Sorption Properties of the Iminodiacetate Ion Exchange Resin, Amberlite IRC-718, Toward Divalent Metal Ions

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ABSTRACT: The sorption properties of the commercially available cationic exchange resin, Amberlite IRC-718, that has the iminodiacetic acid functionality, toward the divalent metal-ions, Fe^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} were investigated by a batch equilibration technique at 25°C as a function of contact time, metal ion concentration, mass of resin used, and pH. Results of the study revealed that the resin exhibited higher capacities and a more pronounced adsorption toward Fe^{2+} and that the metal-ion uptake follows the order: $Fe^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. The adsorption and binding capacity of the resin toward the various metal ions investigated are discussed. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1316–1319, 2008

Key words: Amberlite IRC-718; chelating resin; divalent metal ions exchange; sorption

INTRODUCTION

Heavy metals are commonly found in large quantities in industrial wastewaters. For this reason, the recovery of the metal ions present in these wastewaters is necessary for environmental protection and economical reasons. Solid organic and inorganic ion exchanges constitute the basis of widely employed chemical separation procedures, with applications ranging from analytical and environmental chemistry research to water purification, waste management, and material technologies (such as in nuclear and electroplating industries).[1–4] Stringent environmental regulations require the treatment of wastewater to remove heavy metals; this requirement is very costly for industries.

The most common metals found in wastewater are copper, cadmium, nickel, lead, and zinc which are toxic at high concentrations.[5,6] The use of synthetic resins for chelating toxic metal ions in wastewater is considered as a possible solution for preventing environmental pollution. These resins are mostly based on petroleum synthetic polymers.[7,8]

Synthetic chelating ion exchange resins are receiving considerable attention because of their application in different areas such as the removal of heavy metals, heterogeneous catalysis, solid electrolytes, ion exchange membrane, ion selective electrode, and purification of industrial waste. The use of chelating resins for selective removal of heavy metals from waste streams has been extensively studied.[9–25] Resins with iminodiacetic acid (IDA) functional group such as Chelex 100, Amberlite IRC 718 (formerly, IRC 718), Purolite S930, and Lewatit TP 207 were mainly applied because of their high selectivity and low manufacturing cost.[9] The IDA group could provide electron pairs for chelation; it forms stable coordinate covalent bonds with divalent metal-ions. For example, the resins Chelex 100 and Amberlite IRC-718 have been used to treat the waste effluent discharged from printed circuit board manufacturing, which contains Cu^{2+}, Ni^{2+}, Co^{2+}, and Cd^{2+}.[26]

One of the few commercial chelating ion exchange resins available is Amberlite IRC-718; its chelating ability is attributed to iminodiacetic groups.[27] This acidic chelating resin has a high affinity and selectivity for heavy metal cations; this is achieved by an iminoacetic acid functionality chemically bonded to macroreticular resin matrix.[7,28] The macroreticular structure of Amberlite IRC-718 provides a number of advantages over traditional gel resins; it is highly resistant to osmotic shock and has improved kinetics of ion exchange.[28] Amberlite IRC-718 was used for several purposes such as extraction of heavy metals (Cu^{2+}, Ni^{2+}, Fe^{2+}, and so forth) from solutions like wine,[29] liquor,[30] stored phenol,[31] sludge,[32] and for ion exchange chromatography.[33] In some studies, it was considered as a reference to study other resins.[34]
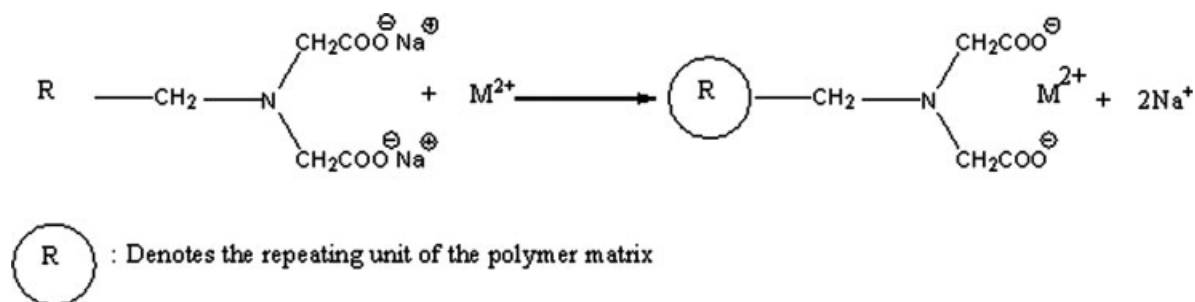
Scheme 1 Ion exchange between metal ions and sodium ions.

In the present work, we have employed the batch equilibration technique and atomic absorption spectrometry to evaluate the sorption properties of the commercially available chelating resin Amberlite IRC-718 toward the divalent metal ions, Fe^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+}, which are present at trace levels in natural aquatic systems. The effect of the different experimental factors such as pH, contact time, metal ion amounts, and mass of resin on the sorption capacity of the resin will be discussed.

EXPERIMENTAL

Reagents

Unless otherwise indicated, all chemicals were obtained from commercial sources and were used as received; the ion exchange resin containing iminodiacetate groups, Amberlite IRC-718, obtained as a sodium salt was purchased from Rohm and Haas, company (USA); bulk density 750 g/L, swelling (%) 30, total exchang capacity 1.35 mequiv/mL,[35] particle size of 16–50 mesh was used without further purification. The following metal ion salts were purchased from Fluka and were also used as received without further purification: Cu(II) acetate, Ni(II) acetate, Zn(II) acetate, and Fe(II) chloride.

Instrumentation

Atomic absorption measurements were carried out with the aid of a Varian Atomic Absorption Spectrophotometer. Samples were shaken using a GFL-1083 shaker thermostated water bath maintained at 25°C.

Sorption of the metal ions on the polymer

The metal chelation characteristics of the resin for each metal ion were studied by the batch equilibrium technique. Duplicate experiments involving 0.100 g of dry, 16–50 mesh size, resin samples were suspended in 25 mL of sodium acetate-acetic acid buffer adjusted to the desired pH with continuous shaking and left for 2 h to equilibrate. To this mixture, 25 mL of metal ion solution containing a total of 15 mg metal-ion were

added. After being shaken for a definite period of time at 25°C, the mixture was filtered, and the amount of metal ion remaining in the filtrate was determined by atomic absorption spectrometry (AAS) using standard solutions for calibration.

The extent of metal-ion uptake was studied under similar experimental conditions, where the contact time was varied from 0.5 to 24 h at 25°C after the solution was equilibrated with distilled water. Similar experiments were also carried out in buffered solutions, in which the pH was varied between 2.0 and 7.0 for a fixed contact time of 6 h.

The effect of resin mass on the metal-ion uptake was also studied using the same general procedure by shaking a suspension of 0.1, 0.2, 0.3, 0.6, 0.8, or 1.0 g of the dry resin in 25 mL of the acetate buffer solution at pH 7.0 for 2 h. To this mixture, 25 mL of buffer solution containing 15 mg of metal-ion were added. The mixtures were then shaken at 25°C for 6 h, filtered, and the amount of metal ion remaining in solution was determined by AAS. The effect of metal-ion concentration was investigated in a similar fashion in buffer solutions containing 0.10 g of dry resin and variable amounts of metal ions at 25°C and a fixed contact time of 6 h.

RESULTS AND DISCUSSION

Rate of metal-ion uptake as a function of contact time

The sorption of various divalent metal ions (Ni^{+2}, Cu^{+2}, Fe^{+2}, and Zn^{+2}) on Amberlite IRC-718 iminodiacetate chelating ion exchanger as a function of contact time was investigated by a batch equilibrium technique. The metal ions displace the sodium ions inside the resin when it was equilibrated with the metal-ion solution as shown in the Scheme 1.

The results for the dependence of the metal ion uptake on contact time for resin are presented in Figure 1. The results indicate fast rates of equilibration; the rates of metal-ion uptake increase in the first 3 h and a steady state is reached within 5–10 h. For Fe(II), about 99% of metal-ion was achieved in the first hour. The rates of metal-ion uptake by various
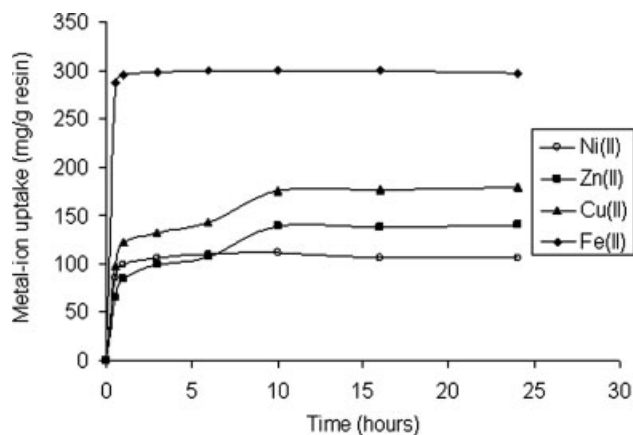
Figure 1 Metal-ion uptake by resin as a function of contact time.

Figure 2 Effect of the pH on metal-ion uptake by the resin.

classes of chelating polymers reported in the literature exhibited a wide range of adsorption rates. In general, the adsorption rates are governed by several factors such as the nature of active chelating groups and repeating units, structural properties of the polymer (porosity, surface area, size, and molar mass), the concentration of metal-ion, the amount of polymer used, and the concentration of other ions that may compete with the metal ion of interest. This makes rate comparisons a subject of great uncertainty.[36]

Results also revealed that the metal-ion uptake follows the order: $Fe^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$; resin shows highest uptake capacity toward Fe(II) and lowest for Ni(II). This difference in capacities observed among the metals by the resin can be explained by the negative steric effect on coordination with the iminodiacetate group.[16] The ionic radius for Fe(II) is 75 pm and for Zn is 88 pm. The stability of the chelate is expected to be less favorable for ions of larger size; this is consistent with earlier investigations.[37–39]

pH dependence of the metal-ion uptake

The binding capacity of the resin toward the investigated metal ions was studied in the pH range 2–7 under continuous shaking for a fixed contact time of 6 h at 25°C; typical pH-binding capacity profiles are displayed in Figure 2. Results reveal that metal-ion uptake increased with pH of the medium and approached a steady state at about pH 6.0. This observation was more pronounced with Fe(II) where the binding capacity of the resin strongly increases with increasing the pH of the medium, whereas the sorption of other metals ions Cu(II), Zn(II), and Ni(II) slightly increases as the pH increases. This behavior could be explained by the nature of the chelating group; the iminodiacetate groups of the Amberlite IRC-718 are weak acids and the degree of
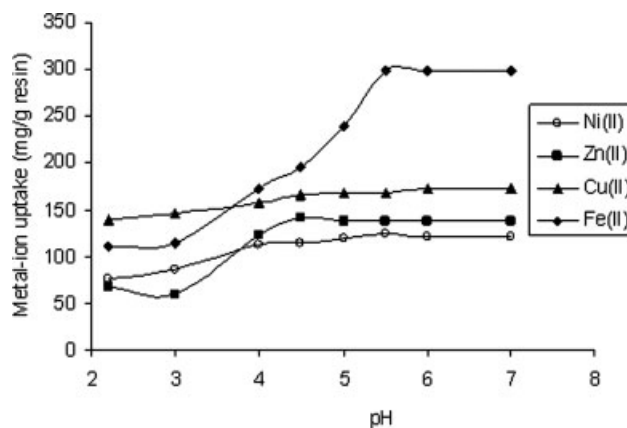
protonation will critically affect the ability of resin to bind metal cations. For this resin, protonation of carboxylate groups and nitrogen atoms is reported to be complete at pH 2.21.[40] A completely deprotonated form of the resin is reached at pH 12.30.[16]

Effect of resin mass on metal-ion uptake

The effect of resin's mass on the rate of metal-ion uptake was investigated using a batch equilibration technique by suspending different masses (0.1, 0.2, 0.3, 0.6, 0.8, or 1.0 g) of the dry resin in 25 mL of the acetate buffer solution at pH = 7.0 for 2 h. Then, 25 mL of buffer solution containing 15 mg of metal-ion was added at 25°C under continuous shaking for 6 h. Results are displayed in Figure 3. Results show that the amount of metal ions adsorbed on the resin increases with the increase of the mass of resin used. This may be explained by the increase of the polymer sites available for chelation when fixed amounts of metal ions are available in solution. In all cases, metal-ions are completely taken out of solution with the presence of 0.8 g of resin.
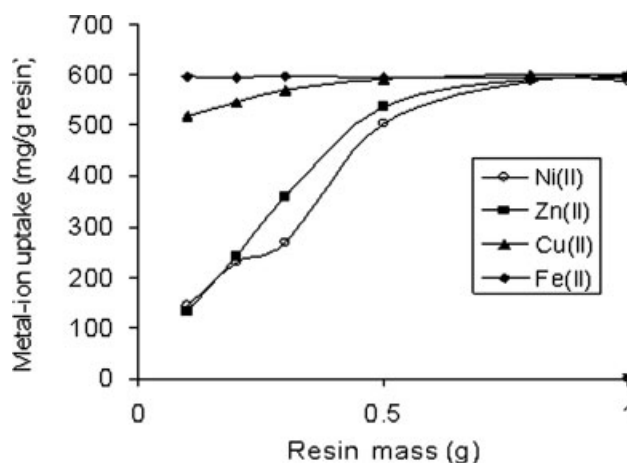

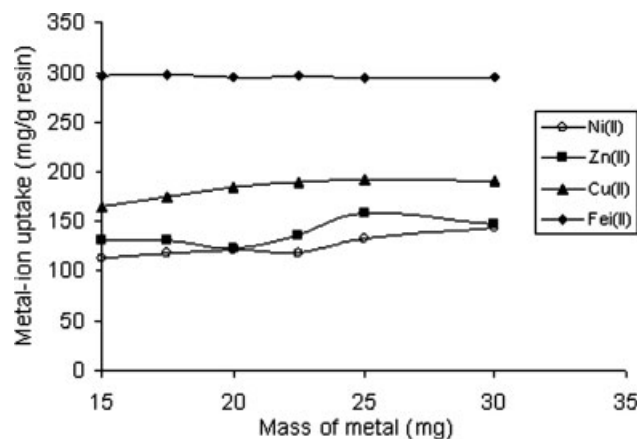**Figure 3** Effect of resin mass on metal-ion uptake by resin.

Figure 4 Effect of initial amount of metal ions on metal-ion uptake by resin.

Effect of metal-ion concentration on metal-ion uptake

The effect of metal-ion concentration on metal-ion uptake was studied by suspending 0.10 g of the dry resin in 25 mL of the acetate buffer solution at pH 7.0 for 2 h followed by the addition of 25 mL of buffer solution containing different amounts of metal-ion. Results shown in Figure 4 reveal that the metal-ion uptake capacity of the resin toward the metal ions does not change considerably with metal ion concentration.

CONCLUSION

In this investigation, we focused on the sorption properties of the commercially available resin, Amberlite IRC-718, a chelating resin containing iminodiacetic acid as ligand attached to the copolymer of styrene and divinyl benzene of macroporous matrix structure, toward some divalent metal-ions in aqueous solutions. The effect of exposure time on the metal-ion uptake was studied by a batch equilibrium technique and showed that a time of 6–10 h was enough to achieve maximum metal-ion sorption and that the extent of metal-ion uptake followed the order $Fe^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. The pH binding capacity profiles showed that the metal-ion uptake of the resin increased with increasing pH and reached a maximum at pH 6.0. The effect of resin mass and metal-ion concentration on the extent of metal-ion uptake were also investigated.

References

1. Karger, B. L.; Martin, M.; Loheac, J.; Guiochon, G. Anal Chem 1973, 45, 496.
2. Helfferich, F. G. Adv Chromatogr 1965, 1, 3.
3. Florence, T. M.; Batley, G. E. Talanta 1976, 23, 179.
4. Brower, J. B.; Ryan R. L.; Pazirandeh, M. Environ Sci Technol 1997, 31, 2910.
5. Vaughan, T.; Seo, C. W.; Marshall, W. E. Biores Technol 2001, 78, 133.
6. Egawas, H.; Nonaka, T.; Abe, S.; Nakayama, M. J Appl Polym Sci 1992, 45, 837.
7. Agrawal, A.; Sahu, K. K.; Rawat, J. P. Solvent Extr Ion Exch 2003, 21, 763.
8. Liu, C. Y.; Chen, M. J.; Lee, N. M.; Hawang, H. C.; Jou, S. T.; Hsu, J. C. Polyhedron 1992, 11, 551.
9. Dabrowski, A.; Hubicki, Z.; Podkoscielny, P.; Robens, E. Chemosphere 2004, 56, 91.
10. Eccles, H.; Greenwood, H. Solvent Extr Ion Exch 1992, 10, 713.
11. Rao, M. G.; Gupta, A. K.; Williams, E. S.; Aguwa, A. A. AICHE Symp Ser 1982, 78, 103.
12. Haas, C. N.; Tare, V. React Polym 1984, 2, 61.
13. Tare, V.; Karra, S. B.; Haas, C. N. Water Air Soil Pollut 1984, 22, 429.
14. Karppinen, T. H.; Pentti, A. Y. Sep Sci Technol 2000, 35, 1619.
15. Korngold, E.; Belayev, N.; Aronov, L.; Titelman, S. Desalination 2001, 13, 383.
16. Malla, M. E.; Alvarez, M. B.; Batistoni, D. A. Talanta 2002, 57, 277.
17. Shah, R.; Devi, S. Anal Chim Acta 1997, 341, 217.
18. Shah, R.; Devi, S. Talanta 1998, 45, 1089.
19. Yang, J.; Renken, A. Chem Eng Technol 2000, 23, 1007.
20. Rao, K. S.; Sarangi, D.; Dash, P. K.; Chaudhury, G. R. J Chem Technol Biotechnol 2002, 77, 1107.
21. Gode, F.; Pehlivan, E. J. Hazard Mater 2003, B100, 231.
22. Mijangos, F.; Diaz, M. Ind Chem Eng Res 1992, 31, 2524.
23. Lehto, J.; Paajanen, A.; Harjula, R.; Leinonen, H. React Polym 1994, 23, 135.
24. Zagorodni, A. A.; Muiraviev, D. N.; Muhammed, M. Sep Sci Technol 1997, 32, 413.
25. Diniz, C. V.; Doyle, F. M.; Ciminelli, V. S. T. Sep Sci Technol 2002, 37, 3169.
26. Lin, L.C.; Juang, R. S. Chem Eng J 2005, 112, 211.
27. Park, C. I.; Cha, K. W. Talanta 1998, 46, 1515.
28. Kocaoba, S.; Akicin, G. Talanta 2002, 57, 23.
29. Kern, M. J.; Wucherpfennig, K. Wein-Wissenschaft 1993, 48, 20.
30. Wucherpfennig, K. Dtsch Lebensm-Rundsch 1992, 88, 313.
31. Brownell, G. L.; Davie, W. R.; Fields, M. C. (Application No US 1981–272141) Ger Offen 1982, 28 pp. DE 3221816 A1 19821230.
32. Lee, I. H.; Kuan, Y.-C.; Chern, J.–M. J Hazard Mater 2006, 138, 549.
33. Cha, K.-W.; Hong, J-W; Choi, B.-D. J Korean Chem Soc 1998, 42, 292.
34. Gonzalez, M. O.; Zamora, R. E.; Diaz, G. C.; Maurelia, R. E.; Guevara, M. A.; Vallejos, L. Congreso Anual-Associacao Brasileira de Metalurgia e Materiais 1995, 9, 109.
35. Fernandez, Y.; Maranon, E.; Castrillon, L.; Vasques, I. J Hazard Mater 2005, 26, 169.
36. Salem, N. M.; Ebraheem, K. A. K.; Mubarak, M. S. React Funct Polym 2004, 59, 63.
37. Ebraheem, K. A. K.; Mubarak, M. S.; Yassien, Z. J.; Khalili, F. Solvent Extr Ion Exch 1998, 16, 637.
38. Ismail, A. I.; Ebraheem, K. A. K.; Mubarak, M. S.; Khalili, F. Solvent Extr Ion Exch 2003, 21, 125.
39. Al-Rimawi, F.; Ahmad, A.; Khalili, F. I.; Mubarak, M. S. Solvent Extr Ion Exch 2004, 22, 721.
40. Schmuckler, G. Talanta 1965, 12, 281.