USE OF IMPREGNATED RESINS AS ADSORBENTS IN VIEW OF HEAVY METALS REMOVAL FROM AQUEOUS SOLUTIONS

Mihaela Ciopec[1*], Zoltán Galbács[2], Corneliu Mircea Davidescu[1], Gabor Galbács[2], Adina Negrea[1], Adriana Popa[3], Petru Negrea[1]

[1] University „Politehnica" Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, Piata Victoriei, no. 2, Timisoara, 300006, ROMANIA
*e-mail: mihaela.ciopec@chim.upt.ro

[2]University of Szeged, Departament of Inorganic and Analytical Chemistry, H-6701 Szeged, P.O.B. 440, Hungary

[3]Romanian Academy, Institute of Chemistry Timisoara of Romanian Academy, Mihai Viteazul Blv., no. 24, Timisoara, 300223, ROMANIA

ABSTRACT

The presence of heavy metal ions in environment is a major concern because of their toxicity to many life forms. Heavy metal ions can be removal from water by adsorption on solid support.
In the present work, we tested the adsorption of metal ions on solvent impregnated resin (SIR). Di-(2-ethylhexyl)-phosphoric acid (D2EHPA) has been chosen as an extractant for the purpose of this study. The interaction between XAD4 resin and D2EHPA was evaluated by physico-chemical methods of analysis (EDX and SEM). The experimental studies on adsorption of metal ions were carried out on Pb^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Ni^{2+}, Fe^{3+}, Zn^{2+} and Ca^{2+}. A separation method was developed for metals ions and was investigated the influence of contact time on the residual concentration of metal ions, on their removal efficiency and on the adsorption capacity of resin towards metal ions.

Keywords: Amberlite XAD4; D2EHPA; Solvent impregnated resin (SIR); Heavy Metals Removal

INTRODUCTION

Heavy metal pollution of industrial wastewaters represents a major problem for the environment, since heavy metal ions are nonbiodegradable, and tend to accumulate in the food chain, which causes varieties of serious health problems. They have remarkably high toxicity; some of them even have been confirmed to be carcinogenic [1-6].
Adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness [1-3, 5]. Many studies are dealing with adsorption and separation of metal with SIR [7]. Amberlite XAD have attractive features are easy regeneration for multiple sorptions-desorption cycles, good mechanical stability and reproducible sorption characteristics.
The present paper investigates the adsorption of metal ions (Pb^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Ni^{2+}, Fe^{3+}, Zn^{2+} and Ca^{2+}) using the SIR prepared by impregnation of Amberlite XAD4 with an organophosphorous extractant D2EHPA. A separation method was developed for metals ions and was investigated the influence of contact time on the residual concentration of metal ions, on their removal efficiency and on the adsorption capacity of resin towards metal ions.

MATERIALS and METODS

The Amberlite XAD4 resin (supplied by Rohm and Hass Co.) was impregnated with D2EHPA trough dry method. The D2EHPA ~ 98.5% used as extractant, was supplied by

BHD Chemicals Ltd Poole England and used as received. Impregnated XAD4 resin was obtained after method previous described [8]. One gram of fresh XAD4 has been placed for 24 h in ethanol (Chimopar Romania) containing 0.1 g/ml extractant (D2EHPA). The polymeric beads have been separated through a porous filter using a vacuum pump, washed with water and dried at 50°C for 24 h.

Adsorption on the XAD4 support macro and interaction between the extractant and support has been emphasized by EDX and SEM analysis using a scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDX) using an Inspect S scanning electron microscope.

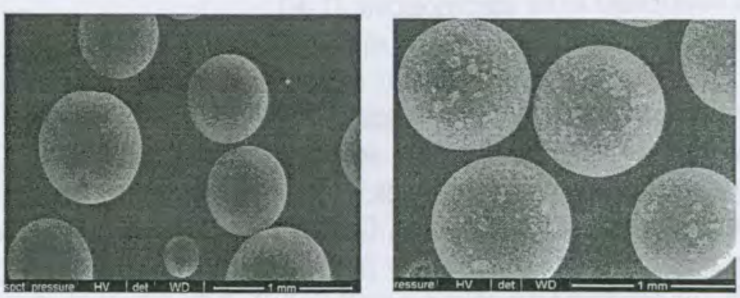
To study the effect of contact time on adsorption of metal ions for experiments was used samples of 0.1g Amberlite XAD4-D2EHPA impregnated resin were mixed at room temperature (27 °C) with 25 mL single metal solution containing 10 mg/L Me^+ (where Me^+ = Pb^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Ni^{2+}, Fe^{3+}, Zn^{2+} and Ca^{2+}) at several shake times (15, 30, 45, 60, 90 and 120min). Adsorption of metal ions on impregnated resin was studied in single component solutions and in solutions containing all cations (in this solution the concentration of each cation was of 10 mg/L). For batch experiments a mechanical shaker bath MTA Kutesz, Hungary was used.

The suspensions were filtered and the concentration of metal ions in the filtrate was determined by means of atomic absorption spectrometry using a Varian SpectrAA 280 Fast Sequential Atomic Absorption Spectrometer with an air-acetylene flame at wavelengths λ=217 nm (Pb^{2+}), λ =324.8 nm (Cu^{2+}), λ=228.8 nm (Cd^{2+}), λ=357.9 nm (Cr^{3+}), λ=232 nm (Ni^{2+}), λ=248.3 nm (Fe^{3+}), λ=213.9 nm (Zn2+) and λ=422.7 nm (Ca^{2+}). All other chemicals used for experiments were of analytical reagent grade, and were used without further purification. Distilled water was used in all experiments.

RESULTS

1. Evaluation of the impregnation process

Adsorption on the XAD4 support macro and interaction between the extractant and support has been emphasized by EDX and SEM analysis. The appearance and morphology of the external protective barrier was examined by scanning electron microscopy. The internal structure of the polymeric adsorbent (Amberlite XAD4) before and after the impregnation is shown in Figure1. The EDX spectrum of Amberlite XAD4 after impregnation is presented in Figure 2. One may notice the presence of the characteristic peak of phosphorus. This also proves the adsorption of D2EHPA on the XAD4 support.



(a) (b)

Figure 1. SEM images of XAD4 (a) before impregnation and (b) after impregnation with D2EHPA

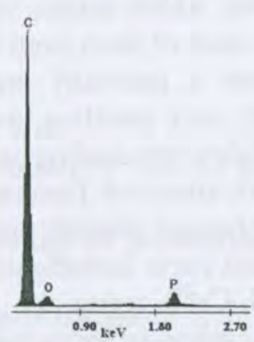


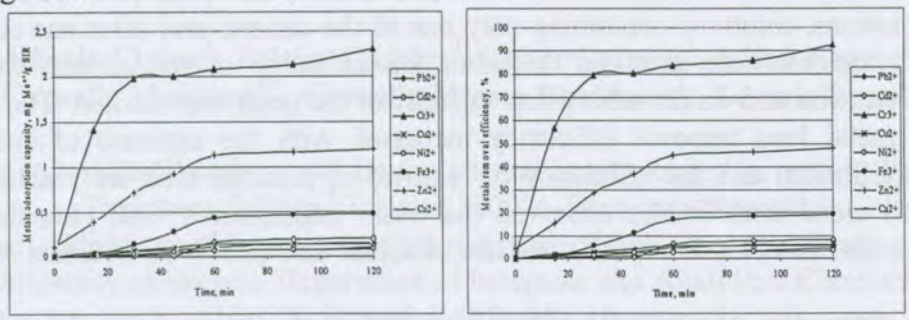
Figure 2. EDX spectrum of XAD4–D2EHPA

We may notice the presence of the characteristic peak of phosphorus and phosphorus content is 1.02%.

2. Retention of metal ions on XAD4-D2EHPA impregnated resin

2.1. Retention of metal ions from single component solutions

Experimental data regarding the influence of contact time on the adsorption capacity and on the efficiency of removal of metal ions on the XAD4-D2EHPA impregnated resin are shown in Figure 3.



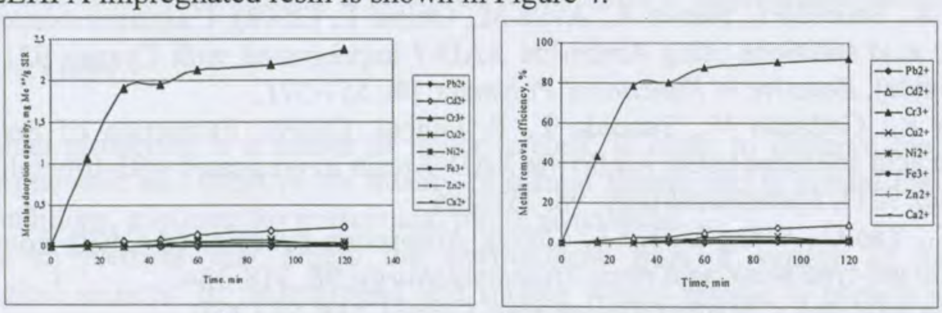
(a) (b)

Figure 3. Influence of contact time on the metal ions adsorption capacity (a) and on the efficiency of removal of metal ions (b) from single component solutions

The experimental data show the increase of the adsorption capacity and the efficiency of removal of metal ions as the contact time increases. Adsorption equilibrium and the efficiency of removal of metallic ions are reached after 60 minutes for all metal ions. The impregnated XAD4 resin with phosphate groups shows higher affinity for trivalent ion (Cr^{3+}) and for divalent ion (Zn^{2+}). One may notice that the efficiency of removal of metallic ions on XAD4-D2EHPA impregnated resin, reaching values ~95% for Cr^{3+} and ~50% for Zn^{2+}. For other metal ions studied the efficiency of removal is lower (<18%).

2.2. Retention of metal ions from mixed cation solutions

Experimental data regarding the influence of contact time on the adsorption capacity and on the efficiency of removal of metal ions from solutions containing a mixture of cations on XAD4- D2EHPA impregnated resin is shown in Figure 4.



(a) (b)

Figure 4. Influence of contact time on the metal ions adsorption capacity (a) and on the efficiency of removal of metal ions (b) from mixed cation solutions

The experimental data show the increase of the adsorption capacity and of the efficiency of removal of metal ions as the contact time increases. Adsorption equilibrium and the efficiency of removal of metallic ions are reached after 60 minutes for all metal ions. One may notice that the resin retains selectively for Cr^{3+} from the cationic mixture. Chromium is not affected by the presence of the other cations in solution; a ~ 95% removal efficiency was reached, as for the solution containing only Cr^{3+}. For other metal ions from the mixture was observed that retention efficiencies are <7%, somehow lower than the values reached for single component solutions.

CONCLUSIONS

Amberlite XAD4 resin was impregnated with D2EHPA by dry method. The impregnation was evaluated by SEM and EDX analysis. These techniques proved the adsorption of D2EHPA on the XAD4 support. To study the possibility of using impregnated resin as adsorbent material in view to remove metal ions (Pb^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Ni^{2+}, Fe^{3+}, Zn^{2+} and Ca^{2+}) from solutions, solutions containing only one of the cations and solutions containing a mixture of all cations were used. In this aim, the influence of the contact time on the efficiency of retention and on the adsorption capacity of the resin was studied. The adsorption capacity and metal ions removal efficiency increased with the increase of contact time. Adsorption equilibrium and the efficiency of removal of metallic ions are reached after 60 minutes for all metal ions. It was observed that resin impregnated with phosphate groups shows affinity for trivalent ion (Cr^{3+}) and for divalent ion (Zn^{2+}) in solution with single component.

At the same time, the adsorption process occurred with the best results when single component solutions were used. When mixed cation solutions were used, the efficiency of adsorption is somehow lower, due to competition between metal ions present in the solutions. Chromium was not affected by the presence of the other cations in solution;
a ~ 95% removal efficiency was reached in both situations.

ACKNOWLEDGEMENTS

This work was partially supported by the strategic grant POSDRU/89/1.5/S/57649, Project ID 57649 (PERFORM-ERA), co-financed by the European Social Fund – Investing in People, within the Sectoral Operational Programme Human Resources Development 2007-2013.

LIST OF REFERENCES

[1] Hosseini-Bandegharaei A., Hosseini M.S., Sarw-Ghadi M., Zowghi S., Hosseini E., Hosseini-Bandegharaei H., (2010), Kinetics, equilibrium and thermodynamic study of Cr(VI) sorption into toluidine blue o-impregnated XAD-7 resin beads and its application for the treatment of wastewaters containing Cr(VI), *Chemical Engineering Journal*, **160**, 190-198.

[2] Navarro R., Saucedo I., Nunez A., Avila M., Guibal E, (2008), Cadmium extraction from hydrochloric acid solutions using Amberlite XAD-7 impregnated with Cyanex 921 (tri-octyl phosphine oxide), *Reactive & Functional Polymers*, **68**, 557-571.

[3] Navarro R., Gallardo V., Saucedo I., E. Guibal, (2009), Extraction of Fe(III) from hydrochloric acid solutions using Amberlite XAD-7 resin impregnated with trioctylphosphine oxide (Cyanex 921), *Hydrometallurgy*, **98**, 257-266.

[4] Xiong C., Yao C., Wang L., Ke J., (2009), Adsorption behavior of Cd(II) from aqueous solutions onto gel-type weak acid resin, *Hydrometallurgy*, **98**, 318-324.
from aqueous solutions, *Chemical Engineering Journal*, **155**, 844-850.

[5] Benamor M., Bouariche Z., Belaid T., Draa M.T., (2008), Kinetic studies on cadmium ions by Amberlite XAD7 impregnated resins containing di(2-ethylhexyl) phosphoric acid as extractant, *Separation and Purification Technology*, **59**, 74-84.

[6] Pehlivan E., Altun T., (2006), The study of various parameters affecting the ion exchange of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solution on Dowex 50W synthetic resin, *Journal of Hazardous Materials*, **B134**, 149-156.

[7] Draa M.T., Belaid T., Benamor M., (2004), Extraction of Pb(II) by XAD7 impregnated resins with organophosphorus extractants (D2EHPA, IONQUEST 801, CYANEX 272), *Separation and Purification Technology*, **40**, 77-86.

[8] Davidescu C. M., Ciopec M., Negrea A., Popa A., Lupa L., Negrea P., Muntean C., Motoc M., Use of Di-(2-Ethylhexyl) Phosphoric Acid (D2EHPA) Impregnated XAD7 Copolymer Resin for the Removal of Chromium (III) from Water, *Rev. Chim. (Bucharest)*, **62(7)**, 2011