Asian Journal of Chemistry Vol. 17, No. 4 (2005), 2184–2190

Adsorption Study of Hexavalent Chromium by Bentonite Clay

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Bentonite, a clay, was used for the adsorption of hexavalent chromium [Cr(VI)] from aqueous solution. Effect of pH, dose of adsorbent and initial concentration was studied on adsorption by bentonite clay. Desorption of Cr(VI) was also studied. Adsorption experiments were conducted in a batch system and found to be maximum at pH 2.0. Equilibrium data fitted well to Langmuir isotherm model. The maximum adsorption capacity of bentonite clay was found to be 5.9 mg/g at an initial pH of 2.0 and 50°C temperature. 0.1 N NaOH could elute > 90% of Cr(VI) and bentonite retains the adsorption capacity without an appreciable loss, for three desorption and adsorption cycles.

Key Words: Chromium, Bentonite clay, Equilibrium, Adsorption, Hexavalent chromium, Desorption.

INTRODUCTION

Metals are ubiquitous to man's environment. With the process of evolution man has developed immunity towards their natural concentration. But with rapid industrialization, the use of metals like Cd, Zn, Hg, Pb, Cu, Ni and Cr has increased many-folds as a consequence of which they are now being found in the environment in objectionable concentration. Chromium is one such metal pollutant, which requires immediate attention. It occurs in variable oxidation states ranging from 0 to 6, out of which trivalent chromium and hexavalent chromium are most stable oxidation states. Cr(III) is relatively non-toxic and no systemic effects have been recorded so far; however, because of its high solubility in water, Cr(VI) is very toxic. The health and environmental effects of Cr(VI) are well documented[1]. It is considered to be a group 'A' carcinogen. The common sources of Cr(VI) into environment are effluents from electroplating, tanning, pigments, dye and chemical manufacturing. The maximum permissible limits of Cr(VI) in potable water and wastewater are 0.05 and 0.1 mg/L, respectively[2]. Keeping in view its toxicity, it becomes an absolute necessity to keep its concentration within

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the permissible limits. The oldest and most widely used method for removal of Cr(VI) is the method of reduction and precipitation. Although this process is effective, it has disadvantages of production of large amount of sludge, operating cost of bulk chemicals and consumption of acids and alkalis[3]. For this reason attention has now been focused on adsorption, which is a simple technique to operate. But it involves the use of adsorbents like activated carbon which is a costly adsorbent, so there is need of some alternate cost effective adsorbents. Many adsorbents have been investigated for their potential for removal of Cr(VI) from the solution. These adsorbents include fly ash[4], aluminum oxide[5], bituminous coal[3], saw dust, sugar cane bagasse[6] and blast furnace flue dust[7]. Keeping in view the low cost and availability, bentonite clay was selected as adsorbent in the present study. Bentonite is a clay mineral derived from the alteration, over geological time periods, of glassy material emitted from volcano stuff and ash or from alteration of silica bearing rocks such as granite and basalt. Bentonite is a naturally occurring material consisting predominantly of the clay mineral montmorillonite. Montmorillonite is a material species in the family of sheet silicates called smectites which are aluminum and magnesium hydrosilicates. The silicate layers have a slightly negative charge that is compensated by exchangeable ions in the intermediate layers. An essential characteristic of all smectite minerals is their ability to absorb large amounts of water and other liquids into their sheet structures. This gives bentonite extraordinary swelling and adhesive properties that are exploited commercially by many industries.

EXPERIMENTAL

Bentonite clay was procured from E. Merck, India Ltd. It was dried in an oven at 80°C for 12 h and was used as the adsorbent. A stock solution (1000 mg/L) of Cr(VI) was prepared by dissolving 2.828 g of $K_2Cr_2O_7$ (AR grade) in 1000 mL of distilled water. The stock solution was then appropriately diluted to get the test solutions of desired strength.

Analysis of Cr(VI) ions

The concentration of the Cr(VI) ions was determined spectrophotometrically after complexing of the metal ion with 1,5-diphenylcarbazide[8]. The absorbance was recorded at 540 nm using UV spectrophotometer (UV-160, Shimadzu) and concentration was determined from the calibration curve.

Effect of pH of solution on Cr(VI) adsorption

The pH of the solution was varied from 1.0 to 6.0. It was adjusted by using 0.1 N HCl/NaOH. 0.1 g dried bentonite clay was added to 100 mL of solution having 100 mg of Cr(VI)/L in 250 mL Erlenmeyer flasks. These flasks were kept on a rotatory shaker at 27 ± 2°C and 120 rpm. After 24 h of agitation the solutions were centrifuged at 3000 rpm for 10 min and further the supernatant solution was analyzed for Cr(VI) concentration.

Effect of dose of adsorbent on Cr(VI) adsorption

The dose of adsorbent was varied from 2.0 to 10.0 g/L in 100 mL of solution having 100 mg Cr(VI)/L at pH 2.0. The flasks were kept on a rotatory shaker at 27 ± 2°C and 120 rpm. After 4 h of shaking, solutions were centrifuged at 3000 rpm for 10 min. The supernatant liquid was analyzed for Cr(VI) concentration.

Effect of initial Cr(VI) concentration on Cr(VI) adsorption

The effect of initial Cr(VI) concentration was studied in the range 10 to 400 mg/L. Bentonite clay (1.0 g) was added to 100 mL of solution having varying Cr(VI) concentration, in 250 mL Erlenmeyer flasks at a pH of 2.0. The flasks were kept on a rotatory shaker at 27, 40 and 50°C and 120 rpm. After 4 h of shaking, the solutions were centrifuged at 3000 rpm for 10 min and the supernatant was analyzed for Cr(VI) concentration.

Equilibrium study

All the data were analyzed using Langmuir and Freundlich isotherm equilibrium. Corresponding correlation were used to draw the plots.

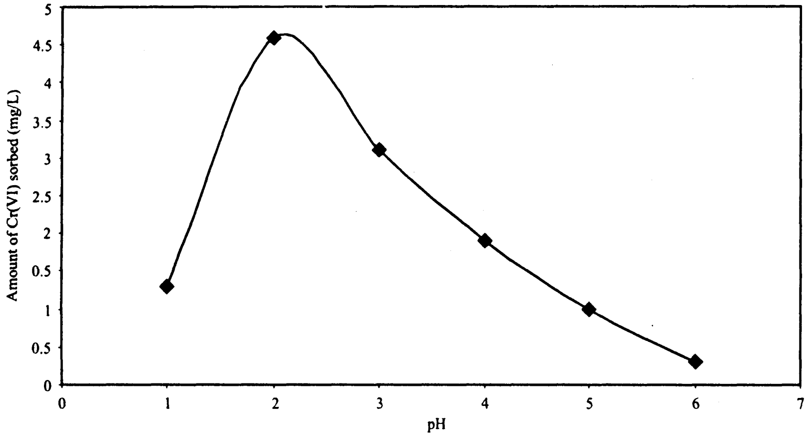
Desorption of Cr(VI)

In order to study the feasibility of using the adsorbents more than once and recovery of the metal, experiments were carried out on the desorption of solute from the bentonite clay. Desorption of Cr(VI) from previously loaded bentonite clay was studied by using NaOH 0.1 N as eluent. For this purpose, 0.2 g of previously loaded bentonite clay was added to 20 mL of eluent in 150 mL conical flasks. After 90 min of shaking at 27 ± 2°C and 120 rpm, solutions were centrifuged at 3000 rpm for 10 min. The supernatant was analyzed for the Cr(VI) concentration. The desorption cycle was carried out five times.

RESULTS AND DISCUSSION

Effect of pH of solution on Cr(VI) adsorption

It was observed that the amount of Cr(VI) adsorbed by clay increased with the lowering of pH of the solution (Fig. 1). Maximum adsorption was observed at pH 2.0. The adsorption capacity of Cr(VI) at pH 2.0 by bentonite clay was 1.3 mg/g, which reduced to 0.3 mg/g at pH 6.0. Cr(VI) occurs as oxy anion[9] as $HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-}, $Cr_4O_{13}^{2-}$ and $Cr_3O_{10}^{2-}$. At lower pH, the surface of the adsorbent becomes positively charged to a higher extent. This results in a stronger attraction for negatively charged Cr(VI) complex ions in the solution. Hence, the adsorption increases with the increase in the acidity of the solution. At higher pH, the concentration of OH^- ions increases and overall charge on the adsorbent surface becomes negative, which causes hindrance in the adsorption of negatively charged chromium ions, which results in the decreased adsorption of Cr(VI) at higher pH.

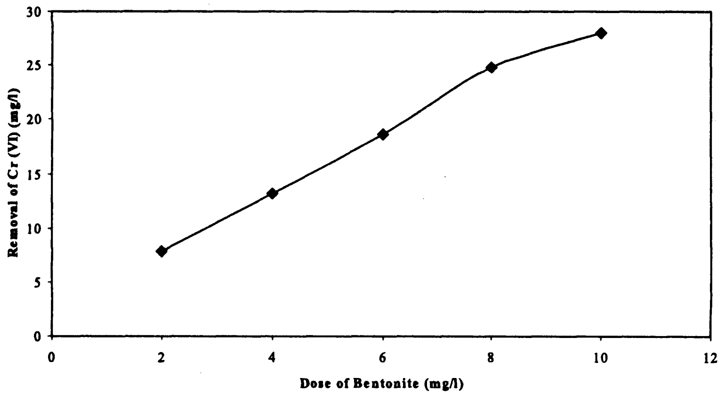


(Initial conc. of Cr(VI) 100 mg/L; Adsorbent dose 1 g/L; Time 24 h temp. 27°C; Agitator speed-20 rpm)

Fig. 1. Effect of pH of solution on adsorption of Cr(VI)

Effect of dose of adsorbent on adsorption of Cr(VI)

The removal of Cr(VI) increased with the increase in the amount of bentonite clay. It was increased from 7.8 to 28.0 mg/L as the adsorbent dose increased from 2.0 to 10.0 g/L (Fig. 2). This is because as the amount of bentonite clay increases, the availability of the potential binding sites also increases leading to higher adsorption of Cr(VI).

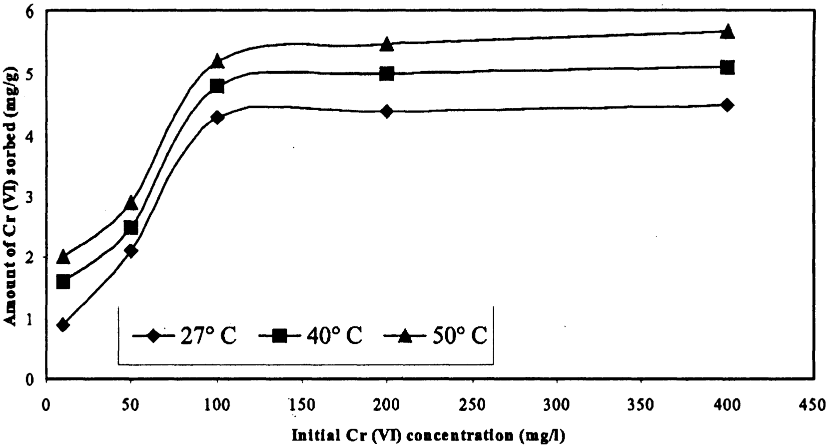


(Initial conc. 100 mg/L; Time 4 h; Temp. 27°C; Agitator speed 120 rpm; pH 2.0)

Fig. 2. Effect of dose of bentonite clay on adsorption of Cr(VI)

Effect of initial concentration of Cr(VI) on its adsorption

The initial concentration of Cr(VI) in the solution remarkably influences the equilibrium uptake of Cr(VI) at all the temperatures (27 to 50°C). It was noted that, as the initial concentration increased the adsorption of Cr(VI) increased as is generally expected due to equilibrium process. When the initial concentration of Cr(VI) increased from 10 to 600 mg/L, the uptake capacity increased from 0.9 to 4.5 mg/g at 27°C, from 1.6 to 5.1 mg/g at 40°C and from 2.0 to 5.7 mg/g at



(Dose of bentonite clay 1.0 g/L; Time 4 h; Temp. 50°C; Agitator speed 120 rpm; pH 2.0)

Fig. 3. Effect of initial concentration of Cr(VI) on its adsorption

50°C (Fig. 3). The increase of uptake capacities of adsorbents with the increase of Cr(VI) ion concentration is due to higher availability of Cr(VI) ions in the solution for the adsorption.

Equilibrium study

The equilibrium established between adsorbed component on the adsorbents and the unadsorbed component in solution can be represented by adsorption isotherms. The most widely used isotherm equations for modelling equilibrium are Freundlich and Langmuir isotherm equations. The Freundlich isotherm equation is an empirical equation based on the adsorption on a heterogeneous surface suggesting that binding sites are not equivalent and/or independent. The mono-component Freundlich isotherm equation[10] is given below:

$$q_{eq} = K_f C_{eq}^{1/n} \tag{1}$$

where K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively. From the linearized plot of log q_e *vs.* log C_{eq}, these constants can be determined.

Langmuir isotherm equation is based on mono-layer adsorption onto a surface with finite number of identical sites, which are homogeneously distributed over the adsorbent surface[11] and is given by the equation (2).

$$q_{eq} = \frac{Q_{max} b C_{eq}}{1 + b C_{eq}} \tag{2}$$

where Q_{max} and b are Langmuir constants denoting maximum adsorption capacity and the affinity of the binding sites, respectively. These constants can be determined from the $1/C_{eq}$ *vs.* $1/q_{eq}$.

In the present study, the data of Cr(VI) adsorption was analyzed for Freundlich and Langmuir isotherms. The linearized plots of Langmuir isotherm model for adsorption of Cr(VI) on Bentonite clay at different temperatures are presented in

Fig. 4. In view of the values of linear regression coefficients, it was noted that the Langmuir isotherm model exhibited better fit to the adsorption data of Cr(VI) than the Freundlich isotherm model, in the studied concentration and temperature range (Table-1). The Q_{max} for Cr(VI) on bentonite clay was increased from 4.9 to 5.9 mg/g with the increase in temperature. It was also observed that as the temperature was increased the maximum adsorption capacity of bentonite clay increased. The rise in adsorption capacity with temperature may be because of rise in the kinetic energy of adsorbent particles. Thus, the collision frequency between adsorbent and adsorbate increases which results in the enhanced adsorption on to the surface of the adsorbent.

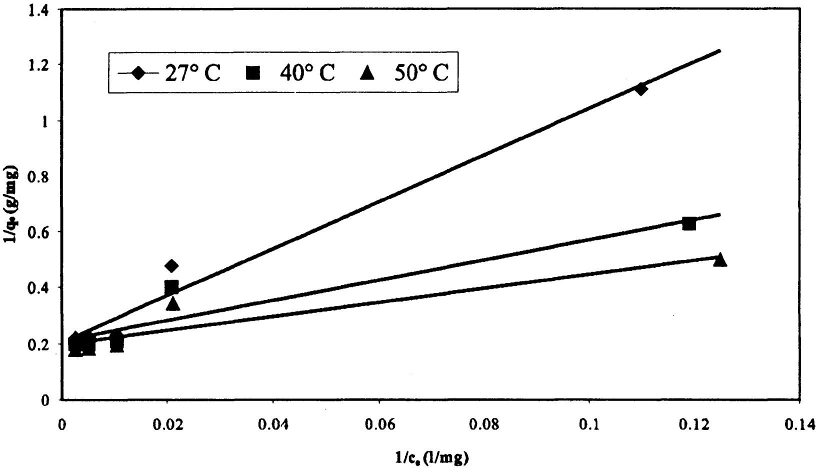


Fig. 4. Linearized plots of Langmuir isotherm for adsorption of Cr(VI) on bentonite clay at different temperatures

TABLE-1
ISOTHERM PARAMETERS FOR Cr(VI) ADSORPTION ON BENTONITE CLAY

Temp. (°C)	Langmuir constants			Freundlich constants		
	Q_{max} (mg/g)	b (L/mg)	r^2	K_f	n	r^2
27	4.9	0.0244	0.9770	1.16	2.17	0.8942
40	5.4	0.0283	0.9773	1.24	3.00	0.8888
50	5.9	0.0321	0.9790	1.28	3.37	0.8985

(pH 2.0; Dose of bentonite clay 1 g/L; Contact time 4 h; Agitator speed 120 rpm).

Desorption of Cr(VI) by NaOH

Desorption studies are important for recovery and reuse of the metal ion. In the present study, adsorption-desorption cycles were carried out five times. It was observed that bentonite clay could be used for three cycles. After three cycles there was appreciable loss in adsorption capacity (Table-2). The loss could be attributed to the loss in the weight of adsorbent and the destruction of surface characteristics due to repeated adsorption-desorption cycle.

TABLE-2
DESORPTION OF Cr(VI) BY NaOH FROM BENTONITE CLAY

Cycles	Adsorption (mg/g)	Desorption (mg/g)	Desorption (%)
I	3.6	3.3	91.7
II	3.4	2.8	82.4
III	3.0	2.8	93.3
IV	2.4	2.1	87.5
V	2.0	1.9	95.0

REFERENCES

1. S.E. Manahan, *Biotech. Progr.*, **11**, 235 (1994).
2. CPCB, The Environmental (Protection) Rules, Pollution control series PCL\2\1992, Schedule I, Delhi, p. 266 (1995).
3. N.S Rawat and C.D Singh, *Asian Environ.*, **14**, 30 (1992).
4. D.C Gupta and U.C Tiwari, *Indian J. Environ. Health*, **27**, 205 (1985).
5. K.K. Panday, G. Prasad and V. N. Singh, *J. Chem. Tech. Biotech., A: Chem. Tech.*, **34**, 367 (1984).
6. D.C. Sharma and C.F. Forester, *Biores. Tech.*, **47**, 257 (1994).
7. L.N. Patnaik and C.P. Das, *Indian J. Environ. Health*, **37**, 35 (1995).
8. D. Eaton, L.S. Clesceri and A.E. Greenberg, Standard methods for examination of water and waste waters, American Public Health Association (APHA), AWWA, WPCF, Washington, DC (USA) (1995).
9. L. Rollinson, Comprehensive Organic Chemistry, Pergamon Press, Oxford (UK), p. 691 (1973).
10. H.M.F. Freundlich, *J. Phys. Chem.*, **57**, 385 (1906).
11. I. Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916).

(*Received*: 15 May 2004; *Accepted*: 20 May 2005) AJC-4235