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G. P. Dasmahapatra[a]; T. K. Pal[a]; A. K. Bhadra[b]; B. Bhattacharya[c]
[a] DEPARTMENT OF PHARMACEUTICAL TECHNOLOGY, JADAVPUR UNIVERSITY, CALCUTTA, INDIA [b] CENTRAL GLASS AND CERAMICS RESEARCH INSTITUTE, CALCUTTA, INDIA [c] DEPARTMENT OF METALLURGICAL ENGINEERING, JADAVPUR UNIVERSITY, CALCUTTA, INDIA

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TECHNICAL NOTE

Studies on Separation Characteristics of Hexavalent Chromium from Aqueous Solution by Fly Ash

G. P. DASMAHAPATRA and T. K. PAL*
DEPARTMENT OF PHARMACEUTICAL TECHNOLOGY

A. K. BHADRA
CENTRAL GLASS AND CERAMICS RESEARCH INSTITUTE

B. BHATTACHARYA
DEPARTMENT OF METALLURGICAL ENGINEERING

JADAVPUR UNIVERSITY
CALCUTTA-700 032, INDIA

ABSTRACT

Hexavalent chromium has been separated from an aqueous solution by fly ash. The particle size distribution and physical properties of fly ash have been illustrated. It is observed that the percent removal of Cr^{6+} by fly ash is affected by its concentration in aqueous solution, temperature, particle size, and pH. Better separation is obtained at acidic pH and at higher temperature. Particle size has a nonsignificant effect on separation. The reaction kinetics of separation follows first-order kinetics more satisfactorily at higher temperature.

Key Words. Chromium; Fly ash; Ion exchange; Separation; Adsorption

INTRODUCTION

Chromium has been used in a variety of industrial process such as tanning, electroplating, pickling, and aluminum anodizing, and in cutting

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* To whom correspondence should be addressed.

tools and glass and wool industries. The presence of chromium metal in the wastewater discharges of these industries is very common, and the concentration ranges much beyond the Indian tolerance limit, i.e., 2 ppm. Of the two stable forms of chromium i.e., Cr^{3+} and Cr^{6+}, the latter is much more toxic (1, 2), thus the environmental tolerance limit for Cr^{6+} in effluent is much stricter, i.e., 0.1 ppm. The most widely used technique for separation of chromium from effluent is hydroxide precipitation after its reduction to Cr^{3+} by ferrous sulfate or sodium bisulfite (3). Other important methods of treatment are ion-exchange (4), sulfide precipitation (5), solvent extraction, activated carbon adsorption (6), adsorption separation by iron hydroxide, alumina, etc. (7–9), and an electrochemical method (10). In the present study an attempt is made to determine the possibility of using fly ash, a by-product of coal burning in a boiler, especially in a thermal power plant, as an absorbing medium in a batch experiment.

MATERIALS AND METHODS

Fly ash is obtained from the electrostatic precipitation (ESP) outlet of the Southern generating station of CESC Ltd., Calcutta. Flyash collected from ESP was found to have substantial moisture due to the water spray used while disposing of fly ash from the ESP hopper in order to minimize its dispersion in the nearby atmosphere. Thus fly ash is heated at 400°C for an hour to make it moisture-free and to activate it before use. Hexavalent chromium bearing water is prepared by dissolving AR Grade potassium dichromate in distilled water. The concentration of Cr^{6+} is determined by the Syn-dithiozone method using a spectrophotometer made by Milton Ray (Model 20D). Syn-dithiozone is obtained from Merck, Germany. Particle size is determined by both an IS sieve and a sedigraph made by Micromerities, USA (Model 5000D). Porosity is determined by an Auto-Scan Mercury intrusion porosimeter made by Quantachrome, USA (Model 60K), and the surface area is determined by a surface area analyzer made by Carlo-Erbe Strumentazione, Italy (Model, 1750 sorpty). Zeta potential is determined by a Zeta meter, USA. For the chemical characterization of fly ash, it is digested in a platinum crucible using Pro-analysis Grade acids i.e., HF, HCl, HNO_3, and $HClO_4$ in succession and made water soluble. The different metal concentrations are determined by an Atomic Absorption Spectrophotometer made by Perkin-Elmer, UK (Model 2380).

EXPERIMENTAL

Batch separation experiments are carried out by shaking 2.0 g fly ash with 50 mL of the Cr^{6+} solution in a connical flask with stopcock in a rotary shaker. The initial pH is adjusted by using either 0.1 N H_2SO_4 or 0.1 N NaOH. The temperature dependence of the separation phenomenon is studied by keeping the Cr^{6+} solution with fly ash over a magnetic shaker in a incubator adjusted to the desired temperature. The progress of the separation experiment is determined by withdrawing a certain volume of the mixture and filtering it through a Whatman 42 filter paper. Blanks without fly ash are also prepared in a similar connical flask to correct for any separation.

RESULTS AND DISCUSSION

From x-ray diffraction studies it is found that the major mineral phase of fly ash is quartz with a minor amount of mullite and traces of magnetite. The chemical composition, physical properties, and particle size analysis of fly ash are illustrated in Tables 1, 2, and 3, respectively.

Effect of Contact Time and Separation Efficiency

The variation of percent removal of Cr^{6+} with time is illustrated in Fig. 1. It is evident from the figure that better removal of Cr^{6+} is obtained at a higher concentration with a limit of 25 mg Cr^{6+}/L solution, beyond which the percent removal declines. It is further found that the percent removal does not depend on the initial concentration. It increases up to 3 hours of contact time, beyond which there is no separation.

TABLE 1
Chemical Composition of Fly Ash

Serial no.	Constituent	% Composition
1	SiO_2	81.730
2	Al_2O_3	4.890
3	CaO	6.570
4	Fe_2O_3	1.286
5	MgO	4.642
6	MnO	0.026
7	CuO	0.001
8	ZnO	0.005
9	Na_2O	0.040
10	K_2O	0.265
11	TiO_2	0.432
Total		99.887

TABLE 2
Physical Characteristics of Fly Ash

Serial no.	Characteristics	Concentration
1	Loss on ignition (at 400°C), %	1.48
	(at 600°C), %	2.98
2	Mean particle size, μ	23.5
3	Porosity, %	0.09
4	Surface area, m^2/g	Below 1
5	Density, g/cm^3	1.06
6	pH zpc	0.9

Effect of pH

The variation of separation efficiency with pH is illustrated in Fig. 2. From the figure it is evident that Cr^{6+} separation efficiency increases steadily in acidic pH and decreases in basic pH. However, there is a marginal increase beyond pH 9.0 up to pH 12.0. The increase of separation efficiency may be due to the accumulation of positive charges over the surface of fly ash which significantly enhances the capacity to attract any Cr^{6+} metal present as the anion $Cr_2O_7^{2-}$.

TABLE 3
Particle Size Distribution of Fly Ash as Determined by Sedigraph

Serial no.	Particle size (range, μ)	% Weight
1	Above 70	3
2	70–60	3
3	60–50	4
4	50–40	8
5	40–30	13
6	30–20	19
7	20–10	24
8	10–8	5
9	8–6	7
10	6–5	4
11	5–4	2
12	4–3	3
13	3–2	3
	Below 2	2

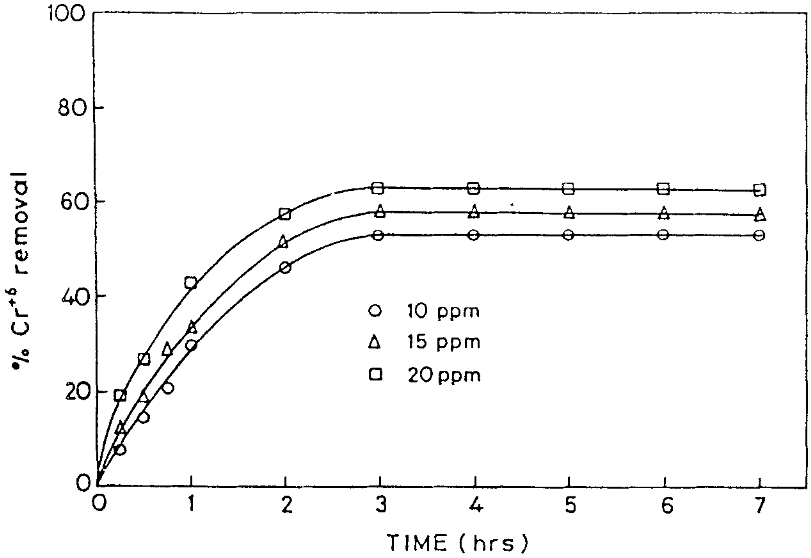

FIG. 1 Effect of contact time with percent removal of Cr^{6+} by fly ash.

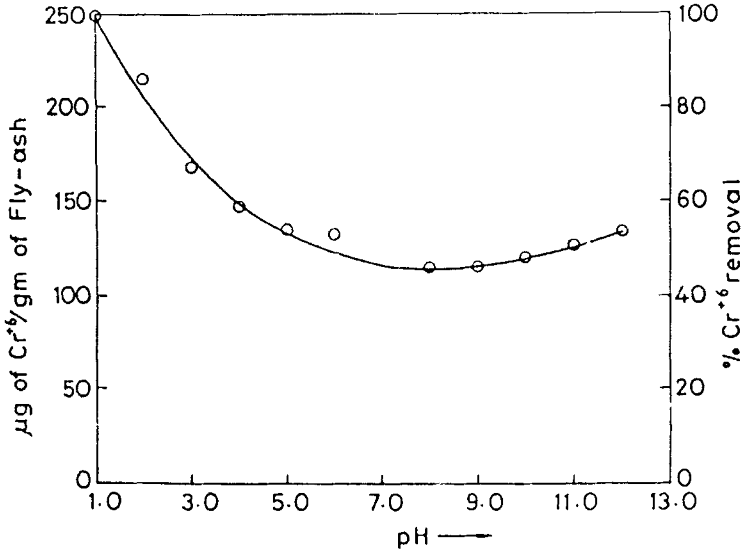

FIG. 2 Effect of pH on the separation efficiency of Cr^{6+} removal by fly ash.

Effect of Temperature

The effect of temperature variation on the separation efficiency of Cr^{6+} from aqueous solution is presented in Fig. 3. From this figure it is seen that the extent of separation increases along with an increase of temperature. Thus it may be concluded that the separation of Cr^{6+} by fly ash is primarily due to ion-exchange and partly due to adsorption. It is also observed that some sort of disorption might occur at higher temperature and the overall separation increases with an increase of temperature.

Effect of Particle Size

An insignificant increase of percent removal of Cr^{6+} is observed as the particle size decreases (Fig. 4). In spite of an increase in surface area due to the presence of finer particles, the percent removal is not increased proportionately. This indicates that the contribution of the adsorption phenomenon in this separation process is not very significant.

Kinetics of the Separation Process

The process of separation follows first-order kinetics with a slight deviation from linearity at the initial reaction stage. The rate equation proposed

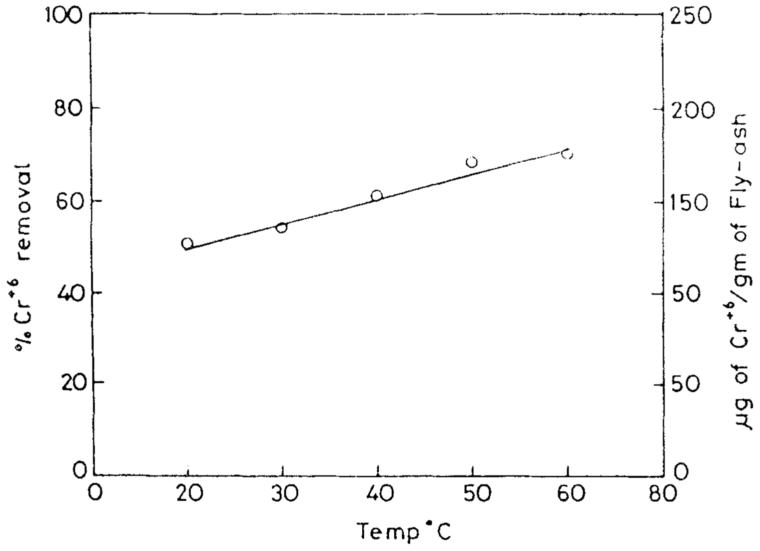

FIG. 3 Effect of temperature on the removal efficiency of Cr^{6+} by fly ash at pH 7.0.

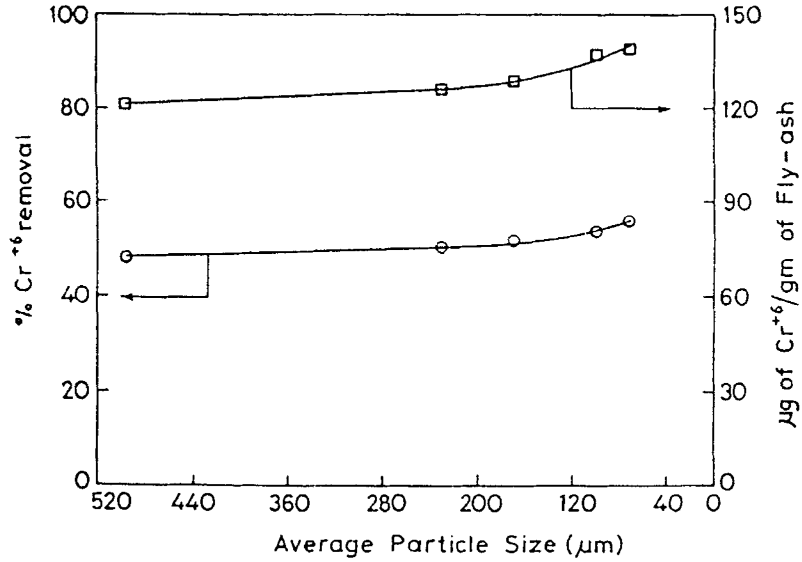

FIG. 4 Effect of particle size on the removal efficiency of Cr^{6+} at pH 7.0.

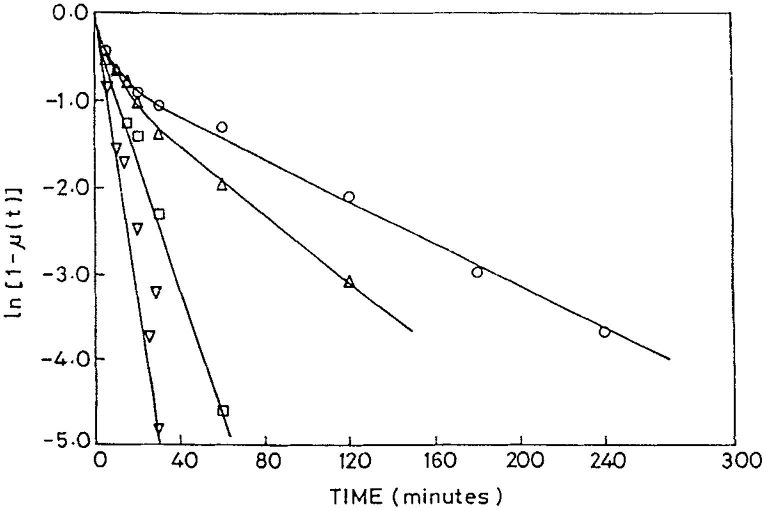

FIG. 5 Plot of $\ln[1 - \mu(t)]$ against t for the rate constant of the Cr^{6+} separation process by fly ash at different temperatures: (○) 20°C, (△) 30°C, (□) 40°C, (▽) 50°C.

by Bhattacharya and Venkobachar (11)

$$\ln[1 - \mu(t)] = k't$$

fits a linear curve at different temperature where $\mu(t)$ is the fractional attainment of equilibrium, t is the time, and k' is the overall rate constant of the process. Plots of $\ln[1 - \mu(t)]$ against t for the rate constant at different temperature are presented in Fig. 5. It is further found that at higher temperatures the initial nonlinearity decreases because the ion-exchange phenomenon is responsible for the total separation of Cr^{6+}. This is confirmed by estimation of the Ca^{2+} and Mg^{2+} ions released from fly ash in the aqueous phase. The overall rate constant of the process is determined from the slope of the curves and is found to be 0.0125, 0.0269, 0.075, and 0.147 min^{-1} at 20, 30, 40, and 50°C, respectively.

CONCLUSION

The present study indicates that the use of fly ash for the separation of Cr^{6+} from the aqueous phase is both economical and convenient. The process holds promise for exploitation on a large scale as a technique for wastewater treatment.

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