	2.1
% Recovery			
Batch technique	81.8	91.4	90.4
Dynamic technique	95	98.8	100
% Relative standard deviation ($n = 4$)	1.02	0.37	3.61

of entropy ($57.53\,\mathrm{J\,K^{-1}\,mol}$) may be indicative of the faster exchange of tested metal ions.

The effect of volume of the sample on the uptake percentage was studied. $100\,\mu\mathrm{g}$ of the alkali metal ions in different sample volumes (25–1000 mL) was allowed to pass through the column at flow rate 3 mL/min. The elution of Li^+, Na^+ and K^+ from IDA-PUF column using 25 mL of 3 M HCl at flow rate 3 mL/min occurred by recovery percentages of 95–110% (Table 4). These results show that the alkali metal ions can be removed from large volumes of the dilute aqueous solutions using IDA-PUF column.

4. Analytical applications

The analytical applicability of the proposed IDA-PUF was tested for the separation and determination of Li^+, Na^+ and K^+ in different samples. Alkali metal ions in different samples of tap water from Fayoum city in Egypt were determined using the IDA-PUF column. The obtained results are shown in Table 5. These results are agreed with the values obtained using AAS measurements. It shows the suitability of the IDA-PUF column for the preconcentration and determination of Li^+, Na^+ and K^+ in water.

5. Sorption mechanism

A zero percentage of the uptake of alkali metal ions onto IDA-PUF was in pH range 1–2 while the maximum uptake percentage at pH values was between 4–5 and 8–10. These results show that at pH 1–2 the hydrogen ion concentration is high in the solution which competes successfully with the protonation of the imino groups to form a quaternary ammonium salt as $R_3NH^+Cl^-$ leading to a decrease in the uptake of metal ions. In pH 4–5, the concentration of hydrogen ion in solution was small which competes with protonation of the imino groups and ionization of the dicarboxylic groups hence, the uptake was very high. While in the alkaline medium (pH 8–10), the dicarboxylic groups are ionized due to the neutralization.
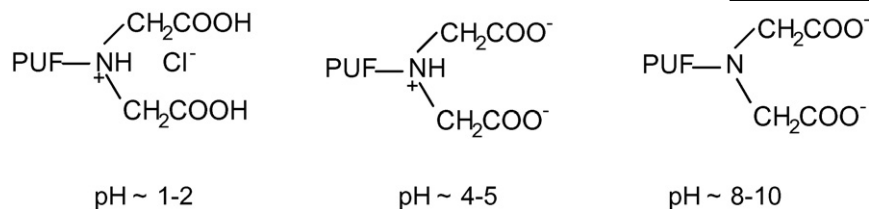
with the polyurethane foam. Characterization of the IDA-PUF indicates that iminodiacetic acid groups are found in the polyurethane foam matrix. The sorption behavior of alkali metal ions onto the IDA-PUF has been studied to optimize the best conditions for removal and preconcentration of metal ions from water (Table 6). These methods offer potential simplicity of use, as well as being inexpensive and rapid.

References

[1] K.C. Bowles, S.C. Apte, G.E. Batley, L.T. Hales, N.J. Rogers, Anal. Chim. Acta 558 (2006) 237.
[2] N. Manouchehri, A. Bermond, Anal. Chim. Acta 557 (2006) 337.
[3] T. Pasinli, A.E. Eroğlu, T. Shahwan, Anal. Chim. Acta 547 (2005) 42.
[4] L. Lin, R.S. Juang, Chem. Eng. J. 112 (2005) 211.
[5] M. Pesavento, G. Alberti, A. Profumo, Anal. Chim. Acta 405 (1–2) (2000) 309.
[6] M. Pesavento, G. Alberti, Water Res. 34 (2000) 4482.
[7] M. Pesavento, R. Biesuz, React. Funct. Polym. 36 (1998) 135.
[8] M. Pesavento, R. Biesuz, M. Gallorini, A. Profumo, Anal. Chem. 65 (1993) 2522.
[9] J.W. Guthrie, R. Mandal, M.S.A. Salam, N.M. Hassan, J. Murimboh, C.L. Chakrabarti, M.H. Back, D.C. Grégoire, Anal. Chim. Acta 480 (2003) 157.
[10] T.S. Lin, J.O. Nriagu, Anal. Chim. Acta 395 (1999) 301.
[11] F. Gode, E. Pehlivan, J. Hazardous Materials 136 (2006) 330.
[12] H. Leinonen, J. Lehto, React. Funct. Polym. 43 (2000) 1.
[13] P.H. Lin, K.S.K. Danadurai, S.D. Huang, J. Anal. At. Spectrom. 16 (2001) 409.
[14] J. Qvarnstrom, Q. Tu, W. Frech, C. Ludke, Analyst 125 (2000) 1193.
[15] S. Hirata, T. Kajiya, M. Aihara, K. Honda, O. Shikino, Anal. Sci. 17 (2001) i5.
[16] D.Q. Trung, C.X. Anh, N.X. Trung, Y. Yasaka, M. Fujita, M. Tanaka, Anal. Sci. 17 (2001) i1219.
[17] E.A. Moawed, M.F. El-Shahat, React. Funct. Polym. 66 (2006) 720.
[18] E.A. Moawed, M.A.A. Zaid, M.F. El-Shahat, J. Anal. Chem. 61 (2006) 458.
[19] E.A. Moawed, Acta Chromatogr. 15 (2005) 220.
[20] E.A. Moawed, J. Indian Chem. Soc. 81 (2004) 395.
[21] M.F. El-Shahat, E.A. Moawed, M.A.A. Zaid, Anal. Bioanal. Chem. 378 (2004) 470.
[22] A.B. Farag, E.A. Moawed, M.F. El-Shahat, Anal. Lett. 38 (2005) 809.
[23] E.A. Moawed, M.A.A. Zaid, M.F. El-Shahat, Int. J. Environ. Anal. Chem. 84 (2004) 935.
[24] S.G. Dmitrienko, O.A. Sviridova, L.N. Pyatkova, E.N. Myshak, O.V. Shelmenkova, Yu.A. Zolotov, Mendeleeve Commun. 6 (2000) 244.

6. Conclusion

The present work deals with the preparation of new chelating resin (IDA-PUF) based on coupling of the monochloro-acetic acid

[25] S.G. Dmitrienko, O.A. Sviridova, L.N. Pyatkova, V.A. Zhukova, Yu.A. Zolotov, Anal. Chim. Acta 405 (2000) 231.
[26] S.G. Dmitrienko, O.A. Sviridova, L.N. Pyatkova, V.M. Senyavin, Anal. Bioanal. Chem. 374 (2002) 361.