

Fly Ash-China Clay for Removal of Cr(VI) from Aqueous Solutions

K K PANDAY, GUR PRASAD & V N SINGH*

Applied Chemistry Section, Institute of Technology, Banaras Hindu University, Varanasi 221 005

Received 8 April 1983; revised and accepted 28 December 1983

The removal of Cr(VI) from aqueous solution by adsorption on a homogeneous mixture of fly ash and china clay (1:1) has been studied at various Cr(VI) concentrations, retention time, pH and temperatures of the solution. The Langmuir's constants have been determined graphically and by regression analysis. Maximum removal of Cr(VI) is observed at pH 2.0 and $30 \pm 1^\circ\text{C}$.

The use of various adsorbents for the removal of Cr(VI), one of the major pollutants, from aqueous solution has been reported in some earlier studies¹⁻³. In this note, we describe the efficacy of a mixture of fly ash and china clay (1:1) as an adsorbent for the removal of Cr(VI) from aqueous solution.

Fly ash and china clay were analysed by chemical methods⁴ and passed through 53 nm sieve. A homogeneous mixture (1 g) of fly ash and china clay (1:1) was taken in stoppered glass bottles and agitated (125 r.p.m) with aqueous solutions (50 ml each) of potassium dichromate of different concentrations, pH and temperatures. The amount of the adsorbent was further increased from 1.0 to 3.0 g and agitated with $1.0 \times 10^{-4} M$ potassium dichromate solution at pH 2.0 and $30 \pm 1^\circ\text{C}$. The progress of adsorption was determined spectrophotometrically using 1,5-diphenylcarbazide⁵. All experiments were done in duplicate with suitable reagent and mixed adsorbent blanks. The desorption studies were carried out in water and in 0.01 N sodium hydroxide solution.

Both the adsorbents, fly ash and china clay, mostly contain oxides of aluminium and silicon with traces of oxides of iron, calcium and magnesium. The adsorption data reveal that with decrease in concentration of Cr(VI) from $1.0 \times 10^{-4} M$ (10.4 mg litre⁻¹ of Cr) to $0.4 \times 10^{-4} M$ (4.16 mg litre⁻¹ of Cr), the adsorption of Cr(VI) by mixed adsorbent increases from 53 to 100% at pH 2.0 and $30 \pm 1^\circ\text{C}$. When the amount of the mixed adsorbent is further increased to 3.0 g, 100% removal is achieved at potassium dichromate concentration of $1.0 \times 10^{-4} M$. With increase in pH from 2.0 to 9.0, the adsorption of Cr(VI) decreases from 100 to 27% at concentration of $0.4 \times 10^{-4} M$, indicating that the acidic medium is favourable for the removal of Cr(VI). Similar results for fly ash-dichromate⁶ and fly ash-phenol⁷ systems

have been reported earlier. The higher adsorption in acidic pH is due to the fact that metal oxides of mixed adsorbent acquire positive charge at low pH (refs 8,9) and attract negatively charged adsorbate ions. The content of alumina in fly ash¹⁰ and clays¹¹ is important in the adsorption of anions. In acidic medium, the edge surface of alumina is positively charged over broad pH range (isoelectric point at pH 8.4). It interacts with dichromate ions to form surface compound at pH values below 8.4. Silica exhibits a steady negative charge at pH values above the isoelectric point (2.5) and thus has a little influence on adsorption of Cr(VI) as dichromate ions. However, at pH values below 2.5, its surface will be favourable for adsorption. The surface of mixed adsorbent becomes negatively charged⁹ and Cr(VI) is converted into Cr(III) in alkaline medium, affecting the nature of the adsorbate-adsorbent system and probably due to this reason adsorption is reduced to 27% at pH 9.0.

It is noted that the equilibrium data for the present system obey the Langmuir isotherm:

$$\frac{C}{(x/m)} = \frac{1}{K_1 K_2} + \frac{C}{K_2} \quad \dots(1)$$

where C is equilibrium concentration ($\mu\text{g litre}^{-1}$), x/m , the amount of Cr(VI) adsorbed per unit weight of adsorbent ($\mu\text{g g}^{-1}$) at equilibrium and K_1 and K_2 are Langmuir constants. The values of K_1 and K_2 were calculated from the Langmuir's plot (Fig. 1) and the values are $2.74 \times 10^{-3} \text{ litre } \mu\text{g}^{-1}$ and $306.06 \mu\text{g g}^{-1}$ respectively. The applicability of isotherm was further tested by regression analysis. The values of K_1 and K_2 calculated come out to be $2.02 \times 10^{-3} \text{ litre } \mu\text{g}^{-1}$ and $309.61 \mu\text{g g}^{-1}$ respectively. The agreement between the two sets of values is fairly good. This suggests the

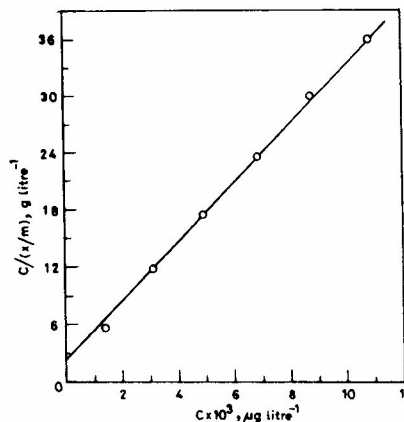


Fig. 1 — Langmuir isotherm for adsorption of Cr(VI) on fly ash-china clay (1:1)

validity of the Langmuir isotherm for the present system. The linearity of the Langmuir's plot indicates the formation of monolayer dichromate ions on the active alumina surface of the mixed adsorbent as the other oxides might have a little contribution in adsorption of Cr(VI).

The thermodynamic parameters for the adsorption of Cr(VI) have been calculated at pH 2.0. The values of ΔG° (-3.76 and -3.58 k cal mol $^{-1}$ at 30° and 40°C respectively) are negative, indicating the adsorption to be spontaneous. The negative value of ΔH° (-9.27 k cal mol $^{-1}$ at 30°C) indicates that the process is exothermic and the adsorption of Cr(VI) on mixed adsorbent occurs by long range attractive forces. The negative value of ΔS° (-0.018 e.u. at 30°C) shows that there is no configurational change and the surface compound is stable.

The adsorptive force between adsorbate and mixed adsorbent is so strong that Cr(VI) does not desorb in water. This is further confirmed by the IR spectra of mixed adsorbent, before and after adsorption of Cr(VI). The characteristic IR bands of $\text{Cr}_2\text{O}_7^{2-}$ ion at 750 and 860 cm $^{-1}$ (ref. 12) were shifted to 780 and 900 cm $^{-1}$ respectively after adsorption on mixed adsorbent surface, indicating the possibility of bonding of dichromate ions with the active sites of mixed adsorbent¹³. Cr(VI) could be completely

desorbed from the adsorbent on treating it with sodium hydroxide solution.

We are grateful to the CSIR, New Delhi for the award of a senior research fellowship to one of us (KKP).

References

- 1 Huang C P & Wu M H, *J Wat Poll Contr Fed*, **47** (1975) 2437.
- 2 Panday K K, Prasad G & Singh V N, *Removal of chromium from water by adsorption process* (Symp Fundamental and Applied Electro-chemistry, Bombay) 1982.
- 3 Jain K K, Singh V N & Prasad G, *Wollastonite for removal of Cr(VI)* (Symp Nuclear and Radiation Chemistry, Varanasi) 1981.
- 4 *Indian standard methods of chemical analysis of fireclay and silica refractory materials*, IS: 1527, 1960.
- 5 *Standard methods for the examination of water and wastewaters* (American public health association, Washington, DC) 1975, 192.
- 6 Gangoli N, Markey D C & Thodos G, *Removal of heavy metal ions from aqueous solution with fly ash* (Proc Natl Conf Complete Wastereuse) 1975, 855.
- 7 Khanna P & Malhotra S K, *Indian J Environ Health*, **19** (1977) 224.
- 8 Singh V N, Singh I S & Rai U S, *Indian J Chem*, **21A** (1982) 247.
- 9 Ahmad S M, *Can J Chem*, **44** (1966) 1663.
- 10 Chu T J, Steiner G R & McEntyre C L, *J Wat Poll Contr Fed*, **50** (1978) 2157.
- 11 Siffert B & Espinasse P, *Clays & Clay Minerals*, **28** (1980) 381.
- 12 Miller F A & Wilkins C H, *Analyt Chem*, **24** (1952) 1253.
- 13 Hair M L, *Infrared spectroscopy in surface chemistry* (Marcel Dekker, New York) 1967, 49.