Asian Journal of Chemistry Vol. 19, No. 5 (2007), 3963-3970

Removal of Cadmium from Water Using Clinoptilolite

MUSTAFA KARATAS
Department of Environmental Engineering, Faculty of Engineering & Architecture
Selcuk University, 42031 Konya, Turkey
E-mail: mkaratas@selcuk.edu.tr

The present study examined the use of clinoptilolite for the removal of cadmium from aqueous solutions. The effects of pH and contact time on the adsorption process were examined. The optimum pH for adsorption was found to be 5.0. A decrease in the clinoptilolite concentration with a constant cadmium concentration or an increase in the cadmium concentration with a constant clinoptilolite concentration, increased cadmium loading per unit weight of the adsorbent. As a result, the maximum removal efficiency levels obtained were as follows; 95.32 % for the clinoptilolite at pH 5.0 and contact time 15 min.

Key Words: Cadmium, Clinoptilolite, Removal efficiency, Adsorption.

INTRODUCTION

Heavy metals are very harmful to humans, animals and plants[1]. Federal and local agencies have therefore established certain limits on quantities of heavy metals being discharged into environment. Cadmium, which was predominantly used in this study show acute toxicity caused by inhalation of cadmium fumes or dust, which are produced by heating this metal[2,3]. Cadmium, released into natural waters by industrial and domestic wastewater discharges[4]. In humans, cadmium is accumulated in the kidneys, which will begin to at overdoses spilling proteins in urine and disrupting protein metabolism[5]. It is well known that chronic cadmium toxicity has been the cause of Japanese Itai-Itai disease[6]. The contamination of surface and ground water by heavy metals as a result of the disposal industrial and domestic waste has become a very serious problem[7]. Low-level heavy metal pollution of river, lake and ocean environments is now widespread and because heavy metals are concentrated in the food-chain, this causes damage to aquatic ecosystems as well as being a danger to human health[8,9].

However, cadmium also has practical applications; *e.g.*, it is highly corrosion resistant and is used as a protective coating for iron, steel and copper. The industrial uses of cadmium are widespread and increasing in electroplating, paint pigments, plastics, silver-cadmium batteries[10], smelting[11], cadmium-nickel batteries, stabilizers, phosphate fertilizer, mining, and alloy industries[12]. The global annual production of cadmium is around 20.000 tons[3].

Removal of cadmium before discharged into environment can be accomplished by a number of processes such as chemical precipitation[13], electrolytic techniques, evaporation exist[14], cementation, solvent extraction, reverse osmosis and ion exchange[15]. Some of these technologies are pH sensitive, they cannot target specific metals, they cannot remove extremely low or high concentrations of metals, and most create sludges that must be disposed as hazardous waste[16]. Traditional methods of removal such as chemical precipitation, coagulation, sorption, ion-exchange and membrane processes are either expensive[17,18] or do not allow one to reduce heavy metals to the levels dictated by the ever more stringent regulations[19]. Among these the ion-exchange process is probably the most attractive, especially because, instead of synthetic ion-exchange resins, it possible to use low-cost sorbents as natural zeolites[20,21].

Contrary to organic resins, natural zeolits show higher cation selective, good resistance to temperature and excellent compatibility with the environment[22]. Regardless of the large volume of research conducted to determine the chemical, surface and ion-exchange properties, practical application of natural zeolites to water treatment technology is still limited. Among the main reasons, one could mention the lack of clear-cut mathematical description of process equilibrium, mainly in multi-component systems[19].

Natural zeolites, due to their large surface areas, high cation exchange capacities, favourable hydraulic characteristics and low cost, are a major class of materials being considered for adsorption of different species. Zeolites possess a net negative structural charge resulting from isomorphic substitution of cations in the crystal lattice[23]. This permanent negative charge results in the favourable ion exchange selectivity of zeolites for certain cations and makes natural zeolites of interest for use in the treatment of nuclear, municipal and industrial wastewaters. This negative charge also causes natural zeolites to have little or no affinity for anions[24-26].

Clinoptilolite has been shown to selectively remove cesium and strontium ions from radioactive wastewater[27] and it use for removing other dissolved heavy metal cations is receiving increasing attention. Considerable research has been conducted to characterize the chemical, surface and ion exchange properties of clinoptilolite[28,29]. Zeolites are highly selective for ion exchange of many toxic metal ions[30] and especially, the natural clinoptilolite zeolite has been applied largely for the removal of pollutants from wastewater[31].

In this study, a detailed study of the effect of natural clinoptilolite addition has been carried out. Clinoptilolite is an economical and easy to find material, on the removal of the cadmium with various dosages, pH and contact time.

EXPERIMENTAL

The clinoptilolite [$Na_6(Al_6Si_3O_{72})\cdot 24H_2O$] samples were provided from Manisa (Turkey). X-ray diffraction analysis showed that this material was 70 % clinoptilolite, and the remainder consisted of mordenite, muscovite and quartz[32]. The chemical composition of zeolite samples was estimated by using X-ray micro-analysis (Table-1).

TABLE-1
CHEMICAL COMPOSITION OF ZEOLITE MATERIALS (%)

Zeolitic material	SiO_2	Al_2O_3	CaO	K_2O	Na_2O	Fe_2O_3	MgO
Rude grains	68.96	12.45	2.53	3.52	1.34	0.82	1.40
Fine grains	69.12	12.05	2.23	3.61	0.32	0.98	1.30

All the chemical compounds used to prepare the reagent solutions, were of analytical reagent grade (Merck). $CdSO_4\cdot 7H_2O$ was used for make up of synthetic cadmium solutions. Analytical grade NaOH and HCl was used to make adjustments in the pH levels of the solution. Distilled water was used throughout the experiments.

Gallenkamp model thermal stirrer was used for the batch experiments. The metal solution was filtered through 0.45 μm pore size membrane filters after settling. It was analyzed using the Perkin Elmer ICP-AES. The pH measurements were performed with Jenway 3010 digital analyzer with a combination electrode.

Dosage studies were conducted at room temperature (22 ± 1ºC) by varying the mass of clinoptilolite. Representative masses (0.05, 0.5, 1, 1.5, 2, 2.2, 2.4, 2.5, 2.6, 2.8, 3, 3.5 and 4 g) of clinoptilolite were mixed with 100 mL of the solution containing 25 mg/L of cadmium with pH of *ca.* 6.7 and the sorption time was 0.5 h. The samples were shaken at 200 rpm. The cadmium concentration at the end of the study period was determined after filtering the samples. The experiment was repeated two times.

pH studies were conducted by shaking 100 mL of metal solution containing *ca.* 25 mg/L of cadmium, 2.4 g of clinoptilolite for 0.5 h, over a range of initial pH values from to 2.0 to 9.0. Filtered samples were used for analyzing the cadmium ion concentrations. The experiment was conducted in duplicates and mean values were used in the analysis of the data. An optimum pH was selected for further studies.

Contact time experiments were conducted at optimum pH to study effects of pH on the equilibrium time required for the adsorption of cadmium on clinoptilolite. The initial cadmium concentration of metal ion was adjusted to approximately 25 mg/L and pH of the solutions was adjusted using 1 N NaOH or HCl solution. After adjusting the pH of the solution 2.4 g of clinoptilolite was added to 100 mL of the metal solutions 250 mL conical flasks.

Upon determining the equilibrium time for the optimum pH, the cadmium removal by clinoptilolite was studied at much closer intervals of time. For this, a separate set of experiments were run at pH 5 and the samples were collected at 5, 10, 15, 30, 45, 60, 90 min and 24 h. Upon collection, samples were filtered and analyzed for cadmium.

RESULTS AND DISCUSSION

At a pH of *ca.* 6.7 the sorption of Cd on the clinoptilolite was around 2.4 g clinoptilolite. Experiments with mixtures of Cd ion in contact with clinoptilolite were performed at different clinoptilolite dosages. The initial concentration of metal ion was approximately 25 mg/L, the solution pH was 6.7 and the adsorption time 0.5 h. The results are shown in Fig. 1.

It was noted that the adsorption performance of these materials was comprable to that of other biomaterials when the tests were carried out under similar conditions; pine bark[3], perlite[4], clinoptilolite[33] and Accacia bark[34], removed about 84.7 % of Cd^{2+}, 55 % of Cd^{2+}, > 95 % of Cd^{2+} and 91 % of Cd^{2+}, from solution, respectively. In this work, 96.3 % of Cd^{2+} removal was obtained with addition of 2.4 g clinoptilolite in 100 mL sample containing 25 mg/L cadmium ion (Fig. 1).

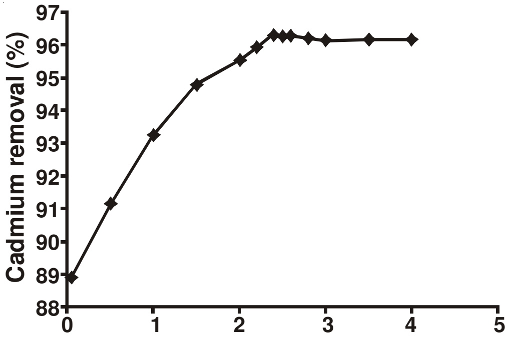

Fig. 1. Effect of clinoptilolite dosage on cadmium adsorption

Additional adsorption experiments with Cd on clinoptilolite were performed at different pH values, the results of which are shown in Fig. 2. The removal of cadmium by adsorption on clinoptilolite was found to increase from 61.04 to 97.28 % when the pH was increased from 2 to 9. The plot of pH *vs.* percentage cadmium removed (Fig. 2) has two inflection points; one at pH 5, where significant adsorption of cadmium actually begins and the other at pH 9, where the adsorption increases drastically.

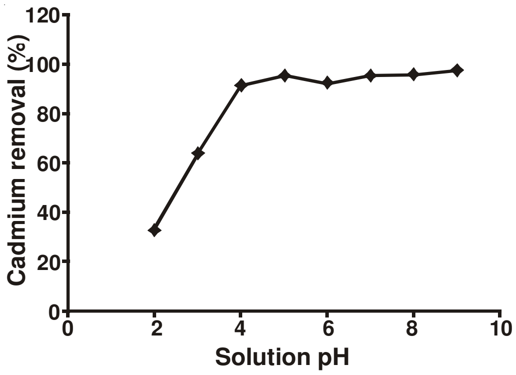

Fig. 2. Effect of pH on cadmium adsorption by clinoptilolite

The adsorption efficiency increased with an increase in the pH of the solution. At low pH values, the higher H^+ concentration reduced the removal of heavy metals significantly, probably because small H^+ ions competed with the divalent cations for sorption sites on clinoptilolite. At higher pH values, the hydrolyzed metal species were more amenable to sorption onto clinoptilolite[35]. In neutral or basic environments, hydrogen bonding of the hydroxy-metal complex with the clinoptilolite surface, chemisorption of the hydrolyzed species and formation and adsorption of the metal hydroxide on the clinoptilolite surface are more likely similar to the adsorption of divalent cations onto quartz[36].

Different researches have observed different pH values at which cadmium precipitates as $Cd(OH)_2(s)$. Bhattacharya and Venkobachar[37] that cadmium precipitates at pH values greater than 10 and Gosset *et. al.*[38] observed cadmium precipitation beyond pH 6.5. Ozer *et. al.*[39] reported that the optimum pH for cadmium adsorption was 6.3. This may be due to the difference in the aqueous medium employed in their experiments. In the present study, an optimum pH of 5.0 was selected for cadmium clinoptilolite system.

The contact times of cadmium adsorption for clinoptilolite at its optimum pH of 5.0 was studied at much closer intervals of time for period longer than 2 h. Fig. 3 shows the contact times of cadmium adsorption on clinoptilolite at closer intervals of time at the optimum pH of 5.0. From the graph, it can be seen adsorption clinoptilolite occurs rapidly, reaching about 97.6 % Cd within 15 min.

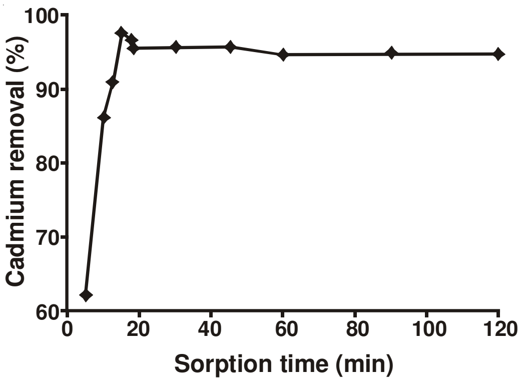

Fig. 3. Effect of contact time on cadmium adsorption by clinoptilolite

On the basis of the experimental results, it can be concluded that clinoptilolite exhibited quite a reasonable capacity for removing cadmium solutions. The maximum cadmium removal at a pH of 5 was 95.32 %. The rate of cadmium adsorption was rapid and the cadmium clinoptilolite system attained equilibrium in 15 min. This results from the fact that natural zeolitic minerals differ in their chemical and mineralogical composition and consequently have different adsorption abilities.

Conclusions

The experimental results showed that using clinoptilolite, a natural zeolite, is particularly suitable for the removal of Cd^{2+} from aqueous solutions similar to those found in industrial effluent streams. The pH studies indicated that the cadmium adsorption on clinoptilolite increased from 61.04 to 97.28 %, when the pH was varied 2 and 9. Beyond pH 9, cadmium removal was probably due to precipitation. The optimum pH was 5.0 and the maximum cadmium removal at this pH was 95.32 %. The contact time studies at pH 5 indicated that equilibrium time for cadmium adsorption on clinoptilolite was 15 min. Clinoptilolite is an easily obtainable and economical zeolite. The other advantages of clinoptilolite are that it can dissolve easily in water and does not produce flock after dissolution. Moreover, these adsorbents could be regenerated and as such, the system could form the basis of more efficient industrial operations.

ACKNOWLEDGEMENT

The author gratefully acknowledges the Selcuk University Research Fund (BAP) for its financial support of the work under taken.

REFERENCES

1. J.N. Lester, Heavy Metals in Wastewater and Sludge Treatment Processes, CRC Press, Boca Raton, FL, USA (1987).
2. M. Sitting, Handbook of Toxic and Hazardous Chemicals, Noyes Publications, Park Ridge, NJ, pp. 119-120, 185-186 (1981).
3. S. Al-Asheh and Z. Duvnjak, *J. Hazard. Mater.*, **56**, 35 (1997).
4. T. Mathialagan and T. Viraraghavan, *J. Hazard. Mater.*, **94**, 291 (2002).
5. J.W. Patterson and R. Passino, Metals Specitaion Separation and Recovery, Lewis Publishers, Chelsea, MA, USA (1987).
6. L. Friberg, M. Piscato, C.G. Nordbert and T. Kjellstrom, Cadmium in the Environment, Springer, Berlin, Germany (1979).
7. M.E. Argun and S. Dursun, *J. Int. Environ. Appl. Sci.*, **1**, 27 (2006).
8. M.E. Argun, S. Dursun, K. Gür, C. Ozdemir, M. Karatas and S. Dogan, *Cell. Chem. Technol.*, **39**, 581 (2005).
9. H. Nagase, D. Inthorn, Y. Isaji, A. Oda, K. Hirata and K. Miyamoto, *J. Ferment. Bioeng.*, **84**, 151 (1997).
10. B. Volesky, Biosorption of Heavy Metals, CRC Press, Boca Raton FL, pp. 13-14, 24 (1992).
11. M.J. Buchauer, *Environ. Sci. Technol.*, **7**, 131 (1973).
12. K.S. Low and C.K. Lee, *Biores. Technol.*, **38**, 1 (1991).
13. N. Nemerow, Liquid Waste of Industry: Theory, Practices and Treatment, Addison-Nesley, Reading, MA, pp. 397-422 (1971).
14. R.W. Peters, in ed.: B.M. Kim, Separation of Heavy Metals and Other Trace Contaminants, AIChE Symposium Series, Vol. 243, pp. 165-203 (1985).
15. M.E. Argun, S. Dursun, K.Gür, C. Ozdemir, M. Karatas and S. Dogan, *Environ. Technol.*, **26**, 479 (2005).
16. L.R. Skubal, N.K. Meshkov, T. Rajh and M. Thurnauer, *J. Photochem. Photobiol. A: Chem.*, **148**, 393 (2002).
17. J.W. Patterson and R.M. Minear, in ed.: P.A. Krenkel, Heavy Metals in the Aquatic Environment, An International Conference, Pergamon Press, pp. 261-272 (1975).
18. C. Ozdemir, M. Karatas, S. Dursun, M.E. Argun and S. Dogan, *Environ. Technol.*, **26**, 397 (2005).
19. R. Petrus and J.K. Warchol, *Water Res.*, **39**, 819 (2005).
20. S.E. Bailey, T.J. Olin, R.M. Bricka and D.D. Adrian, *Water Res.*, **33**, 2469 (1999).
21. S. Kesraoui-Ouki, C.R. Cheeseman and R. Perry, *J. Chem. Technol. Biotechnol.*, **59**, 121 (1994).
22. C. Colella, *Miner. Deposita*, **31**, 554 (1996).
23. H. Faghihian and R.S. Bowman, *Water Res.*, **39**, 1099 (2005).
24. Z. Li, T. Burt and R.S. Bowman, *Environ. Sci. Technol.*, **34**, 3756 (2000).
25. E. Chmielewska-Hortvathova and J. Lesny, *J. Radional. Nucl. Chem. Lett.*, **214**, 209 (1996).
26. H. Faghihian, A. Malekpour and G.M. Maragheh, *Int. J. Environ. Pollut.*, **18**, 181 (2002)
27. P. Lukac and M. Foldesova, *J. Radional. Nucl. Chem. Lett.*, **188**, 427 (1994).
28. M.W. Ackley and R.T. Yang, *AlChE J.*, **37**, 1645 (1991).

29. R.M. Carland and F.F. Aplan, *Miner. Metallur. Process.*, **12**, 210 (1995).
30. R.M. Barrer, Zeolites and Clay Minerals as Sorbents and Molecular Sieves, Academic Press, London.
31. A. Dyer, *Chem. Ind.*, **7**, 241 (1984).
32. M. Vace-Mier, C.B. Jimenez, R. Gehr and G.P. Bosch, Effect of Phenol on Heavy Metals Uptake by Clinoptilolite from Etla, Mexico, In Zeolite 97, 5th International Conference on the Occurrence, Properties and Utilization of Natural Zeolites, Napoli, Italy (1997).
33. M.V. Mier, R.L. Callejas, R. Gehr, B.E.J. Cisneros and P.J.J. Alvarez, *Water Res.*, **35**, 373 (2001).
34. P. Kumar and S.S. Dara, *Indian J. Environ. Health*, **22**, 196 (1980).
35. R.O. James and T.W. Healy, *J. Coll. Interf. Sci.*, **40**, 40 (1972).
36. M.C. Fuerstenau and B.R. Palmer, Anionic Flotation of Oxides and Silicates, Flotation-A.M. Gaudin Memorial, Ch. 7, pp. 148-196 (1976).
37. A.K. Bhattacharya and C. Venkobachar, *J. Environ. Eng.*, **110**, 110 (1984).
38. T. Gosset, J. Trancart and D.R. Thevenot, *Water Res.*, **20**, 21 (1986).
39. A. Ozer, M.S. Tanyildizi and F. Tumen, *Environ. Technol.*, **19**, 1119 (1998).

(*Received*: 22 September 2006; *Accepted*: 9 March 2007) AJC-5505