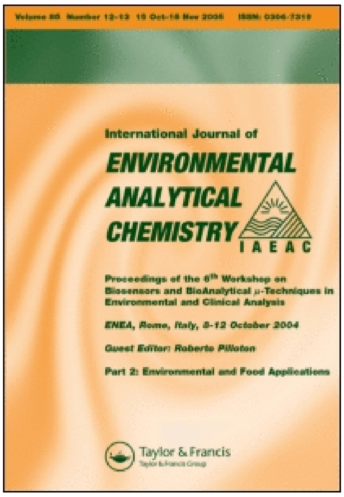

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Inexpensive Adsorption Technique to Remove Cr(VI) from Aqueous Solutions

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INEXPENSIVE ADSORPTION TECHNIQUE TO REMOVE Cr(VI) FROM AQUEOUS SOLUTIONS

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The removal of Cr(VI) from aqueous solutions by using an inexpensive adsorbent, viz. China clay has been investigated. Maximum uptake (68%) was observed at a solution concentration of 0.5×10^{-4} M, pH 2.5 and 30 °C. The kinetics of the process have been explained using the Lagergren equation; the average rate constant of adsorption was found to be 0.148 min^{-1}. Langmuir's isotherm was found to be valid; the constants are calculated for different temperatures. The rate-limiting factor is the intraparticle diffusion. The coefficients of mass transfer and intraparticle diffusion are determined at different temperatures. In the present study low temperatures as well as low pH favour the uptake of Cr(VI) species.

KEY WORDS: Inexpensive, adsorption, China clay, Cr(VI), isotherm, mass transfer.

INTRODUCTION

Chromium does not occur in its native state and is found primarily in chromite or chrome iron ore in nature. It has a wide variety of uses and is an important constituent of useful alloys such as stainless steel. The use of chromium in the dye and pigment industry, for the production of electric cells, for printing, and the manufacture of rubber is well recognised.[1] Chromium is a potential carcinogen which produces cancer of the lung, the nose and other sites of the body. It was shown in a recent study that workers involved in the production of chromates from chromium ores are 30-fold more prone to suffer from lung cancer than those working in the production of other metallic salts.[2] Chromium(VI) is toxic to various species of fish[3] and adversely affects the life of plants.[4] Various techniques, e.g., reduction and precipitation, ion-exchange, precipitation of chromates with barium or lead, ion flotation, electrolysis and reverse osmosis, are available for the removal of Cr(VI) from aqueous solutions.[5] The most widely used method of treatment is to first detoxify Cr(VI) by reducing it to the lesser toxic Cr(III), followed by the precipitation of the hydrated chromium oxide by the addition of a base. However, this process suffers from a serious disadvantage regarding the disposal of the precipitated chromium hydroxide.[6–8] An ion–exchange treatment, of course, does not present a sludge disposal problem; however, it is quite expensive and poorly selective for chromate over other anions. Furthermore, a critical flow rate has to be maintained for an efficient removal of the metal.

In recent years, adsorption processes have become popular among environmental scientists for the removal of various species from polluted water.[9–12] For a long time, the removal of various pollutants from wastewater by adsorption on activated carbon has been quite popular.[13,14] However, in a developing country like India it is rather difficult to use it extensively in wastewater treatment. In the past decade we have tried to remove various pollutants by using non-conventional cheap adsorbents.[9–12] The present study deals with the removal of Cr(VI) by adsorption on China clay, a very cheap clay mineral.

EXPERIMENTAL

All the chemicals used in our experiments were of analytical reagent grade and were obtained from BDH (Bombay, India). China clay was obtained from Pathar Ghatt (Bihar, India). The particle size of the adsorbent was measured with the HIAG PC-320, model Q 002917 (Royco Instrument Division, N.Y., USA).[15] The surface area was determined by a three-point N_2 gas adsorption method using a Quantasorb surface area analyser, model Q5–7[16] (Quantachrome Corp., N.Y., USA). The adsorbent was passed through a 100 μm sieve and used as such to avoid extra expenditure.

Batch adsorption experiments were performed with 1.0 g of adsorbent. The adsorbent was agitated with 50 ml of the chromium solution of different concentrations in polythene bottles at pH 2.5 and 30 °C. The speed of agitation was 125 rpm throughout the experiments. After agitation the solutions were centrifuged at 10 000 rpm and the amount of metal ion in the aliquot was determined spectrophotometrically using a Spectronic 20 (Bausch and Lomb, N.Y., USA). Data for the isotherm study were obtained by allowing the adsorbent to remain in contact with the solution for 70 minutes—the period necessary to attain equilibrium.

RESULTS AND DISCUSSION

Characterization of the Adsorbent

It is clear from Table 1 that silica and alumina are the major constituents of China clay; traces of the oxides of iron, calcium and magnesium are also present. The XRD analysis results of China clay are presented in Table 2; these show the predominance of kaolinite and α-quartz. Muscovite, calcite and hematite are present in traces.

Effect of Contact Time and Concentration

The effects of chromium concentration and time of contact are shown in Figure 1.

Table 1 Characterization of China clay

Constituents	*% by weight*
SiO_2	46.22
Al_2O_3	38.40
Fe_2O_3	0.68
CaO	0.86
MgO	0.37
Loss of ignition (%)	13.47
Surface area ($m^2 g^{-1}$)	9.78
Porosity	0.33
Density ($g cm^{-3}$)	2.692

Table 2 "d" values of China clay

d(A°)	*Possible mineral*
7.1833	Kaolinite
3.5840	Kaolinite
2.5661	Kaolinite
2.3862	Kaolinite
2.3429	Kaolinite
2.2986	Kaolinite
1.9912	Kaolinite
4.4581	Muscovite
4.2655	α-Quartz
3.3478	α-Quartz
1.8193	α-Quartz
1.6670	α-Quartz
1.5427	α-Quartz
1.3741	α-Quartz
1.8960	Calcite
1.4901	Hematite

The uptake of chromium(VI) increases with time and reaches plateau conditions after 1 hr. The percentage uptake increased from 35 to 68% with a solution concentration decreasing from 2.0×10^{-4} M to 0.5×10^{-4} M. It is clear that uptake is highly dependent on the initial concentration of the metal ions in the solution. The finding that a high removal occurs in the low concentration range can be exploited for industrial purposes.

The rate constant for the process, K_u(min^{-1}), for the uptake of Cr(VI) on China clay followed Lagergren's first order rate equation:[17]

$$\log(q_e - q) = \log q_e - \frac{K_u}{2.303} \cdot t \qquad (1)$$

where q_e and q (both in mg g^{-1}) are the amounts of Cr(VI) ion adsorbed at equilibrium and at time t, respectively. The linear plots of log $(q_e - q)$ vs. t (Figure 2) at various temperatures confirm the validity of the equation. The values of K_u

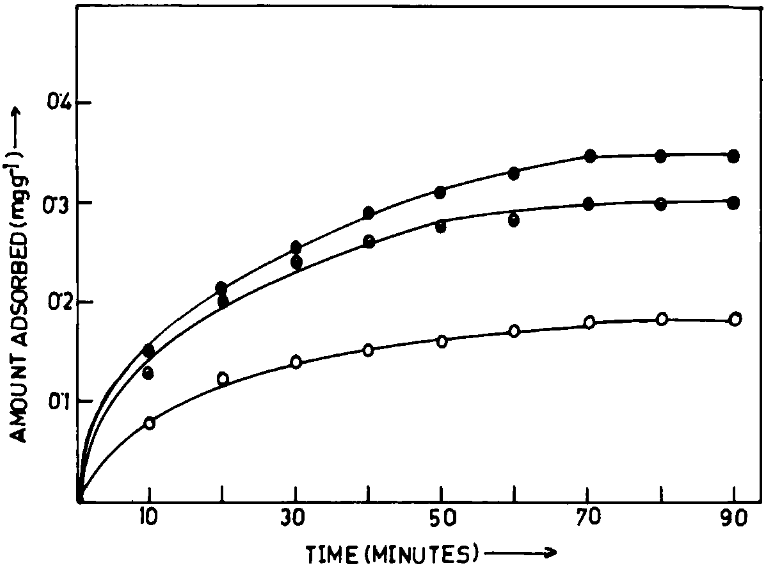


Figure 1 Effect of concentration on removal of Cr(VI) by China clay: (○) 0.5×10^{-4} M, (⊖) 1.0×10^{-4} M and (●) 1.5×10^{-4} M. Conditions: 0.01 M $NaClO_4$ for ionic strength; pH 2.5; temperature 30 °C.

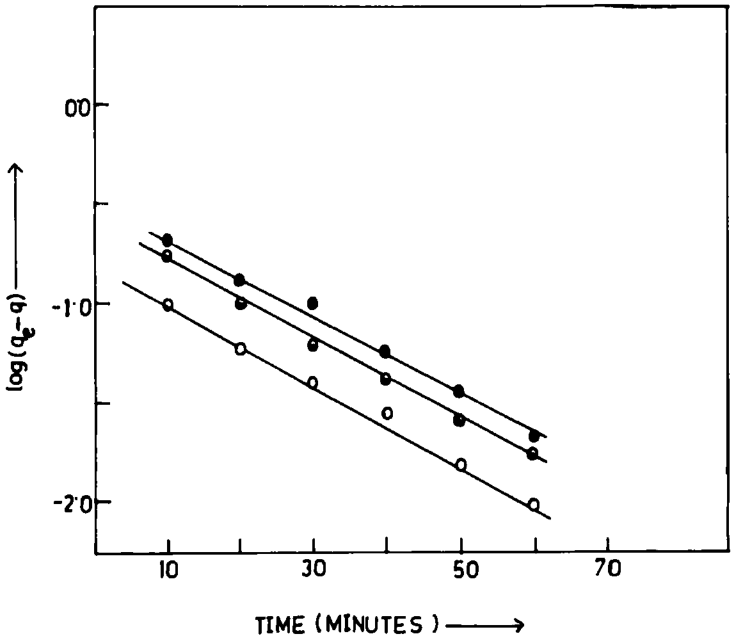


Figure 2 Lagergren plot for the adsorption of Cr(VI) on China clay; (○) 30 °C, (⊖) 40 °C and (●) 50 °C. Conditions: 0.5×10^{-4} M Cr(VI), 0.01 M $NaClO_4$ and pH 2.5.

Table 3 Kinetic parameters of adsorption at different temperatures

Temperature (°C)	K_u (*min*$^{-1}$)	K_1 (*min*$^{-1/2}$)
30	7.15×10^{-2}	4.2×10^{-2}
40	6.75×10^{-2}	3.0×10^{-2}
50	6.5×10^{-2}	0.5×10^{-2}

Table 4 Langmuir constants at different temperatures

Temperature (°C)	Q^0 (*mgg*$^{-1}$)	*b* (*lmg*$^{-1}$)	*k* (*lg*$^{-1}$)
30	1.0834	0.205	0.222
40	0.5862	0.126	0.074
50	0.4286	0.097	0.042

at 30, 40 and 50 °C were calculated from the plots and are given in Table 3. The overall rate constant is $6.80 \times 10^{-2}\,\mathrm{min}^{-1}$.

Adsorption Isotherm

The experimental data fit the Langmuir isotherm model:[10]

$$\frac{C_e}{q_e} = \frac{1}{Q^0 \cdot b} + \frac{C_e}{Q^0} \tag{2}$$

where C_e ($\mathrm{mg\,l^{-1}}$) is the concentration of the adsorbate at equilibrium and Q^0 ($\mathrm{mg\,g^{-1}}$) and b ($\mathrm{l\,mg^{-1}}$) are the Langmuir constants related to capacity and energy of adsorption, respectively. Straight-line plots of C_e/q_e vs. C_e (Figure 3) at different temperatures also confirm the monolayer coverage of the Cr(VI) species on China clay.[21] The adsorption capacity of China clay decreases from $1.08\,\mathrm{mg\,g^{-1}}$ to $0.43\,\mathrm{mg\,g^{-1}}$ when increasing the temperature from 30 to 50 °C at 2.5 pH (Table 4). This shows that lower temperature favours the adsorption of Cr(VI) ions.[21,22]

Mass Transfer and Intraparticle Diffusion

The study regarding the mass transfer from solution onto the surface of adsorbent was performed in the light of the well known model of McKay *et al.*:[14]

$$\ln\left(\frac{C_t}{C_0} - \frac{1}{1+mk}\right) = \ln\frac{mk}{1+mk} - \frac{1+mk}{mk} \cdot \beta_L \cdot S_s \cdot t \tag{3}$$

where C_t and C_0 (both in $\mathrm{mg\,l^{-1}}$) are the concentrations of Cr(VI) at time t and time zero, respectively, m ($\mathrm{g\,l^{-1}}$) is the mass of the adsorbent, k ($\mathrm{l\,g^{-1}}$) is the

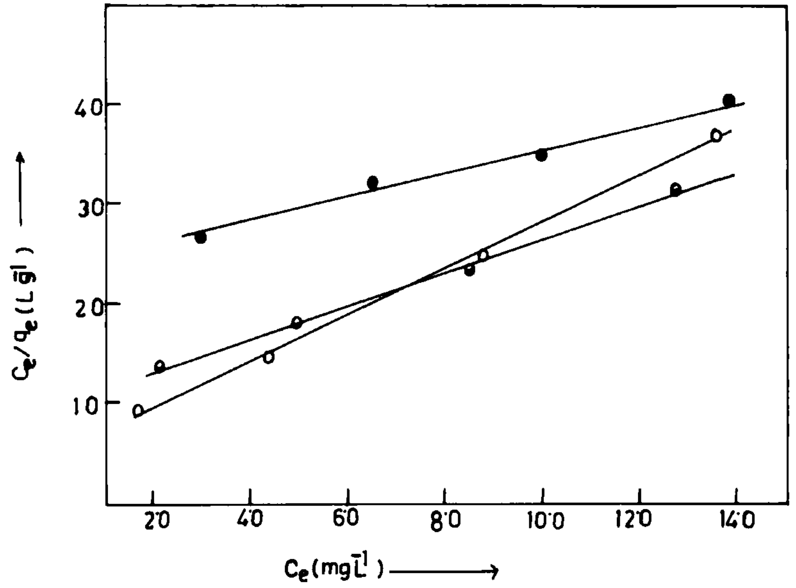


Figure 3 Langmuir plot for the removal of Cr(VI) by adsorption on China clay; (○) 30 °C, (◒) 40 °C and (●) 50 °C. Conditions: 0.5×10^{-4} M Cr(VI), 0.01 M $NaIO_4$ and pH 2.5.

Langmuir constant and β_L (cm sec^{-1}) and S_s (cm^{-1}) are the mass transfer coefficient and outer surface of the adsorbent per unit volume, respectively. The value of S_s, the outer surface of the adsorbent, was calculated by means of

$$S_s=\frac{m}{d_p\cdot\rho_p(1-\varepsilon_p)} \tag{4}$$

in which d_p (cm) and ρ_p (g cm^{-3}) are the mean particle diameter and density of the adsorbent used, respectively; ε_p, a dimensionless quantity, is the porosity of the China clay sample. A linear plot of

$$\ln\left(\frac{C_t}{C_0}-\frac{1}{1+mk}\right)\text{vs. } t$$

(Figure 4) confirms the applicability of the McKay model[23] for the adsorption of Cr(VI) on China clay. The value of the mass transfer coefficient, β_L, was calculated from the slope and intercept of this plot and found to be 5.6×10^{-3} cm sec^{-1} at 30 °C and pH 2.5. This value indicates that the rate of mass transfer on China clay is rapid enough for the present system and that the adsorbent can be used for purification of wastewaters rich in Cr(VI).

Along with the mass transfer there is the possibility of intraparticle diffusion in most adsorption processes, which is a rate-limiting step in such type of reactions.

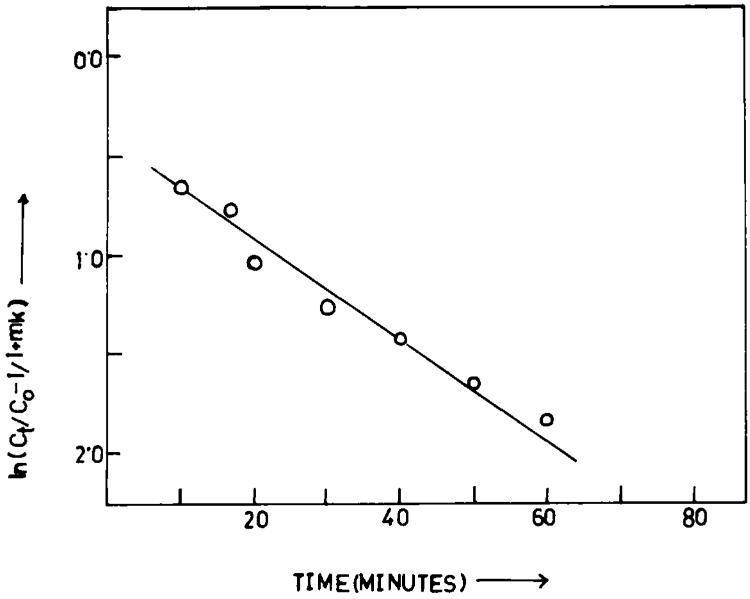


Figure 4 McKay plot for mass transfer of Cr(VI) during its removal by adsorption on China clay; temperature 30°C. Conditions: 0.5×10^{-4} M Cr(VI), 0.01 M $NaClO_4$ and pH 2.5.

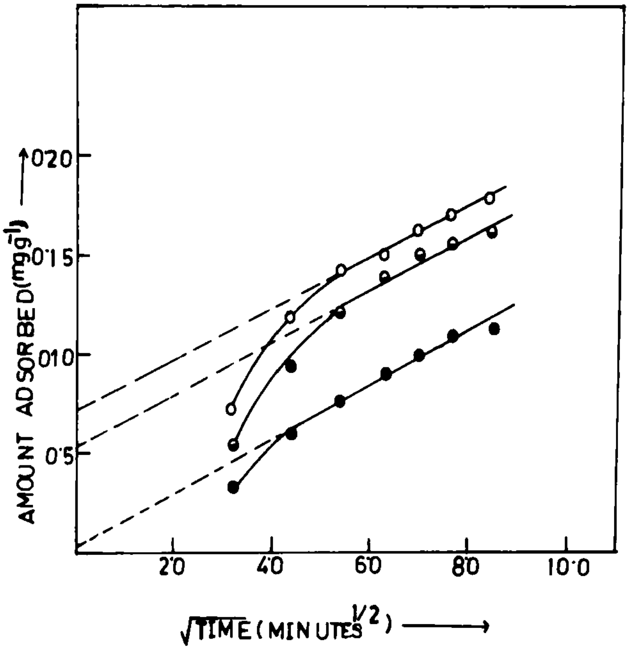


Figure 5 Intraparticle diffusion plot for the removal of Cr(VI) by China clay; (○) 30°C, (◒) 40°C and (●) 50°C. Conditions: 0.5×10^{-4} M Cr(VI), 0.01 M $NaClO_4$ and pH 2.5.

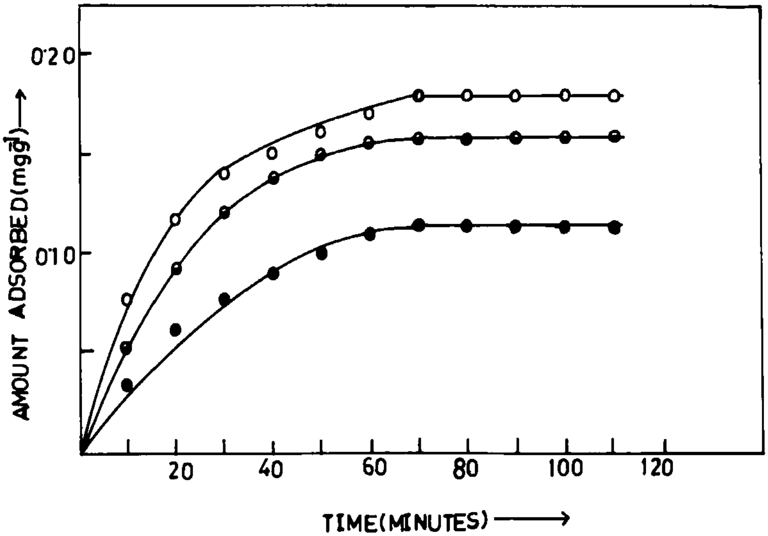


Figure 6 Plot showing the effect of temperature on the removal of Cr(VI) by adsorption on China clay; (○) 30 °C, (◒) 40 °C and (●) 50 °C. Conditions: 0.5×10^{-4} M Cr(VI), 0.01 M $NaC10_4$ and pH 2.5.

Testing of this possibility was done by plotting the amounts of Cr(VI) adsorbed ($mg\,g^{-1}$) against the square root of time (Figure 5). The curved nature of these plots is explained by the fact that the initial portion of the curve reflects the boundary-layer diffusion effect[23] and the final linear portions are due to intraparticle effects. The rate constants for intraparticle diffusion, K_1, at different temperatures were determined from the slopes of the straight-line plots of Figure 5; the values are given in Table 3. The intercept is proportional to the boundary layer thickness. It is also clear from the figure that the film thickness decreases with increasing temperature. The increased escaping tendency of adsorbate molecules from the adsorbent surface at increased temperatures seems to be the proper explanation of the decreased boundary layer thickness.

Effect of Temperature

The uptake of Cr(VI) by adsorption on China clay was found to decrease from 68 to 41% with a temperature increase from 30 to 50 °C (Figure 6) at a solution concentration of 0.5×10^{-4} M and pH 2.5. It is due to an increased escaping tendency of the adsorbate molecules at increasing temperatures and a reduction in the boundary layer thickness (Figure 5).

Effect of pH

China clay contains different metal oxides which, through amphoteric dissociation, develop charges on the surface in aqueous solutions:

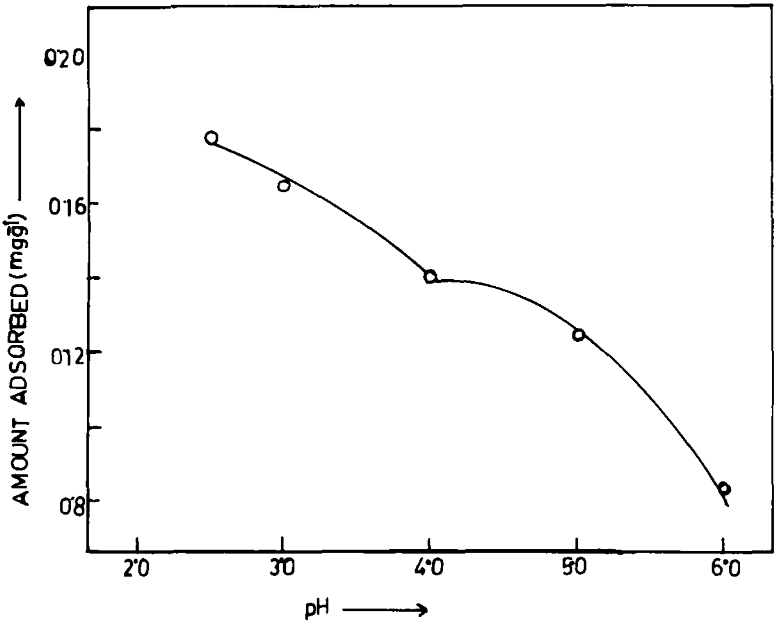
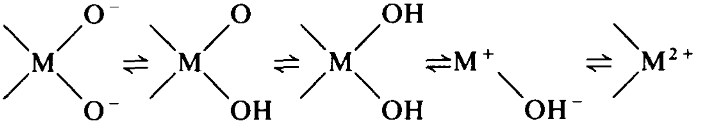


Figure 7 Effect of pH on the removal of Cr(VI) by China clay. Conditions: 0.5×10^{-4} M Cr(VI) 0.01 M $NaClO_4$ and 30 °C.



(5)

where 'M' stands for aluminium, silicon, etc.

In our experiment maximum uptake (68 %) of the Cr(VI) species was found at pH 2.5 (Figure 7) at a Cr(VI) concentration of 0.5×10^{-4} M and 30 °C. Our results agree with the earlier findings[19,20] that Cr(VI) uptake continuously decreases with increasing pH.

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