

Removal of Heavy Metals from Wastewater Using Synthetic Ion Exchange Resin

T. BORKLU BUDAK

Department of Chemistry, Faculty of Science and Art, Yildiz Technical University, 34220 Davutpasa, Istanbul, Turkey

Corresponding author: Tel: +90 212 3834150; E-mail: tborklu@yildiz.edu.tr; turkanborklu@yahoo.com

(Received: 13 April 2012;

Accepted: 4 February 2013)

AJC-12928

There are many methods available to remove heavy metal ions from wastewater and default water alike. Among all the available methods, ion exchange is considered to be the most simple and efficient one. Two strong acid cation-exchanger resins, Amberlite 252 and Amberjet 1200 were used for the removal of copper(II) and zinc(II) from synthetic rinsewater. The accumulated information of the comparison mentioned above was shown in column system as concentration copper(II) 350 mg/L and zinc(II) 600 mg/L, flow rate of 2.5 mL/min and 35 g of adsorbent. The results obtained show that the Amberjet 1200 strong cation-exchange resin performed well for the adsorbed these two metals from synthetic rinsewater of the electroplating industries.

Key Words: Copper(II), Zinc(II), Ion exchange resin, Wastewater.

INTRODUCTION

Now-days, water plays an important role in human beings, natural environment and social development, but the subsequences of water use are municipal wastewaters and industrial wastewaters. Therefore, how to treat wastewaters and make them reusable is not only an important task but also an urgent problem to be solved¹. Pollution by heavy metals is currently of great concern, due to the increased awareness of the potentially hazardous effects of elevated levels of these materials in the environment^{2,3}.

Many plating industries release heavy metals such as cadmium, lead, chromium, copper, zinc, iron and nickel in wastewaters. These heavy metals that find many useful applications in our life are very harmful if discharged into natural water resources and pose a serious health hazard⁴⁻¹².

The most popular method to treat heavy metal containing wastewaters is chemical precipitation that uses alkaline to raise the solution pH to allow the formation of heavy metal hydroxide precipitate followed by filtration or other solid/liquid separation processes. Although the chemical precipitation method is quite effective for heavy metal removal, the resultant heavy metal sludge is classified as a hazardous solid waste and needs to be adequately treated. Sometimes, treating heavy metal sludge is more difficult than treating heavy metal-containing wastewaters. Therefore, other methods such as electrodialysis¹³⁻¹⁷, reverse osmosis^{16,17}, biosorption including some economic bio-adsorbent¹⁸⁻²³, adsorption²⁴⁻²⁸ and ion exchange process are developed to remove heavy metals from industrial wastewaters. Among

the heavy metal removal processes, ion exchange process is very effective to remove various heavy metals and can be easily recovered and reused by regeneration operation. Ion-exchange resins are a variety of different types of exchange materials, which are distinguished into natural or synthetic resin. Furthermore, it can be as well categorized on the basis of functional groups such as cationic exchange resins, anion exchange resins and chelating exchange resins. Depending on the functional groups, ion-exchange resin can deal properly with several heavy metals such as copper, nickel, cobalt, cadmium, zinc and aluminum²⁹⁻³² in addition to remove heavy metals from industrial wastewater, ion-exchange resin can facilitate heavy metal extraction from sludge by shifting the thermodynamic equilibrium of $M(OH)_{2(s)} \leftrightarrow M^{2+} + 2OH^{-}$.

Ion exchange using polymeric resins has been used successfully to recover heavy metals from wastewaters and process streams³³⁻³⁷. Many studies on the removal of metal ions by ion exchange resins have been conducted³⁸⁻⁴⁹. It has been reported that ion exchange is able to overcome some of the problems encountered in other techniques.

In this work, the comparison of the exchange capacity of Cu^{2+} and Zn^{2+} from synthetic rinsewater of electroplating industry with Amberlite 252 and Amberjet 1200 strong acid cation-exchanger resins were investigated. Successful design of column system generally requires prediction of the break-through curves for the effluents. The maximum exchange capacity of resin column is also needed in design. Hence, breakthrough curves are investigated in the system⁵⁰.

EXPERIMENTAL

Commercial synthetic Amberlite 252 and Amberjet 1200 strong acid cation-exchange resin in hydrogen form was obtained from Rohm and Haas Company. The properties of the resin are given in Table-1. For conditioning of resin, after three preliminary recycling of the resin in column system with 1 M HCl and NaOH solutions to remove eventual chemicals residues (solvents, functionalizing agents) trapped in the resins' matrixes during their preparation, the samples were finally converted in hydrogen forms by 1 M HCl.

TADIE 1

PROPERTIES OF AMBERJET 1200 AND AMBERLITE 252 RESINS		
Properties	Amberjet 1200 (Na ⁺	Amberlite 252 (Na ⁺
•	form)	form)
Functional groups	- SO ₃ -	-SO ₃ -
Ionic form as shipped	Na ⁺	Na ⁺
Total exchange capacity	\leq 2.0 eq/L (Na ⁺ form)	\geq 1.8 eq/L (Na ⁺ form)
Minimum bed depth	800 mm	700 mm
Service flow rate	5 to 50 BV*/h	5 to 170 BV*/h
Regenerant	HCl	HCl
Flow rate (BV/h)	2 to 5	4 to 6
Concentration (%)	4 to 10	4 to 10
Level (g/L)	40 to 150	45 to 150
Minimum contact time	20 min	30 min
Slow rinse	2 BV at regeneration	2 BV at regeneration
	flow rate	flow rate
Fast rinse	1 to 3 BV at service	2 to 4 BV at service
	flow rate	flow rate
$(1 \text{ DV} (D + 1) \text{ V} + 1)$ $(1 \text{ m}^3 + 1)$		

 $1 \text{ BV} (\text{Bed Volume}) = 1 \text{ m}^3 \text{ solution per m}^3 \text{ resin}$

Solution preparation and reagents: The solutions of Cu(II) (350 mg/L) and Zn(II) (600 mg/L) were prepared by dissolving of analytical grade CuCl₂.2H₂O and ZnCl₂ from Merck, Germany, respectively. HCl and NaOH were purchased from Merck. Water was deionized and purified further with a Milli-Q water purification system (Millipore, USA). Freshly prepared solutions were used throughout the experiments.

Varian 220 AA model atomic absorption spectrometer operating with an air-acetylene flame was used to analyze the concentration of Cu(II) and Zn(II) in solutions. Calibration curves were prepared between 2 and 10 mg/L. Precision of the paralel measurements was as ±3 % SD. The pH measurements were carried out with a glass electrode (WTW 440i Model pH meter).

Data analysis: In addition, the percentage of Cu(II) and Zn(II) ions removed from the aqueous solution by Amberlite 252 and Amberjet 1200 resins were calculated using eqn. (1):

$$\% R = [(C_i - C_t)/C_i] \times 100$$
(1)

where R per cent of removed metal from aqueous solution (%); C_i initial metal ions concentration (mg/L); C_t metal ion concentration in solution at time t (mg/L).

Column experiments: In the column experiment, sorption in system was performed in a fixed-bed glass column with 1.0 cm internal diameter and 35 cm height, packed with 30 cm³ of resin. The addition of glass wool beads was added to improve the flow distribution. The schematic diagram of the fixed-bed glass column system is shown in Fig. 1. Copper (II) and zinc(II) ions solution having an initial concentration

of 350 mg/L and 600 mg/L, respectively, synthetic waste rinsewater from plating industry were used through column at a constant flow rate of 2.5 mL/min and 4 mL/min respectively. The effluent solution outlet of the ion-exchanger column was collected at different time intervals and analyzed for Cu(II) and Zn(II) content using atomic absorption spectrometer. The solutions were diluted appropriately prior to analysis. Breakthrough curves for the copper and zinc adsorption on the resin were obtained by plotting volume of the passing solution against the ratio of Cu(II) and Zn(II) ions concentrations in the effluent and in the influent solutions (C_i/C_t) throughout the column.



Fig. 1. Equipment for column adsorption experiment

RESULTS AND DISCUSSION

In this study, adsorption properties of copper(II) and zinc(II) on Amberlite 252 and Amberjet 1200 strong cationic resins has been studied by using columns technique. The results are given in Figs. 2-5.





0,5

Fig. 3. Breakthrough curve of copper(II) for Amberjet 1200



Fig. 5. Breakthrough curve of zinc(II) for Amberjet 1200

Effect of adsorbent type: The adsorbent type is important parameter to obtain the quantitative uptake of metal ion. The retention of metals was examined in the relation to the type of adsorbent. The results of the dependence of Cu(II) and Zn(II) adsorption on the Amberlite 252 and Amberjet 1200 are shown in Figs. 6 and 7. For this purpose, the concentration of metals were fixed at 350 mg/L of Cu(II) and 600 mg/L of Zn(II) and 2.5 mL/min and 4.0 mL/min, respectively, while the amount of resin was 30 cm. The percentage adsorption values were increased with Amberjet 1200 strong cationic resin for Cu(II) and Zin(II).



Fig. 6. Comparison of Amberjet 1200 and Amberlite 252 performance for removal of copper(II)

Conclusion

In this study, the effects of the types of resin on removal of copper and zinc metal ions from synthetic waste rinsewater were investigated. According to these experimental results, it was demonstrated that Amberjet 1200 is a strong acid cationexchange resin has good capability and efficiency for the removal of these metals from waste rinsewater medium. Studied conditions were found at a 350 mg/L of Cu(II) and 600 mg/L of Zn(II) and 2.5 mL/min and 4.0 mL/min, respectively, while the amount of resin was 30 cm³.



Fig. 7. Comparison of Amberjet1200 and Amberlite252 performance for removal of zinc(II)

The postulated reaction scheme for ion exchange is as follows:

 $2R\text{-}SO_3\,H+M^{2+} \rightarrow (R\text{-}SO_3)_2\,M+2H^+$ (on strongly acidic resin) $M=Cu^{2+},\,Zn^{2+}$

The experimental results were showed that Amberjet 1200 strongly cation exchange resin is more useful to recovery of Cu(II) and Zn(II) from electroplating industry waste rinse water than Amberlite 252. Amberjet 1200 has more capacity than the Amberlite 252.

The treatment for the recovery of copper(II) and zinc(II) from electroplating industry waste rinse water has been proposed that is applicable to small and medium metal plating plants. Thus, when the amounts of rinse water relatively small, recycling of copper and zinc may be economical in such plants and consequently, the municipal sewage system would not be severely contaminated with these toxic pollutants.

REFERENCES

- 1. I.H. Lee, Y.C. Kuan and J.M. Chern, J. Chinese Inst. Chem. Eng., 38, 71 (2007).
- 2. S. Kocaoba, J. Hazard. Mater., 147, 488 (2007).
- 3. S.S. Gupta and K.G. Bhattacharyya, J. Colloid Interf. Sci., 295, 21 (2006).
- P.G. Priya, C.A. Basha, V. Ramamurthi and S.N. Begum, J. Hazard. Mater., 163, 899 (2009).
- 5. E. Denkhaus and K. Salnikow, Oncol./Hematol., 42, 35 (2002).
- 6. E.F. Pane, J.G. Richards and C.M. Wood, Aquat. Toxicol., 63, 65 (2003).
- N.R. Axtell, S.P.K. Sternberg and K. Claussen, *Bioresour. Technol.*, 89, 41 (2003).
- 8. N. Akhtar, J. Iqbal and M. Iqbal, J. Hazard. Mater., B108, 85 (2004).
- 9. E.F. Pane, A. Haque and C.M. Wood, Aquat. Toxicol., 69, 11 (2004).
- 10. E.F. Pane, C. Bucking, M. Patel and C.M. Wood, *Aquat. Toxicol.*, **72**, 119 (2005).
- E.F. Pane, M.D. McDonald, H.N. Curry, J. Blanchard, C.M. Wood and M. Grosell, *Aquat. Toxicol.*, 80, 70 (2006).
- E.F. Pane, M. Patel and C.M. Wood, *Comp. Biochem. Physiol.*, *Part C*, 143, 78 (2006).
- T. Mohammadi, A. Razmi and M. Sadrzadeh, *Desalination*, 167, 379 (2004).
- T. Mohammadi, A. Moheb, M. Sadrzadeh and A. Razmi, Sep. Purif. Technol., 41, 73 (2005).
- 15. B. Schlichter, V. Mavrov, T. Erwe and H. Chmiel, *J. Membr. Sci.*, **232**, 99 (2004).
- A.P. Kryvoruchko, I.D. Atamanenko and L.Y. Yurlova, *J. Membr. Sci.*, 228, 77 (2004).

- 17. Z. Ujang and G.K. Anderson, Water Sci. Technol., 38, 521 (1998).
- 18. Z. Aksu and G. Do"nmez, J. Environ. Sci. Health, A36, 367 (2001).
- 19. K.G. Bhattacharyya and A. Sharma, J. Hazard. Mater., B113, 97 (2004).
- J.R. Evans, W.G. Davids, J.D. MacRae and A. Amirbahman, *Water Res.*, 36, 3219 (2002).
- 21. A. Kapoor and T. Viraraghavan, Bioresour. Technol., 63, 109 (1998).
- 22. Y. Sag and T. Kutsal, Chem. Eng. J., 60, 181 (1995).
- 23. C.R.T. Tarley and M.A.Z. Arruda, Chemosphere, 54, 987 (2004).
- J.H. Choi, S.D. Kim, S.H. Noh, S.J. Oh and W.J. Kim, *Micropor. Mesopor. Mater.*, 87, 163 (2006).
- 25. M.A. Tandel And B.N. Oza, Asian J. Chem., 17, 415 (2005).
- 26. S.J. Park and Y.M. Kim, Mater. Sci. Eng., A391, 121 (2005).
- 27. J.H. Suh and D.S. Kim, J. Chem. Technol. Biotechnol., 75, 279 (2000).
- B. Yu, Y. Zhang, A. Shukla, S. Shukla and K.L. Dorris, J. Hazard. Mater., B80, 33 (2000).
- M. Ersoz, E. Pehlivan, H.J. Duncan, S. Yildiz and M. Pehlivan, *Reactive Polym.*, 24, 195 (1995).
- Y. Ferna´ndez, E. maranon, L. Castrillon and I. Vazquez, J. Hazard. Mater., B126, 169 (2005).
- 31. R. Kiefer and W.H. Holl, Ind. Eng. Chem. Res., 40, 4570 (2001).
- 32. A. Kilislioglu and B. Bilgin, Appl. Radiat. Isot., 58, 155 (2003).
- 33. J. Yang and A. Renken, Chem. Eng. Technol., 23, 1007 (2000).
- 34. S. Chand, Seema, Arti and C.V. Chahal, Asian J. Chem., 24, 1297 (2012).

- 35. F. Gode and E. Pehlivan, J. Hazard. Mater., B100, 231 (2003).
- 36. S.H. Lin and C.D. Kiang, Chem. Eng. J., 92, 193 (2003).
- A. Dabrowski, Z. Hubicki, P. Podkoscielny and E. Robens, *Chemosphere*, 56, 91 (2004).
- 38. S. Rengaraj and S.H. Moon, Water Res., 36, 1783 (2002).
- M.E. Malla, M.B. Alvarez and D.A. Batistoni, *Talanta*, **57**, 277 (2002).
 R.K. Sharma, N. Bhojak, S. Mittal and B.S. Garg, *Microchem. J.*, **61**,
- 94 (1999).
 41. J. Lehto, A. Paajanen, R. Harjula and H. Leinonen, *React. Polym.*, 23, 135 (1994).
- 42. L.C. Lin and R.S. Juang, Chem. Eng. J., 112, 211 (2005).
- M.G. Rao, A.K. Gupta, E.S. Williams and A.A. Aguwa, *AIChE Symp. Ser.*, 78, 103 (1982).
- 44. C.N. Haas and V. Tare, *React. Polym.*, 2, 61 (1984).
- 45. V. Tare, S.B. Karra and C.N. Haas, *Water, Air, Soil Pollut.*, **22**, 429 (1984).
- E. Korngold, N. Belayev, L. Aronov and S. Titelman, *Desalination*, 133, 83 (2001).
- 47. T.H. Karppinen and A.Y. Pentti, Sep. Sci. Technol., 35, 1619 (2000).
- 48. F. Gode and E. Pehlivan, J. Hazard. Mater. B, 100, 231 (2003).
- 49. F. Mijangos and M. Diaz, Ind. Chem. Eng. Res., 31, 2524 (1992).
- 50. H.A. Thomas, J. Am. Chem. Soc., 66, 1664 (1944).