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Removal of Chromate from Aqueous System by Activated Red-Mud

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In this investigation, red-mud which is the semi-waste of the Seydisehir Aluminium Factory in Turkey was used as an adsorbent material after activation processes. Firstly, the red-mud was treated with different concentration of HCl acid and was washed up with deionized water to clean the acid and other residues. Then, activate adsorbent was used in different doses and at the different pH values for each experimental test. Furthermore, optimum activated red-mud dosage was added in the water containing different chromate concentration. So, the capability of the red-mud for the chromate removal from the water was investigated. In the experiments, the chromate added tap water was used for synthetic water samples. About 70 % chromate removal efficiency was obtained by the optimum red-mud dose and pH value. This investigation indicated that waste of aluminium factories might be used for heavy metal removal processes from the water.

Key Words: Chromate, Heavy metals, Treatment, Adsorption, Red mud, Recycling.

INTRODUCTION

Industrial wastewaters contain many heavy metals, which have very important effects on the environmental pollution. The discharge of toxic metals into the watercourses is a serious pollution problem which may affect the quality of water supply. Increasing concentrations of these metals in the water constitute a serious health hazard mainly due to their non-degradability, toxicity in relatively low concentration and tendency to bioaccumulation[1,2].

Wastewater streams frequently contain combinations of metals, some of which are anionic. There are several anions of environmental concern to the US Environmental Protection Agency (US EPA) and three important anions contain chromium, arsenic or selenium[3]. Chromium is the most ubiquitous of these three elements and is widely used in electroplating, leather tanning, metal finishing, chromate preparation, textile dyeing, the canning industry, steel fabrication, wood industry, and paint and pigments[4-6]. Chromium usually exists in both trivalent and hexavalent forms in aqueous systems[7,8]. The hexavalent form is 100 to 1000 times more toxic than the trivalent form and its accumulation in the environment is a great cause for concern[4].

While Cr(III) may be considered as an essential trace element for the proper functioning of living organisms, *e.g.* for the maintenance of the glucose tolerance factor in the human body, Cr(VI) can be toxic and carcinogenic[9]. Chromium contaminated wastes are usually discharged to the environment as hexavalent chromium in the form of chromate (CrO_4^{2-}) and dichromate (CrO_7^{2-}) anions which are thermodynamically stable over a large pH range[10]. The high toxicity (acute and chronic) and carcinogenity of chromium(VI) make this element one of the most alarming and urgent metal that needs to be controlled[11].

There are various established methods for the removal of heavy metals such as chemical precipitation, adsorption on activated carbon, ion-exchange and reverse osmosis or electrodialysis[12,13], but these methods have some disadvantages different than each other. Conventional precipitation method is less efficient and creates high quantity of toxic waste sludge. Ion-exchange and reverse osmosis, even though effective and efficient, are expensive and need pre-treatment[14-16]. Adsorption is the most popular method for wastewater treatment due to its easy and inexpensive operation, but there are certain problems using activated carbon as adsorbents due to the high cost of use and regeneration[17].

In order to minimize processing costs for these effluents, recent investigations have focused on the use of low-cost-adsorbents[18,19]. Industrial wastes are also one of the potentially low-cost adsorbent for heavy metal removal. It requires little processing to increase its sorption capacity. Generally industrial wastes are generated as by-products such as red-mud. Since these materials are locally available in large quantities and obtained inexpensively[20].

Red mud, due to high aluminium, iron and calcium, has been suggested as an economic adsorbent for removal of toxic metals as well as for water or wastewater treatment[21]. The basic advantage of red-mud is its versatility in application. Red-mud is a by-product of the Bayer Process of alumina production in the aluminium industries[22]. For every ton of alumina produced, between 1 and 2 tonnes (dry weight) of red-mud residues are produced. It is composed primarily of fine particles of silica, aluminium, iron, calcium and titanium oxides and hydroxide, which are responsible for its high surface reactivity[23,24]. Because of these characteristics red-muds have been the subject of many investigations including some on the removal of toxic heavy metals from wastewater in recent years[25-28]. However, little research has been conducted to utilize red-mud for chromate removal[29-32].

In the present study, the adsorption of chromate on the activated red-mud was evaluated under various conditions such as pH, chromate concentrations and red-mud dosages. This study provided some information on the possibility of increasing the chromate sorption capacity of red-mud, and the possibility of using these substances as an unconventional means of removing chromate from the water. To determine the optimum conditions of adsorption capacity was also aimed.

EXPERIMENTAL

Red-mud used in the present experiments was supplied from Seydisehir Aluminium Plant in Turkey. It has the following average chemical composition (% by wt): Al_2O_3, 19.88; Fe_2O_3, 36.47; CaO, 2.33; SiO_2, 15.95; Na_2O, 10.03; TiO_2, 4.97; CO_2, 2.48; S, 0.09; V_2O_5, 0.074; P_2O_5, 0.041 and loss on ignition, % 8.04. After arrival in the laboratory, red-mud was air dried and sieved by 250 mesh size steal sieve. The studies were carried out with the red mud of particle size of 0.1-1.0 mm diameter. Sieved red-mud was stored at laboratory conditions until activation processes.

Activation of red-mud: Red-mud was activated through acid treatment with concentrated HCl acid. For this purpose, four 25 g of dry red-mud were prepared and suspended in 50 mL distilled water (2 mL distilled water per gram red-mud) by adding 0.5, 1.0, 1.5, 2.0, 4.0, 6.0 and 8.0 mL HCl (% 36 purity, Merck Co. Germany) and the suspensions were stirred for 0.5 h. Then, they were washed twice with 100 mL of distilled water to remove the residual acid and soluble compounds. The treated red-mud was filtrated by using Whatmann filter to remove the solution content. Mud cakes were dried at 105 °C overnight and stored in vacuum desiccators.

Adsorption experiments: In the adsorption study, chromate adsorption characteristics of activated red-mud were investigated. Adsorption experiments were performed by Jar Test Method (Armfield W1-A, UK) at room temperature. A preliminary jar-test procedure was used to select coagulant dosage range and the optimal pH value ranging from 5 to 8. The pH of the solutions was adjusted with either an acid (HCl) or a base (NaOH) solution to achieve the desired pH. Finally, activated red-mud with polyelectrolyte was tested with different doses to determine the relative effectiveness of activated red-mud.

All experiments were run at 8 mg L^{-1} constant chromate concentration using analytic grade K_2CrO_4. (Merck Co., Germany). Chromate concentration was analyzed by a spectrophotometric method with Cuvettes-Test by using CADAS-200 UV-Vis spectrophotometer (Dr. Bruno Lange GmbH & Co. KG, Düsseldorf). Initial and final concentrations were determined at each experiment run.

RESULTS AND DISCUSSION

In this recent work, the measurement of adsorption capacity of red-mud was investigated in three stages. Adsorption experiments were studied with preliminary activated red-mud waste of Seydisehir Aluminium Factory. Preliminary activation was made with conc. HCl acid addition (0.5, 1.0, 1.5, 2.0, 4.0, 6.0 and 8.0 mL) on 25 g of raw red-mud in 50 mL distilled water. Fig. 1 shows that chromate removal rate was the highest with addition of 1.0 mL HCl and removal rates were decreased with increasing HCl addition. Therefore, red-mud activation was performed with addition of 1.0 mL concentrate acid addition and secondary experiments were continued with this activated red-mud materials.

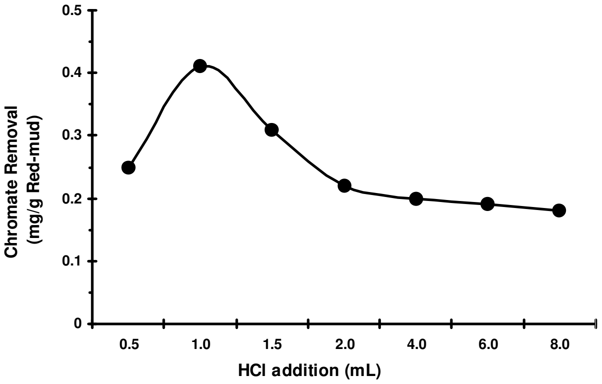

Fig. 1. Effect of red-mud (0.5 g in 50 mL chromate solutions) activated with different amount of HCl addition (0.5, 1.0, 1.5, 2.0, 4.0, 6.0 and 8.0 mL concentrated HCl in 25 g red-mud) on chromate adsorption

In the secondary experiment, chromate adsorption characteristics of activated red-mud were investigated. Coagulant dosage range was selected with jar-test procedure that its results were given in Fig. 2. It was observed that the adsorption rate of chromate was at maximum (about 40 %) with 1.0 g activated red mud addition. However, Fig. 2 shows that the highest removal per gram red-mud was with 0.1 g red-mud addition but this addition was not possible to remove enough chromate removal which was about 20 % removal efficiency.

The variation of chromate adsorption is illustrated in Fig. 3. As seen in the figure, chromate removal is approximately at the same level up to 4.0 mg L^{-1} with increasing chromate addition. Up to 4.0 mg L^{-1}, chromate removal efficiency rate was not changed then it was slightly lowered at 8.0 mg L^{-1}. 4 mg L^{-1} chromate concentration was used at the experiments afterwards. Chromate residue in the solution was the minimum at the lowest concentration.

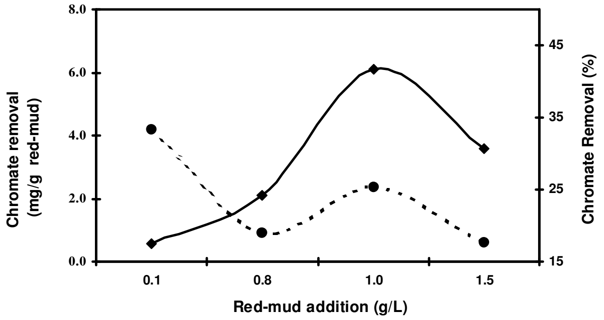

Fig. 2. Chromate removal for per gram red-mud activated with 1.0 mL HCl on the adsorption of as a function of the amount of the adsorbent. Chromate removal for per g red-mud (●), chromate removal rate (◆)

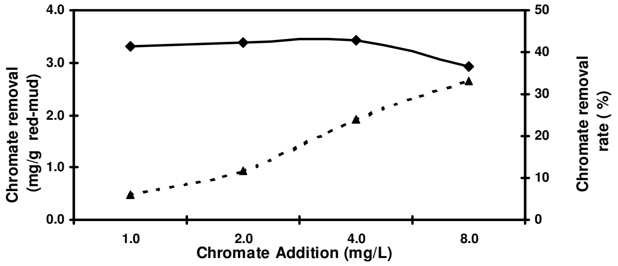

Fig. 3. Chromate concentration change with addition of 1 g red-mud activated 1 mL HCl and chromate adsorption efficiency as a function of the chromate concentration. Chromate removal for per gram red-mud (◆), chromate removal rate (▲)

At the last step, effect of pH values ranging from 5 to 8 on the chromate adsorption capacity of activated red-mud was investigated. The results are presented in Fig. 4 and it shows that, the maximum chromate removal (69 %) at constant chromate concentration with 1 g activated re-mud addition was obtained at pH 7. Chromate adsorption capacity of activated red-mud was also maximum at pH 7.

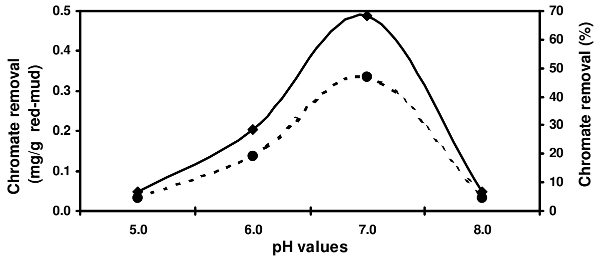

Fig. 4. Effect of 1 g red mud activated with 1 mL HCl on the adsorption of 1 mg L^{-1} chromate as a function of pH. Chromate removal for per gram red-mud (●), chromate removal efficiency rates (◆)

Conclusion

The waste product of aluminium factory and activated red-mud is found to be economical and suitable material for chromium metal removal from the aqueous environment. This usage for water treatment would be given another change for disposal and reuse of the aluminium plants.

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REFERENCES

1. S. Larous, A.H. Meniai and M.B. Lehocine, *Desalination*, **185**, 483 (2005).
2. M. Karatas and S. Dursun, *J. Int. Environ. Appl. Sci.*, **1**, 54 (2006).
3. US-EPA, Ground Water and Drinking Water, Current Drinking Water Standards, EPA 8s16-F-02, Washington (2002).
4. H. Lynda, L.H. Wartelle and W.E. Marshall, *Water Res.*, **39**, 2869 (2005).
5. M.E. Argun and S. Dursun, *J. Int. Environ. Appl. Sci.*, **1**, 27 (2006).
6. A. Nakajima and Y. Baba, *Water Res.*, **38**, 2859 (2004).
7. M.K. Banks, A.P. Schwab and C. Henderson, *Chemosphere*, **62**, 255 (2006).
8. M.E. Argun and S. Dursun, *J. Int. Environ. Appl. Sci.*, **2**, 5 (2007).
9. S. Yalcin and R. Apak, *Anal. Chim. Acta*, **505**, 25 (2004).
10. C.S. Uyguner and M. Bekbolet, *Appl. Catalysis B: Environ.*, **49**, 267 (2004).
11. A. Syla, A. Veliu, K. Berisha, E. Karakashi and I. Fejza, *J. Int. Environ. Appl. Sci.*, **2**, 51 (2007).
12. A. Ucer, A. Uyanik and S.F. Aygun, *Sep. Purif. Technol.*, **47**, 113 (2006).
13. S. Dursun and A. Pala, *J. Int. Environ. Appl. Sci.*, **2**, 11 (2007).
14. S.R. Shukla, R.S. Pai and A.D. Shendarkar, *Sep. Purif. Technol.*, **47**, 141 (2006).
15. T.G. Chuah, A. Jumasiah, I. Azni, S. Katayon and S.Y.T. Choong, *Desalination*, **175**, 305 (2005).
16. S.A. Dean and J.M. Tobin, *Resources, Conservation Recycling*, **27**, 151 (1999).
17. S. Wang, Y. Boyjo, A. Choueib and Z.H. Zhu, *Water Res.*, **39**, 129 (2005).
18. S. Kocaoba and T. Akyuz, *Desalination*, **181**, 313 (2005).
19. S.E. Bailey, T.J. Olin, R.M. Bricka and D.D. Adrian, *Water Res.*, **33**, 2469 (1999).
20. S. Babel and T.A. Kurniawan, *J. Hazardous Mater.*, **B97**, 219 (2003).
21. C. Brunori, C. Cremisini, P. Massanisso, V. Pinto and L. Torricelli, *J. Hazardous Mater.*, **B117**, 55 (2005).
22. S. Dursun, D. Guclu and M. Bas, *J. Int. Environ. Appl. Sci.*, **1**, 98 (2006).
23. Ü. Danis and B. Keskinler, *J. Int. Environ. Appl. Sci.*, **1**, 91 (2006).
24. D. Chvedov, S. Ostap and T. Le, *Colloids Surf.*, **A182**, 131 (2001).
25. H. Genc-Fuhrman, C.H. Tjell and D Mcconchi, *J. Colloid Interface Sci.*, **271**, 313 (2004).
26. K. Guclu and R. Apak, *J. Colloid Interface Sci.*, **260**, 280 (2003).
27. H.S. Altundogan, S. Altundogan, F. Tumen and M. Bildik, *Waste Manag.*, **22**, 357 (2002).
28. R. Apak, E. Tutem, M. Hugul and J. Hizal, *Water Res.*, **32**, 430 (1998).
29. J. Pradhan, S.N. Das, R.S. Thakur, *J. Colloid Interface Sci.*, **217**, 137 (1999).
30. V.K. Gupta, M.M. Gupt and S. Sharma, *Water Res.*, **35**, 1125 (2001).
31. M.E. Argun, S. Dursun, K. Gur, C. Ozdemir, M. Karatas and S. Dogan, *Environ. Technol.*, **26**, 479 (2005).
32. D. Couillard, *Sci. Total Environ.*, **25**, 181 (1982).

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