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Removal of chromium(VI) from electroplating industry wastewater using bagasse fly ash—a sugar industry waste material

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Abstract. A waste product generated in the sugar industry in India has been converted into a cheap potential adsorbent. This has been characterised and utilized for the removal of chromium (VI) from synthetic and actual wastewater. The sorption efficiency decreases with increase in pH. Adsorption of Cr (VI) on bagasse fly ash follows the Freundlich and Langmuir isotherms and these have been used to obtain the thermodynamic parameters of the process. The sorption capacity of this adsorbent for chromium removal is found to be comparable to other low cost adsorbents.

Introduction

Pollution by chromium and its compounds is of considerable concern as the metal is highly reactive and has found widespread use in leather tanning, electroplating, metal finishing and chromate preparation processes. Two predominant forms of chromium, namely Cr(III) and Cr(VI), occur in aqueous systems. Hexavalent chromium is known to be detrimental to human beings and animals. Over exposure of chrome workers to chromium dusts and mists has been related to irritation and corrosion of the skin and the respiratory tract and, probably, to lung carcinoma. Ingestion may cause epigastric pain, nausea, vomiting, severe diarrhoea and haemorrhage (Hung and Wu, 1975). Much has been reported on the treatment of chromium wastewater. The methods adopted include ion exchange, evaporation, chemical reduction and precipitation, electrolysis and electroplating, ion flotation and carbon adsorption. Activated carbon adsorption, one of the most efficient processes for the removal of Cr(VI) from wastewater has seldom been reported (Kim and Zoltek, 1977; Hung and Wu, 1977). The economics of the recovery and recycling of chromium in the case of certain Indian tanneries is quite well understood.

Most of these methods suffer from some drawbacks such as high capital and operational costs or the treatment and disposal of the residual metal sludges. Efforts made to develop low cost materials as possible media for the metal's removal from aqueous solutions, including natural water and industrial wastewaters, are quite well documented. Such materials range from industrial waste products (*e.g.*, waste rubber tyres, blast furnace slag), to agricultural products like wool, rice straw, coconut husk, sawdust and peat moss. Contributions have been made by many workers (Tan *et al.*, 1985; Periasamay *et al.*, 1991; Alves *et al.*, 1993; Sharma and Forester, 1993; Namasivayam and Ranganathan, 1994; Ajmal *et al.*, 1996; Dimitrova, 1996).

Earlier studies, undertaken at the Roorkee University laboratory, were concerned with the application of some metal hydroxides (Srivastava *et al.*, 1988), clays (Srivastava *et al.*, 1989), carbon developed from fertilizer waste material (Srivastava *et al.*, 1996; Gupta *et al.*, 1997a), activated slag developed from blast furnace waste

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(Srivastava *et al.*, 1997; Gupta *et al.*, 1997b; Gupta, 1998), lignin—a paper industry waste (Srivastava *et al.*, 1994), gels (Srivastava *et al.*, 1995), etc.

This present study reports on the continuing work on the treatment and utilization of bagasse fly ash generated in the sugar industry (Srivastava *et al.*, 1995a; 1995b; Gupta *et al.*, 1998a; 1998b). This waste product normally causes a disposal problem, but may possibly be used for the removal and recovery of Cr(VI) from wastewater. Results obtained with Pb^{2+} and some phenols were quite promising (Srivastava *et al.*, 1995a; 1995b; Gupta *et al.*, 1998a; 1998b). The factors that affect the interfacial reactions between chromium and fly ash have been investigated.

Materials and Methods

Bagasse fly ash was obtained from a local sugar refinery at Bijnor, Uttar Pardesh, India. Various reagents used were of AR grade. $K_2Cr_2O_7$ was used for Cr(VI). All solutions were prepared using double distilled water. pH measurements were made with a pH meter, model CT. No. CL46 Toshniwal, India. Concentrations of the metal ions were determined by atomic absorption spectrophotometer, model, Perkin Elmer 3100. A Phillips X-ray diffractometer was used for X-ray measurements of the material. The surface area of the adsorbent was determined by using a Quantasorb (USA) surface analyser.

The waste material was treated with hydrogen peroxide (100 volumes) at 60°C for 24 h to oxidize the adhering organic matter. Resulting material was then washed with distilled water, dried at 100°C and stored in a vacuum desiccator. The adsorbent was powdered, ground and sieved to the desired particle size before use. The analysis, characterization and batch to batch reproducibility of the material were strictly controlled.

Adsorption studies were mainly undertaken by batch technique with a solution of chromium of varying concentrations (1000 to 100 $\mu g\ cm^{-3}$). The contact time and conditions were based on extensive preliminary experiments which demonstrated the equilibrium uptake of Cr (VI) in almost ten hours. Shaking for any time between 10 and 24 hours gave practically the same uptake. As such, all adsorption experiments were run after equilibrating a 10 cm^3 of adsorbate solution for 10h, at temperatures 30, 40 and 50°C with 0.1g of adsorbent in all the sets run for this purpose. The effect of pH, temperature, interference by other metal ions and detergents on the uptake of chromium was observed as a function of adsorbate concentration.

The kinetics of adsorption of Cr (VI) on the prepared adsorbent was studied by batch technique (Finite Bath). A number of stoppered pyrex glass tubes containing a definite volume (10 cm^3 in each case) of solutions of Cr (VI) of known concentration were placed in a thermostatic shaking assembly. After attaining the desired temperature, a known amount of adsorbent was added in each tube. The solutions in various test tubes, were separated from the sorbent material and the concentration of Cr (VI) was determined.

Results and Discussion

The different constituents of bagasse fly ash, used in these studies were SiO_2-61.44, Al_2O_3-14.5, CaO-2.82, Fe_2O_3-4.86, MgO-0.71 and Loss on ignition-17.12 percent by weight. X-ray diffraction patterns of the product provided d-spacing values which reflected the presence of goethite, mullite, haematite, kaolinite, α-quartz and γ-alumina (Srivastava *et al.*, 1995). The fly ash is quite stable in water, salt solutions, acids, bases and organic solvents. The product under investigation slightly lowers the pH of deionized water, when kept in contact with it for more than 24 hours, thereby, it is classified as 'L' type according to the Steenberg classification (Mattson *et al.*, 1976). The surface area of the adsorbent material as determined by the Brunauer, Emmett and Teller (BET) method was 440 m^2g^{-1}.

The uptake of Cr (VI) as a function of hydrogen ion concentration was examined over a pH range of 1-6 (Fig. 1). The optimum pH for the removal of Cr (VI) is 1.0. The higher adsorption of Cr (VI) on bagasse fly ash at low pH may be due to the neutralization of negative surface charge by an excess of hydrogen ions, thereby facilitating the diffusion of dichromate ions and their adsorption on the prepared adsorbent. A significant reduction in the adsorption of Cr (VI) at higher pH is possibly due to the abundance of

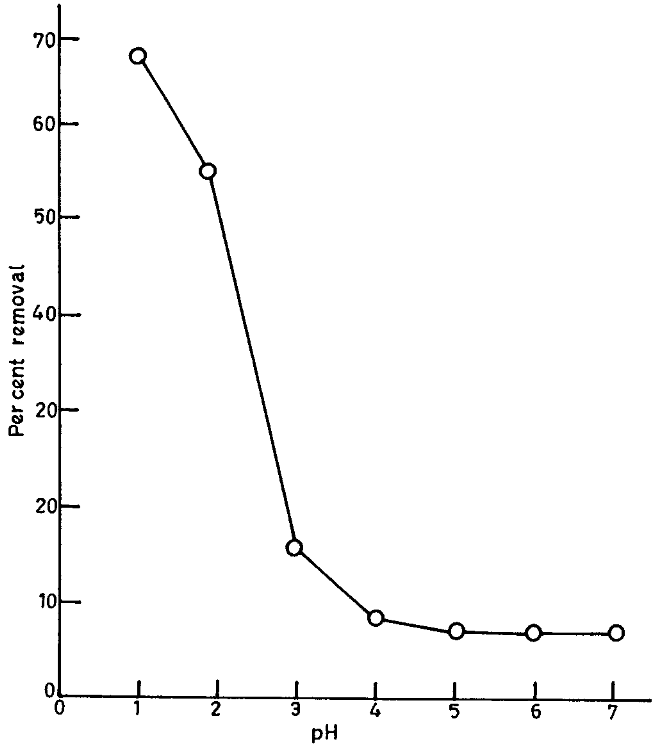

Figure 1. Effect of pH on the adsorption of Cr (VI) on bagasse fly ash.

OH^- ions resulting in an increased hindrance to the diffusion species.

The adsorption isotherms of Cr (VI) at different temperatures under optimum conditions are depicted in Fig. 2. The curves are regular and concave to the concentration axis indicating a positive adsorption. Further, the removal of Cr (VI) decreases with increase in temperature suggesting, the process to be exothermic in nature. The sorption data correlates well with the Freundlich and Langmuir models (equations 1 and 2)

$$q_e = K_F C^{1/n} \tag{1}$$

$$q_e = \frac{Q^\circ bC}{1 + bC} \tag{2}$$

where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent, C is the solute phase concentration, Q° is the solid phase concentration corresponding to complete coverage of available adsorption sites, K_F, $1/n$ and b are the characteristic constants where K_F and $1/n$ determines the adsorption capacity and adsorption intensity respectively, while b signifies the enthalpy of the adsorption process.

The values of Freundlich and Langmuir parameters are given in Table 1. The Langmuir constant Q° decreases with increase in temperature, thereby, indicating the process to be exothermic in nature. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L, which describes the type of isotherm (Weber and Chakraborti, 1974) and is defined by, $R_L = 1/(1 + bC_0)$, where b is the Langmuir constant and C_0 is initial concentration of Cr(VI). The value of R_L confirms whether the process is unfavourable ($R_L > 1$) or favourable ($R_L < 1$). For the adsorption of Cr (VI) on bagasse fly ash the calculated value of R_L is 0.016 which indicate a highly favourable adsorption since $R_L \ll 1$.

Thermodynamic parameters, obtained for the system, under investigation using equations 3, 4

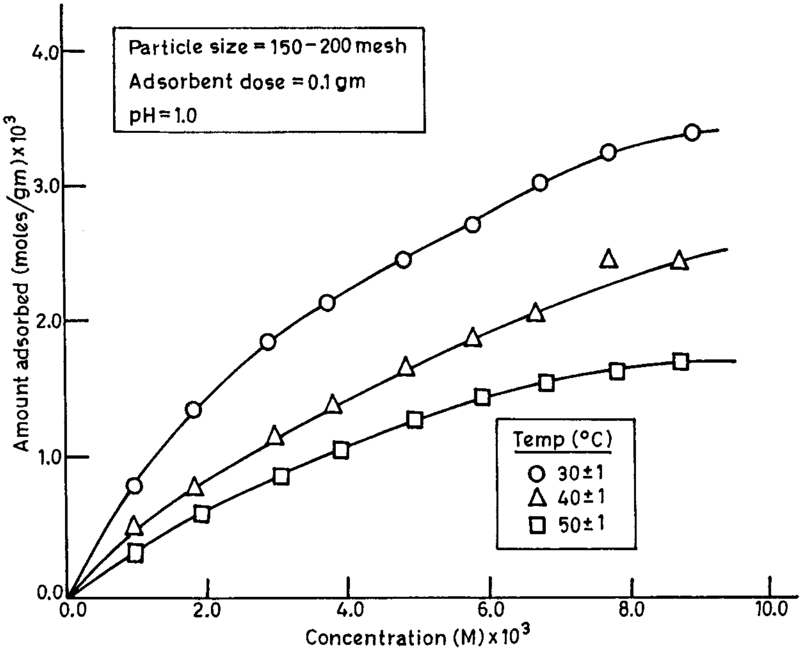

Figure 2. Adsorption isotherms of Cr (VI) at different temperatures on bagasse fly ash.

and 5 are given in Table 1.

$$\Delta G^\circ = -RT \ln K \tag{3}$$

$$\Delta H^\circ = -R\left[\frac{T_2 T_1}{T_2 - T_1}\right]\ln\frac{K_2}{K_1} \tag{4}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{5}$$

where K, K_1, and K_2 are equilibrium constants at 30, 40 and 50°C. Other terms have their usual significance. The negative free energy value indicates the feasibility of the process and the spontaneous nature of the adsorption. Free energy increases with increase in temperature indicating a decrease in adsorption at higher temperature. The negative values of enthalpy change (ΔH°) of the process suggest the exothermic nature and the possibility of strong bonding between chromium and bagasse fly ash. A negative ΔS° entropy of adsorption also reflects the affinity of the adsorbent material towards chromium.

In order to determine the effect of other metal ions (Na^+, Cd^{2+}, Zn^{2+}, Hg^{2+}, Al^{3+}) as well as an anionic detergent (Manoxol 1B) on chromium uptake by bagasse fly ash, experiments were per-

Table 1. Freundlich, Langmuir and Thermodynamic Parameters for Chromium Removal

Temp.	Freundlich Constant		Langmuir Constants		Thermodynamic Parameters		
	$\frac{1}{n}$	$K_F \times 10^4$	$Q^\circ \times 10^3$ (mol g^{-1})	$b \times 10^{-4}$ (1 mol^{-1})	$-\Delta G^\circ$ (kJ mol^{-1})	ΔH° (kJ mol^{-1}) (mean)	$-\Delta S^\circ$ (kJ mol^{-1}K^{-1}) (mean)
30°C	0.43	6.33	5.00	6.37	16.26	50.43	112.76
40°C	0.68	1.99	2.38	3.36	15.14		

formed at the optimum pH of the primary metal ion. The maximum interference was observed with Na^+ and minimum with Cd^{2+} while the others (Zn^{2+}, Hg^{2+}, Al^{3+}, Manoxol 1B) fell in between the two (Fig. 3). The reduction in chromium uptake might be due to the competitive ion effect between the interfering metal ions and chromium for the sorption sites on the bagasse fly ash.

The removal of chromium (Fig. 4) at different concentrations of adsorbent takes places in two stages. The first stage of solute uptake, the 'immediate solute removal', was obtained within first two hours, the 'subsequent removal', continued for a longer period of time. Thus the initial external/surface mass transfer was followed by a slower rate of internal diffusion within the bagasse fly ash itself. Although solute removal (%) increases with increasing adsorbent concentrations, the adsorption efficiency under identical conditions goes down. It was observed that after 8 hours of equilibrium, 46%, 48% and 50% of Cr (VI) (concentration 500 μg cm^{-3}, pH 1.0) was removed with 0.5, 1.0 and 2.0 gl^{-1} of bagasse fly ash, respectively. Such an enhanced quantity of absorbent (0.5–2.0 gl^1) was able to remove only an additional 4.0% amount of Cr (VI). Taking into account the handling problem associated with large quantities of bagasse fly ash and also considering a relatively smaller solute removal with smaller amounts of adsorbent, 1.0 gl^{-1} of bagasse fly ash has been taken as an optimum absorbent concentration.

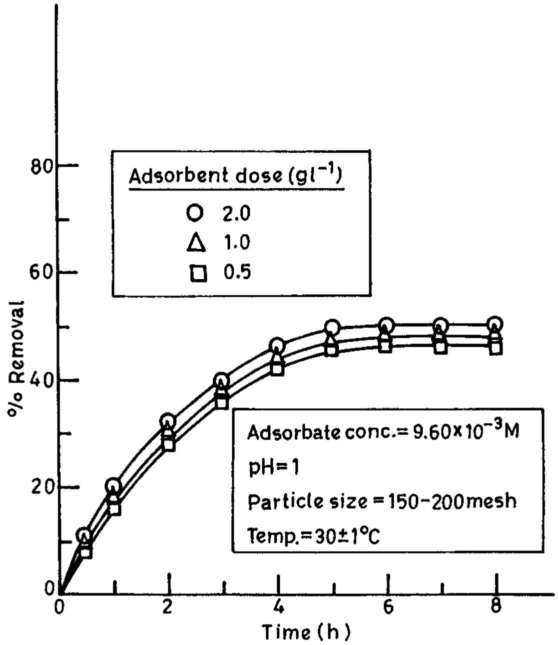

Figure 4. Effect of amount of bagasse fly ash on the rate of uptake Cr (VI).

The relationship between percent removal and initial adsorbate concentration (Fig. 5), depicts

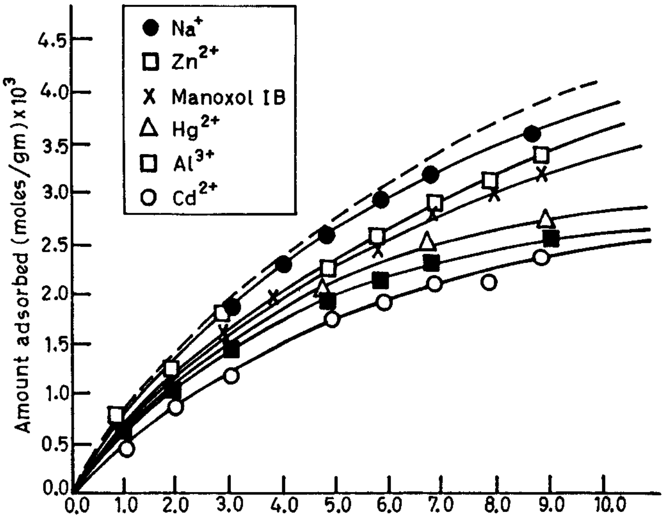

Figure 3. Competitive adsorption of Cr (VI) in absence (------) and in presence (——) of interfering metal ions and surfactant.

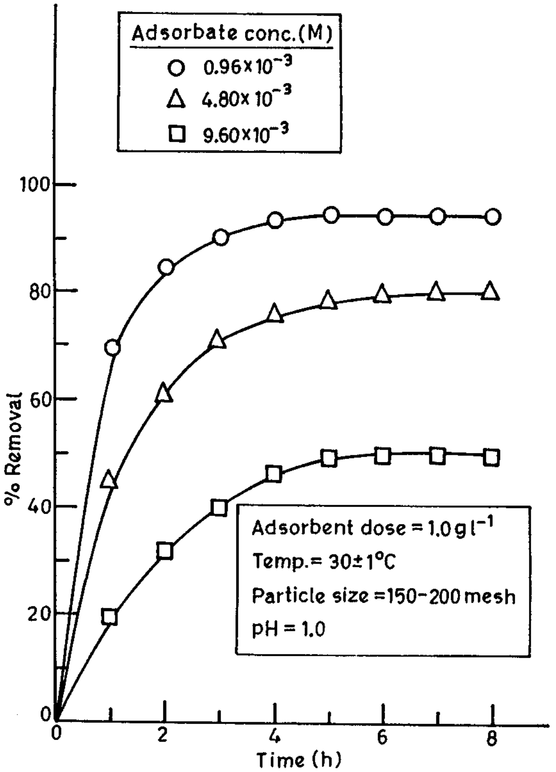

Figure 5. Effect of adsorbate concentration on the rate of uptake of Cr (VI) on baggase fly ash.

that the removal of adsorbate decreases with increasing metal ion concentration and so the removal of even trace quantities of pollutants from the solution, is not expected to pose any special problem in the system under investigation.

For practical application and designing of sorption reactors it is necessary to determine the steps involved in the process of adsorption which govern the overall rate of removal. The same was done using the ingenious treatment of Boyd *et al.*, (1947) and Reichenberg (1953).

A quantitative understanding of the sorption dynamics and other mechanistic aspects was possible with the help of following expressions (6–9).

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[\frac{-D_i t \pi^2 n^2}{r_0^2}\right] \qquad (6)$$

or

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp[-n^2 Bt] \qquad (7)$$

Where F is the fractional attainment of equilibrium at time 't' and is obtained by the expression 8.

$$F = \frac{Q_t}{Q_0} \qquad (8)$$

and

$$B = \frac{\pi^2 D_i}{r_0^2} \qquad (9)$$

where Q_t is the amount taken up at time 't' and Q_0 is the maximum uptake, D_i is the effective diffusion coefficient of ion in adsorbent phase, r_0 is the radius of the adsorbent particle assumed to be spherical and $n = 1, 2, 3\ldots$ are the integers defining the infinite series solution obtained by a Fourier type of analysis.

For every observed value of F, corresponding Bt values as derived from equation (7) have been obtained from the Reichenberg Table (Reichenberg, 1953). The linearity test of Bt versus time plots are employed to distinguish between controlled rates of exchange. At low concentrations (500 μg cm^{-3}) the Bt versus time plots deviated from linearity and did not pass through the origin, signifying the adsorption to be film diffusion while at high concentrations ($>$ 500 μg cm^{-3}) the same were linear and passed through the origin indicating the adsorption to be particle diffusion in nature.

The experimental conditions were set up for particle diffusion as the sole rate determining step to study the thermodynamics of the sorption process. The energy of activation, E_a, the pre-exponential factor D_0 (analogous to Arrhenius frequency factor), entropy of activation, $\Delta S^{\#}$ have been determined using the following expressions.

$$D_i = D_0 \exp\left[\frac{-E_a}{RT}\right] \qquad (10)$$

$$D_0 = 2.72\ d^2 \left[\frac{kT}{h}\right] \exp\left[\frac{\Delta S^{\#}}{R}\right] \qquad (11)$$

where 'd' is the average distance between the successive exchange sites and is taken as 5.0×10^{-10}m. R, h, k are the gas, Plank and Boltzmann constants respectively.

The values of E_a, $\Delta S^{\#}$ and D_0 for the diffusion of Cr (VI) in bagasse fly ash are listed in Table 2. The negative value of entropy of activation obtained from the adsorption of Cr (VI) reflect that no significant change occurs in the internal structure of bagasse fly ash. The effective diffusion coefficient (D_i) values at different temperatures (Table 2) follow the same order in which Cr (VI) gets adsorbed on the developed adsorbent.

Recovery of Adsorbate and Regeneration of Adsorbent Material

Recovery of the adsorbate material as well as regeneration of adsorbent is also quite an important process in wastewater treatment. In order to achieve this and to assess the practical utility of the adsorbent, column studies were performed. A glass column (40 cm long × 1.0 cm diameter) was filled with 0.5g (size, 200-250 mesh) of bagasse fly ash. The column was loaded with Cr (VI) (concentration 500 μg cm^{-3}) solution percolated downwards at a flow rate of 0.4 cm^3 min^{-1}. Desorption was tried with a number of eluting agents but the best results were obtained with 3M $NH_{3(aq)}$ solution, as 98 percent of chromium loaded on the column is eluted by this reagent. The column, of course, suffers a loss in adsorption efficiency and a decrease by 2 to 6 percent is recorded after the first run. It was further observed that a treatment of the column with 1M HNO_3 restores it back to original state and no loss in sorption capacity is noted in subsequent runs. When put to use with live wastes, it proved advisable to regenerate the column after every 4 to 5 cycles.

Wastewater obtained from a chrome tanning plant (analysis: pH 1.8-2.0; SS 330 μg cm^{-3}, TS 1200 μg cm^{-3}; Cr-3700 μg cm^{-3}) was tried with the column mentioned above. Adsorption of chromium was 100 percent but only 90 percent could be desorbed for reuse. If suspended and total solids are quite large in wastewater, it should be centrifuged at a higher speed before feeding the supernatant liquid into the column for the removal of chromium metal ions.

Conclusions

The results presented in this paper clearly reveal the economic feasibility of the use of waste bagasse fly ash which is available in abundance, as an adsorbent. The material can be utilized for Cr (VI) removal from wastewater even in the presence of other metal ions and surfactants. Economically this material would always be cheaper than the cheapest variety of commercially available carbon (Srivastava *et al*., 1995a). Recovery of metal ions and the chemical regeneration of the columns without the need for dismantling, will further bring down the cost.

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References

Ajmal, M., Ali Khan Rao, R. and Siddique, B. A. (1996) Studies on removal and recovery of Cr(VI) from electroplating wastes. *Water Research*, **30,** 1478–1482.

Alves, M. M., Beca, C. G., Guedes De Carvalho, R., Castanheira, J. M., Pereira, M. C. and Vasconcelos, L. A. T. (1993) Chromium removal in tannery wastewaters "polishing' by Pinus sylvestris bark. *Water Research*, **27,** 1333–1338.

Boyd, G. E., Adamson, A. N., and Meyers, L. S. (1947) The exchange adsorption of ions from aqueous solution by organic zeolites II kinetics. *J. Am. Chem. Soc.*, **69,** 2836–2848.

Dimitrova, S. V. (1996) Metal sorption on blast furnance slag. *Water Research*, **30,** 228–232.

Table 2. Effective Diffusion Coefficients (D_i), D_0, E_a, $\Delta S^{\#}$ Values for the Diffusion of Chromium (VI) in Bagasse Fly Ash

D_i (Effective diffusion coefficient) (cm^2 sec^{-1})		$D_0 \times 10^{-10}$	$E_a \times 10^{-3}$	$\Delta S^{\#}$
30°C	40°C	(cm^2 sec^{-1})	(J mol^{-1})	(JK^{-1} mol^{-1})
5.46	4.48	2.39	−3.25	−512.6

Gupta, V. K., Rastogi, A., Dwivedi, M. K., and Mohan, D. (1997) Process development for the removal of Zinc and Cadmium from wastewater using slag—A blast furnace waste material, *Sep. Sci. Technol.*, **32,** 2883–2912.

Gupta, V. K., Srivastava, S. K., and Mohan, D. (1997a) Sorption dynamics, process optimization, equilibrium uptake and column operations for the removal and recovery of malachite green using activated carbon and activated slag. *Ind. Engg. Chem. Res.*, **36,** 2207–2218.

Gupta, V. K. (1998) Equilibrium uptake, sorption dynamics, process development, and column operations for the removal of copper and nickel from aqueous solution and wastewater using activated slag, a low-cost adsorbent. *Ind. Eng. Chem. Res.* **37,** 192–202.

Gupta, V. K., Mohan, D., and Sharma, S. (1998a) Removal of lead from wastewater using bagasse fly ash—A sugar industry waste, *Sep. Sci. Technol.*, **33,** 1331–1343.

Gupta, V. K., Sharma, S., Yadav, I. S., and Mohan, D. (1998b) Utilization of bagasse fly ash generated in the sugar industry for the removal and recovery of phenol and p-nitrophenol from wastewater, *J. Chem. Technol. Biotechnol.*, **71,** 180–186.

Hung, C. P. and Wu, M. H. (1975) Chromium removal by carbon adsorption. *J. Water Pollun. Control Fed.*, **47,** 2437–2446.

Hung, C. P. and Wu, M. H. (1977) The removal of chromium (VI) from dilute aqueous solution by activated carbons. *Water Research*, **11,** 673–679.

Kim, J. I. and Zoltek, J. (Jr.) (1977) Chromium removal with activated carbon. *Prog. Wat. Technol.*, **9**, 143–155.

Mattson, J. S. and Mark, H. B. (1976) *Activated Carbon Surface Chemistry and Adsorption from Aqueous Solution*, New York, Marcel and Dekker.

Namasivayam, C. and Ranganathan, K. (1994) Removal of Fe(II) by waste Fe(II)/Cr(II) hydroxide from aqueous solution and electroplating industry wastewater. *Indian J. Chem. Technol.*, **1**, 351–355.

Periasamy, K., Srinivasan, K., and Murugan, P. K. (1991) Studies on chromium (VI) removal by activated groundnut husk carbon. *Indian J. Environ. Health*, **33,** 433–439.

Reichenberg, D. (1953) Properties of ion exchange resins in relation to their structures III kinetics of exchange. *J. Am. Chem. Soc.*, **75,** 589–597.

Sharma, D. C. and Forester, C. F. (1993) Removal of hexavalent chromium using sphagnum moss peat. *Water Research*, **22,** 1201–1208.

Srivastava, S. K., Bhattacharjee, G., Tyagi, R., Pant, N., and Pal, N. (1988) Studies on the removal of some toxic metal ions from aqueous solutions and industrial waste part I (removal of lead and cadmium by hydrous iron and aluminium oxide). *Environ. Technol. Lett.*, **9**, 1173–1185.

Srivastava, S. K., Tyagi, R., Pant, N., and Pal, N. (1989) Studies on the removal of some toxic metal ions part II (removal of lead and cadmium by montmorillonite and kaolinite). *Environ. Technol. Lett.*, **10,** 275–282.

Srivastava, S. K., Singh, A. K., and Sharma, A. (1994) Studies on the uptake of lead and zinc by lignin obtained from black-liquor-A paper industry waste material. *Environ. Technol. Lett.*, **15,** 353–361.

Srivastava, S. K., Gupta, V. K., Anupam and Mohan, D. (1995), Removal of some anionic and cationic detergents using an inorganic gel adsorbent. *Indian J. Chem.*, **34A,** 342–350.

Srivastava, S. K., Gupta, V. K., Yadav, I. S., and Mohan, D. (1995a) Removal of 2,4-dinitrophenol using bagasse fly ash—A sugar industry waste material. *Fresenius Envir. Bull.*, **4**, 550–557.

Srivastava, S. K., Gupta, V. K., Johri, N., and Mohan, D. (1995b). Removal of 2,4,6-trinitrophenol using bagasse fly ash—A sugar industry waste material. *Indian J. Chem. Technol.*, **2**, 333–336.

Srivastava, S. K., Gupta, V. K., and Mohan, D. (1996) Kinetic parameters for the removal of lead and chromium from wastewater using activated carbon developed from fertilizer waste material. *Environ. Model. and Assess.*, **1**, 281–290.

Srivastava, S. K., Gupta, V. K., and Mohan, D. (1997) Removal of lead and chromium using activated slag developed from blast furnace waste material. *J. Environ. Engg. ASCE.*, **123,** 461–468.

Tan, T. C., Chia, C. K., and Teo, C. K. (1985) Uptake of metal ions by chemically treated human hair. *Water Research*, **19,** 157–162.

Weber, T. W. and Chakraborti, R. K. (1974) Pore and solid diffusion models for fixed bed adsorbers. *J. Am. Inst. Chem. Engg.*, **20,** 228–238.