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Arsenic (III) removal from aqueous solutions by mixed adsorbent

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The removal of As(III) from its aqueous solutions by adsorption on homogeneous mixture of china clay and fly ash in equal proportions has been found to be dependent on various operating parameters such as concentration, temperature and *p*H. The As(III) removal is favourable at low concentration, high temperature and slightly basic condition at *p*H 8.0. The applicability of Langmuir isotherm in present system suggests the formation of monolayer coverage of As(III) molecules at the outer surface of the adsorbent. Thermodynamic parameters indicate the spontaneous and endothermic nature of the process. Adsorption kinetics studied using the model suggested by Lagergren infers a first order rate expression.

Keywords: As(III) adsorption, Adsorption kinetics, China clay, Fly ash, Langmuir isotherm

Arsenic is highly toxic[1-3] and is often used as herbicide and insecticide. The permissible limit of 0.06 ppm of arsenic in drinking water has been recommended by WHO and ICMR. The presence of arsenic in water beyond the permissible limit causes carcinogenic effects on living being. Its ingestion disturbs the nervous system and also acts as a casual factor for Haff's diseasse. Acute and choronic arsenic poisoning from the consumption of arsenic contaminated drinking water have been observed. Arsenic is recognized as a cause of skin, lung and liver cancer. It is suspected of causing mouth, esophagus, larynx bladder and paranasal sinus cancer. The toxicity of arsenic varies with its oxidation state. Arsenic(III) has been reported to be more toxic than arsenic(V). Arsenic(III) exerts its toxic action by attacking –SH groups of an enzyme thereby inhibiting enzyme action. The enzyme which generate cellular energy in the citric acid cycle are adversely affected. It precipitates the proteins. Presence of arsenic in natural water may originate from effluents of pesticides and fertilizers, plant desicants, tannery operations, metallurgical industries, dyes, detergents, glassware and ceramic production. Other sources include organic and inorganic chemicals, poultry feed additives, pharmaceuticals and petroleum refining industries and rare earth industries. Arsenic is also released from smelting and roasting of mineral ores, combustion of fossils fuels, leaching of mine wastes, volcanism and land erosion. Coal and oil burning contribute about 5000 metric tones of arsenic per year. High temperature processes involved in cement production add another approximately 3200 metric tones of arsenic per year. Among several techniques available for separation/extraction of metal ions from its solution, adsorption is preferred because of its sludge free operation and easy handling of the overall operation. In recent past much interest has been exhibited in the use of adsorption technique[4] for the removal of As(III) from water and wastewater by activated carbon[5] and several low cost adsorbents. In the present investigation a mixture of low cost china clay and fly ash has been used for the removal of As(III) from aquous solution by batch adsorption technique.

Experimental Procedure

Materials and method

China clay was obtained from Patharghatt village of Bhagalpur district of Bihar in India. Fly ash was obtained from Obra Thermal Power Plant, Mirzapur, India. Both adsorbents were sieved through 53 μm sieve and a homogeneous mixture of (1:1 ratio by weight) was obtained. The average particle size was measured by HIAC-320 Model 8002917 (ROYCO institute Division, U.S.A.). The surface area of individual and mixed adsorbents was determined by a "Three-point" N_2 gas adsorption method using a model QS-7 Quantasorb Surface Area Analyzer (Quantachrome Corp., U.S.A) and the porosity was determined by Mercury Porosimeter. The density measurement was carried out using specific gravity bottle at 30°C. The chemicals used were of analytical reagent grade and obtained from BDH, Bombay, India. All solutions were prepared[6] using distilled deionised water.

Batch adsorption experiments[7] were carried out by shaking 1.0 g of adsorbent mixure with 50 mL aqueous solutions of As(III) of desired concentrations at various *p*H and temperatures in different polythene bottles for various retention times using temperature controlled shaker at a constant speed of 220 rpm. The concentrations of As(III) remained in each sample after adsorption were determined, at desirable time intervals, by iodine monochloride method[8] using a systonics UV-VIS spectrophotometer, 118 at 520 nm wavelength.

Results and Discussion

Main constituents of the mixed adsorbent are silica and alumina while other oxides are also present in traces, as reported earlier[9]. It is thus expected that most of the As(III) in aqueous medium would be removed either by alumina, silica or by a combined effect of the both oxides. Intraparticle diffusion of adsorbate species within the porses of adsorbents is also explected because of porous nature of the adsorbents. The findings of the present investigation may be discussed in the light of the following factors.

Effect of concentration

The removal of As(III) by adsorption on mixed adsorbent increases with time and the equilibrium is attained in 120 min. The time of saturation (Fig. 1) is independent of concentration of As(III). The nature of curve which is single, smooth and continuous leading to saturation suggests the possibility of formation of monolayer coverage[10] on the surface of adsorbent. The arsenic uptake per unit mass of the adsorbent increases with increase in the initial concentration. However, the percentage removal increases with decrease in initial concentration. With change in concentration of As(III) from 2.5 to 10.0 ppm, the adsorbed amount increases from 0.1125 (90% removal) to 0.33 mg.g^{-1} (66% removal) at temperature 30°C and *p*H 8.0. The aqua – complexes of metal oxides present in the adsorbent are formed probably due to the chemisorption of water dipoles on the surface of adsorbent particles. These complexes are amphoteric in nature and may either dissociate proton from co-ordinately bonded water molecules [Eq. (1)] or may donate protons to hydroxyl ions [Eq. (2)] as follows:

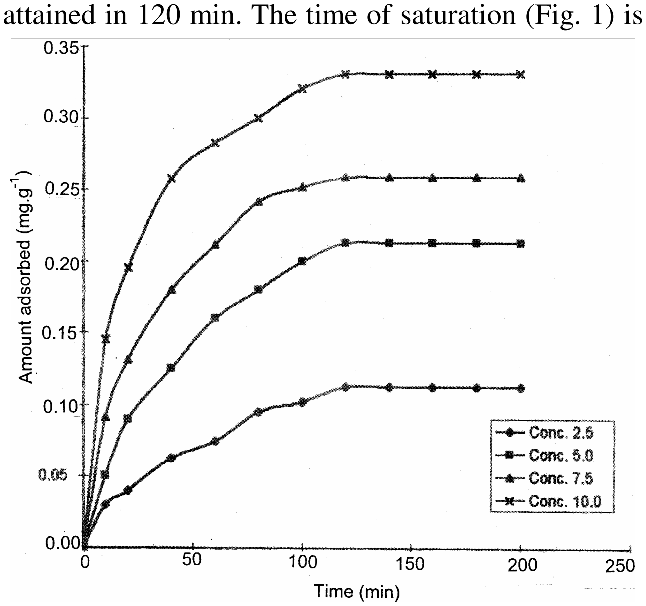


Fig. 1— Time variation of adsorption of As(III) on China clay and fly ash mixed adsorbent at different concentrations. Conditions: particle size<53 μm, Temp. = 30°C and *p*H = 8.0

$$M^{n+}(OH)_n(OH_2)_m \rightleftharpoons [M^{n+}(OH)_{n+1}(OH_2)_{m-1}]^- + H^+ \quad \ldots(1)$$

$$M^{n+}(OH)_n(OH_2)_m + H^+ \rightleftharpoons [M^{n+}(OH)_{n-1}(OH_2)_{m+1}]^+ \quad \ldots(2)$$

In the above equilibria, it is assumed that the coordination number of the metal ions remains constant. Basicity or acidity of the metal ions depends on the polarization of hydroxyl ion or, water molecules which further depends on the charge and radius of the metal ions.

Adsorption kinetics

The kinetics of adsorption of As(III) on mixed adsorbent was studied in the light of Lagergren equation[11]:

$$log(q_e - q) = log\ q_e - \frac{K_{ad}}{2.303}t \quad \ldots (3)$$

where q and q_e represent amount adsorbed (mg.g^{-1}) at any time t, and at equilibrium respectively, K_{ad} is the rate constant of adsorption. The straight line obtained from the plot of log (q_e-q) versus time (Fig. 2) indicates the first order adsorption process. The rate constant (K_{ad}) was found to be 0.0219, 0.0221 and 0.0226 min^{-1} at 30, 40 and 50°C respectively. Intraparticle diffusion during adsorption was recorded at different temperatures (30, 40 and 50°C). The rate constant of intraparticle diffusion (K_{id}) of As(III) at different temperatures was determined from the slop of the plot of amount adsorbed versus square root of time (Fig. 3). The linear portion of the plot may be attributed to the nature of intraparticle diffusion process of adsorbate species and it is the expected rate determining step during the adsorption.

Pore diffusion coefficient

The pore diffusion coefficient for the intraparticle transport of As(III) within the pores of mixed adsorbent was calculated using following equation:

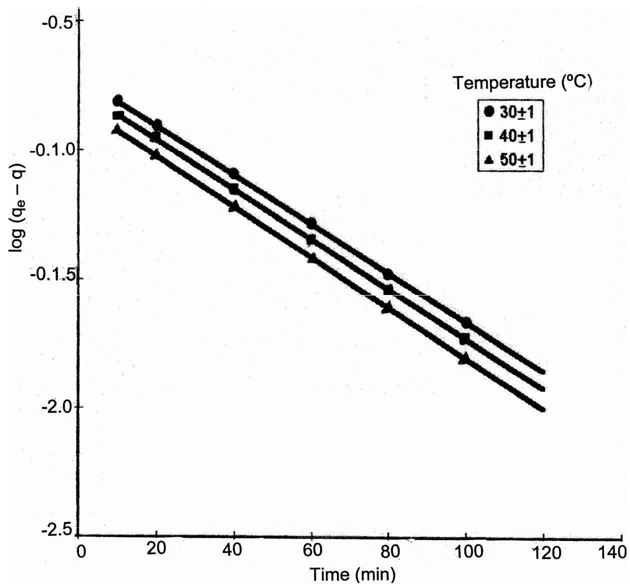


Fig. 2— Rate constant plot for As(III) adsorption at different temperatures. Conditions: conc. = 5.0 mg/L, particle size <53 μm and *p*H = 8.0

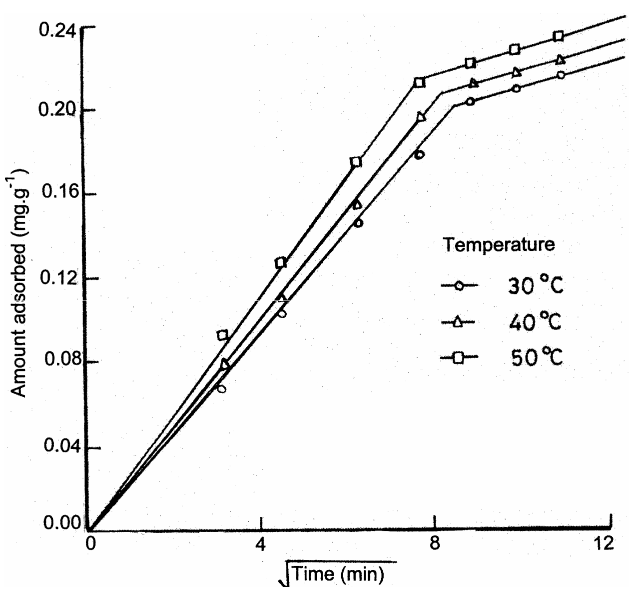


Fig. 3— Intraparticle diffusion plot for As(III) absorption on China clay-fly ash adsorbent at different temperatures. Conditions: conc. = 5.0 mg/L, particle size <53 μm and *p*H= 8.0

$$D = \frac{0.03 r_0^2}{t_{1/2}} \qquad \ldots (4)$$

where $t_{1/2}$ is the time for the half adsorption, r_o is the radius of the mixed adsorbent particle and D is the diffusion coefficient. The value of D is found to be 8.75×10^{-11} cm^{2}s^{-1} indicating that the process is goverened by diffusion[12] but pore diffusion is not the only rate limiting step.

Effect of temperature

With increase in temperature from 30 to 50°C, the adsorption of As(III) was found to increase from 85 to 93% (Fig. 4) at a concentration of 5.0 ppm and *p*H 8.0. The increase in the extent of adsorption with the rise of temperature implies the endothermic adsorption. It has been reported[13] that the increase in uptake with temperature is mainly due to an increase in the number of adsorption sites created by the breaking of some of the internal bonds near the edge of the crystal.

Thermodynamics parameters (Table 1), the change in standard free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) of the adsorption on the china clay-fly ash mixed adsorbent have been calculated at 30, 40 and 50°C using the following equations:

$$\Delta G^o = -RT \ln K \qquad \ldots (5)$$

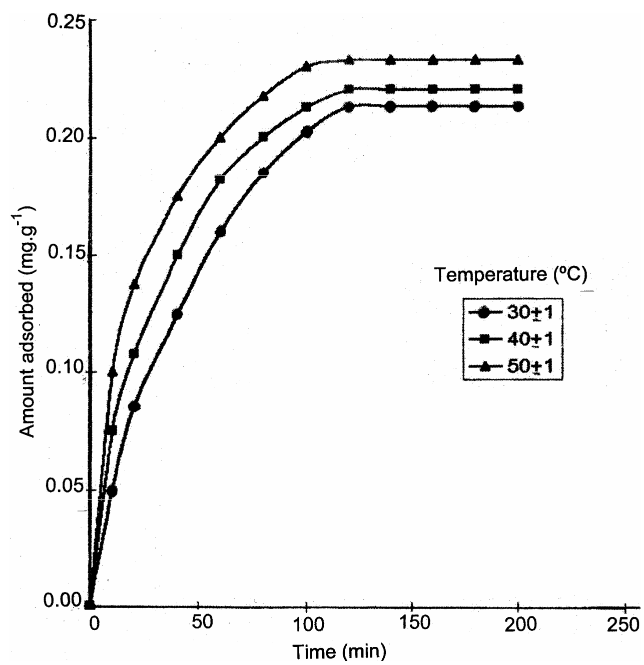


Fig. 4— Time variation of adsorption of As(III) on China clay and fly ash mixed adsorbent at different temperatures. Conditions: conc. = 5.0 mg/L, particle size4 <53 μm and *p*H= 8.0

$$\Delta H^0 = R\left[\frac{T_2.T_1}{T_2 - T_1}\right] \ln\frac{K_2}{K_1} \quad \ldots (6)$$

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} \quad \ldots (7)$$

where K, K_1 and K_2 are equilibrium constants at temperature T, T_1 and T_2 respectively, derived from Langmuir plots. The negative values of free energy change (ΔG°) at different temperatures indicate the spontaneous nature of adsorption. The positive value of enthalpy change (ΔH°) shows the endothermic nature of the adsorption process. The positive value of entropy (ΔS°) indicates some structural change at the solid-solution interface. The values of thermodynamic parameters provide information for understanding the nature of adsorption mechanism[14] as well as in predicting the optimum condition for the removal of arsenic from water.

Adsorption isotherm

The equilibrium distribution of adsorbate species at the solid-solution interface and also in the bulk at a particular temperature is of paramount importance to the environmentalists, dealing with the study of wastewater treatment by adsorption. The purpose of the adsorption isotherm is to provide an idea about the capacity of the adsorbent for the removal of As(III) through adsorption process. The maximum possible adsorption of the adsorbate species at the solid surface is a function of its concentration at constant temperature:

$$q_e = f\,(C_e) \quad \ldots (8)$$

where q_e (mg g^{-1}) is the amount of adsorbate adsorbed at equilibrium and C_e (mg L^{-1}) is the equilibrium concentration of the adsorbate in solution. The validity of a particular isotherm to any adsorbate-adsorbent system is highly limited and quite specific in nature for a definite range of concentrations. However, the equilibrium data have been analysed in the light of Langmuir adsorption isotherm. The adsorption capacity of the adsorbent has been determined for the uptake of adsorbates undertaken for the study at different temperatures and results are also compared with non-linear regression to prove the validity of the Langmuir isotherm[15].

The equilibrium data for the adsorption of As(III) on the adsorbent used at various temperatures were calculated with the help of Langmuir isotherm equation, which is based on the monolayer coverage of adsorbate on the surface of adsorbent. The rearranged linear form of Langmuir equation is written as:

$$\frac{Ce}{qe} = \frac{1}{Q^{\circ}.B} + \frac{Ce}{Q^0} \quad \ldots (9)$$

where Q° and b are Langmuir constants related to the capacity and energy of adsorption respectively. The values of Q° and b at different temperatures were determined (Table 2) from the slopes and intercepts of the linear plots of C_e/q_e versus C_e (Fig. 5). The study

Table 1— Thermodynamic parameters for adsorption of As(III) on china clay and fly ash mixture

Temp. ($^{\circ}$C)	ΔG^{o} (kCal/mol)	ΔH^{o} (kCal/mol)	ΔS^{o} (kCal/mol)
30	-1.045	-	-
40	-1.239	4.839	17.9
50	-1.660	11.953	42.15

Concentration = 5 mg/L and *p*H = 8

Table 2— Values of Langmuir constant (Q^{o}), separation factor (b), equilibrium parameter (R_L) and rate constant of intraparticle diffusion (K_{id})

Temp. (°C)	Q°	b (mg.g^{-1})	R_L	k_{id} (mg.g^{-1}min$^{-1/2}$)
30	0.389	1.590	0.112	0.0093
40	0.396	2.065	0.088	0.0096
50	0.399	3.548	0.0534	0.0106

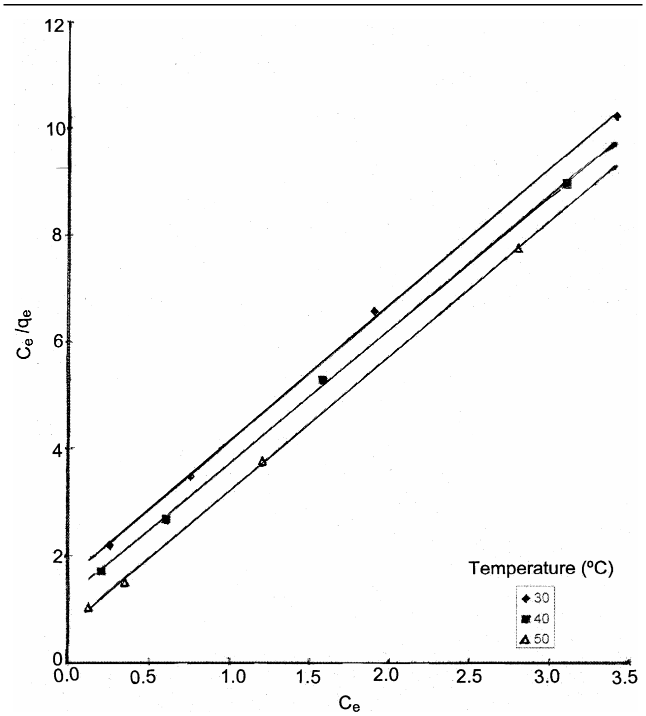


Fig: 5— Langmuir isotherm plot for As(III) adsorption at different temperatures. Condition: conc. = 5.0 mg/L, particle size <53 μm and *p*H = 8.0

of adsorption isotherm is useful in determining the adsorption capacities of mixed adsorbent of china clay and fly ash for the removal of As(III) at certain temperature. The equilibrium data for the adsorption of As(III) on mixed adsorbents at various temperatures and *p*H 8.0 follow the rearranged Langmuir equation. Further a dimensionless equilibrium parameter R_L supports the finding of Langmuir process, which is expressed as:

$$R_L = \frac{1}{1 + bC_0} \qquad \ldots (10)$$

The value of R_L for the system at different temperatures has been found to be between zero and one (Table 2) showing favourable adsorption of As(III) on mixed adsorbent (1:1).

Effect of *p*H

The change in the extent of adsorption of As(III) from 0.125 to 0.213 $mg.g^{-1}$ has been found with the increase in *p*H from 4.0 to 8.0 and maximum removal (85%) has been found at *p*H 8 (Fig. 6). The major constituents of mixed adsorbent are oxides of aluminum and silica; with the increase in *p*H, the positive surface charge density on constituent oxide

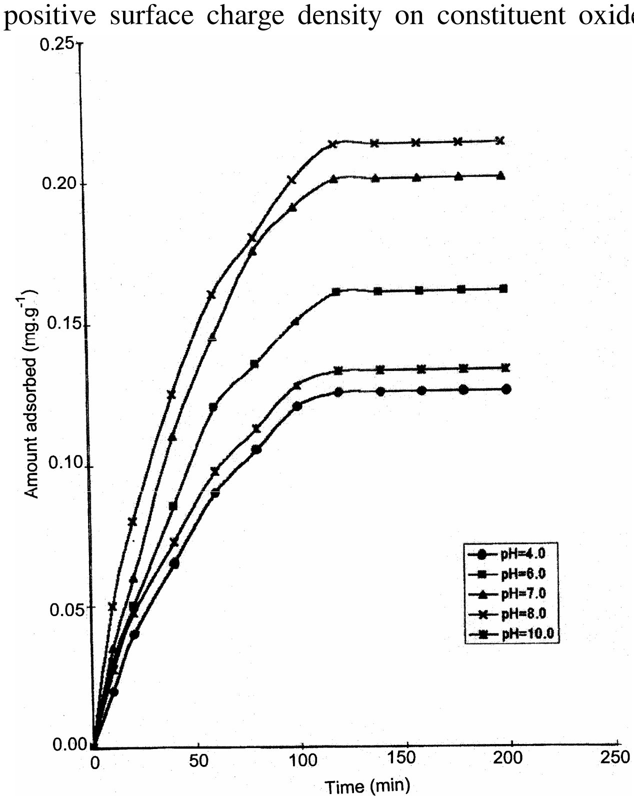
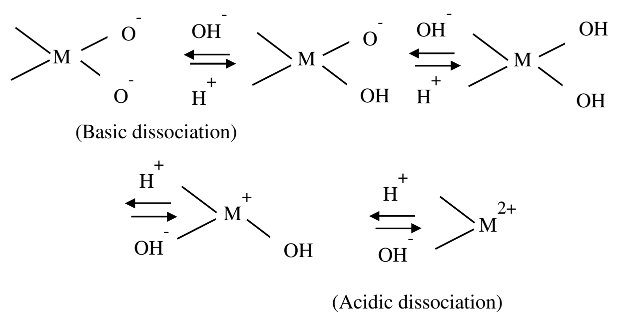


Fig. 6— Time variation of As(III) adsorption at different *p*H values. Conditions: conc. = 5.0 mg/L, particle size <53 μm and Temp. = 30°C.

(Al_2O_3) of adsorbent decreases and the negative surface charge density on SiO_2 increases. Due to this either fact the surface becomes slightly positive or negative or becomes neutral depending on the extent of the changes in the surface charge density of oxides. The probability of maximum adsorption of As(III) in the form of neutral species H_3AsO_3 at *p*H 8.0 is supported by the present findings. Thus, the results obtained at various *p*H values may be explained on the basis of aqua complex formation and its subsequent acid-base dissociation at the solid solution interface[16]. Change in surface charge occurs in the following manner:



where M stands for Al, Si, Fe, Ca etc. Further, in extreme acidic conditions, the adsorbent surfaces are highly protonated and such a situation is not favourable for As(III) removal resulting almost no change in the extent of adsorption within the *p*H range 2.5-5.0. With the increase in *p*H of system, the degree of protonation of the surface reduces gradually and approaches to zero near zero point charge (zpc) of the adsorbent. The species like $H_2AsO_4^-$ and $HAsO_4^{2-}$ which may be formed during the adsorption process may play a role in the molecule surface interaction or occlusion phenomena[17] and may also affect the arsenic adsorption mechanism.

Conclusion

The following conclusions may be drawn from the present investigations:

(1) An homogeneous mixture of chin clay and fly ash shows a good adsorption capacity towards As(III).

(2) The fitness of Langmuir adsorption isotherm in the present system shows the formation of monolayer coverage of the As(III) at the outer surface of the mixed adsorbent and the process is endothermic in nature.

(3) The adsorption process has been found to be partially diffusion controlled phenomena.

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References

1 Irgolic K J, *Arsenic Environment*, in *Frontier in Bioinorganic Chemistry*, edited by A V Xavier (VCH Publishers, Weinheim, Germany), 1986.
2 Wilson R, *Chronic Arsenic Poisoning: History, Study and Remediation* (Cambridge, Hardward University), 2001.
3 Mckee J E & Wolf H W, *Water Quality Criteria* (California State Water Quality Control Board, Pub), 3A, 1963.
4 Raji C, Manju G N & Anirudhan T S, *Indian J Eng Mater Sci,* 4 (1997) 254.
5 Kula I, Urlu M, Karaoglu H & Celik A, *Biores Technol*, 99 (2007) 492.
6 Singh A P, Srivastava K K & Shekhar H, *Proc Nat Acad Sci, India Sect* A, 78 (2008) 282.
7 Meena A K, Mishra G K, Kumar S, Rajagopal C & Nagar P N, *J Sci Ind Res*, 63 (2004) 410.
8 Howard A G & Arbab-Zabar M H, *Analyst*, 105 (1980) 338.
9 Singh A P, Srivastava K K & Shekhar H, *J Sci Ind Res*, 66 (2007) 952.
10 Pandey K K, Prasad G & Singh V N, *J Chem Technol Biotechnol,* 34A (1984) 367.
11 Sen A K & De A K, *Water Res*, 21 (1987) 885.
12 Michelson L D, Gideon P G, Pace E G & Kutul L H, *Water Res Technol Bull,* USDI Office, 74 (1975) 425.
13 Bercket G, Arog A Z & Ozel M Z, *J Colloid Interface Sci,* 187 (1997) 338.
14 Wang Z, Liu F & Zhange Q, *Indian J Chem*, 44A (2005) 2051.
15 Bhattacharya A K & Venkobachar C, *J Environ Eng, ASCE,* 110 (1984) 110.
16 Ahmed S M, *Can J Chem*, 44 (1966) 1663.
17 Benjamin M M & Bloom N S, In *Adsorption from Aquous Solutions,* edited by P H Tewari (Plenum Press, New York), 1981.