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Removal of Lead from Wastewater Using Bagasse Fly Ash—A Sugar Industry Waste Material

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ABSTRACT

Bagasse fly ash, a waste generated in sugar industries in India, has been converted into a low cost adsorbent and has been used for the removal of lead from aqueous solutions in the 4.80×10^{-4} to 4.83×10^{-3} M concentration range. Maximum removal takes place at pH 3.0 using 10 $g{\cdot}L^{-1}$ of the adsorbent of particle size 150–200 mesh. The effect of the presence of other metal ions, temperature, and contact time has also been studied. Sorption data have been correlated with both Langmuir and Freundlich adsorption models. The adsorbent has been satisfactorily used for the removal of Pb^{2+} from the effluent of a metal-finishing plant.

Key Words. Lead; Wastewater treatment; Low cost adsorbent; Adsorption; Bagasse fly ash; Metal ions; Solid waste utilization

INTRODUCTION

Safe and effective disposal of heavy metal-bearing wastewater is a difficult task due, in part, to the fact that cost-effective treatment alternatives are not available, especially in less-developed countries (1). Lead is ubiquitous in the environment and is hazardous (2). As per the Indian Standard Institution (ISI) specification, the tolerance limit for the discharge of lead into drinking water is 0.05 $mg{\cdot}L^{-1}$ (3) and in land surface waters is 0.1 $mg{\cdot}L^{-1}$ (4). A

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number of methods are available for the removal of metal ions from aqueous solutions. These include ion exchange, solvent extraction, reverse osmosis, precipitation, coprecipitation, and adsorption. The process of adsorption by activated carbon and other adsorbents has long been a subject of study. Research interests in recent years have grown into the production of low cost alternatives to activated carbon which remains an expensive material. Efforts made in this direction up to 1992 are reviewed by Pollard et al. (5). Other reports include the use of coral sand (6), clays (7, 8), metal hydroxides (2), chelating resins (9), crown ethers (10, 11), metal oxides (12, 13), zeolites (14, 15), etc.

The sugar industry is one of the most important agricultural-based industries in India. Bagasse fly ash, a waste generated from this industry, causes a disposal problem. Currently this is being used as a filler in building materials, and no proper methodology of treatment or application of this waste has been worked out. Our earlier efforts to use wastes of some prime industries for the removal of metals and other toxic substances have been very successful (16–22). Continuing our efforts, we have developed an adsorbent from bagasse fly ash and tried it for the removal of lead from aqueous solutions. The results are described in this communication.

MATERIALS AND METHODS

All reagents used were of AR grade. A stock solution (1.0×10^{-2} M) of the test sorbate was made by dissolving reagent-grade $Pb(NO_3)_2$ in double distilled water. The ionic strength was kept constant using different amounts of $NaNO_3$ after accounting for the ionic concentration due to HCl and NaOH used for adjusting the pH.

Equipments

pH measurements were made on a pH meter (Model CT No. CL46, Toshniwal, India). Atomic absorption spectra were recorded on an atomic absorption/emission spectrophotometer (Model 3100 Perkin-Elmer). Scanning electron microscopy was performed using a Phillips SEM 501 electron microscope.

Material Development

The waste material was obtained from a local sugar industry at Bijnor (U.P.). This material was treated with excess hydrogen peroxide (100 volume) at 60°C for 24 hours until the evolution of bubbles stopped. This indicated the complete oxidation of adhering organic matter. The resulting product was then washed with distilled water and dried at 100°C for 24 hours and sieved before use to obtain particles of uniform mesh size (100–150, 150–200, and 200–250 BSS mesh). Finally, the product was stored in a vacuum desiccator.

Determination of Lead

Pb^{2+} was determined by AAS at 283.30 nm using an air-acetylene flame (light source: hollow cathode). For this purpose, $Pb(NO_3)_2$ solutions of various concentrations (1.0×10^{-5} to 1.0×10^{-2} M) were prepared and their absorbance recorded by AAS. A calibration plot was drawn, from which the concentration of the test solution was calculated.

Sorption Studies

Sorption studies were performed by the batch technique to obtain the rate and equilibrium data. A series of 50 mL test tubes filled with 10 mL of lead solution of varying concentrations maintained at pH 3.0 and at constant ionic strength were placed in a thermostat cum shaking assembly. At the desired temperature a known amount of adsorbent (0.1 g; particle size 150–200 mesh) was added into each tube and agitated intermittently. Preliminary investigations showed that equilibrium uptake was attained in 6–8 hours with practically no change observed up to a period of 24 hours. All adsorption experiments were, however, run after equilibrating 10 mL of adsorbate solution for 24 hours to ensure complete uptake. After this period the supernatant solution was centrifuged and the amount of uptake of lead was determined. The initial sorbate concentration ranged from 4.80×10^{-4} to 4.83×10^{-3} M. Sorption studies were carried out at 30, 40, and 50°C to assess the effect of temperature. To obtain the adsorption vs time data, solutions of the specified tubes (at a fixed $[Pb^{2+}] = 4.80 \times 10^{-4}$ M) were separated at different times from the sorbent material and analyzed for lead content. The effect of pH was studied over a pH range of 2–6 by adjusting the pH with dilute HCl and NaOH. The influence of an anionic surfactant, Manoxol-IB [sodium di(2-ethylhexyl)sulfosuccinate], on the sorption of lead was studied at the optimum pH (3.0) as a function of the concentration of surfactant. Stoppered glass tubes containing adsorbate solution along with the detergent and fixed amount of adsorbent ($10\ g \cdot L^{-1}$) were equilibrated for 24 hours. The supernatant was centrifuged and analyzed for aqueous metal.

A similar procedure was adopted to study the interferences caused by the presence of other metal ions.

RESULTS AND DISCUSSION

The waste material obtained from the sugar industry was found to be stable in water, electrolytes, acids, and bases. One gram of the adsorbent was stirred with 100 mL of deionized water (pH 6.8) for 2 hours and left for 24 hours in an air-tight stoppered conical flask. A lowering of the pH (6.4) was observed and, therefore, according to Steenberg's classification (23), the mate-

TABLE 1
Chemical Constituents and Other Characteristics of Bagasse Fly Ash

	Percentage by weight
Constituents:	
SiO_2	61.44
Al_2O_3	14.5
CaO	2.82
Fe_2O_3	4.86
MgO	0.71
Other characteristics:	
Loss on ignition	17.12%
Porosity	0.36 (fraction)
Surface area	440 $m^2 \cdot g^{-1}$

rial may be treated as an "L" type in nature. Chemical composition and characteristics of the material (18, 19) are presented in Table 1, and *d*-spacing values (x-ray diffraction) which reflect the presence of different minerals are given in Table 2. The surface area as determined by malachite green adsorption isotherm (18) was 440 $m^2 \cdot g^{-1}$. A SEM photograph of the bagasse fly ash (Fig. 1) clearly reveals the porous nature of the product. The material was so fragile that it could be easily crushed by hand.

The effect of pH on the uptake of lead (Fig. 2) shows that the percentage adsorption increases with pH to attain a maximum at pH 3.0 and thereafter it decreases with any further increase in pH. A similar behavior has been reported by Sen and De (24) for Hg(II) adsorption on fly ash. Therefore, all

TABLE 2
d-Spacing Values Obtained from X-ray Diffraction of Bagasse Fly Ash

d (Å)	Probable minerals[a]
4.690	Goethite
3.740	Mullite
2.730	Hematite
2.528	Kaolinite
2.234	α-Quartz
2.012	γ-Alumina
1.496	Hematite
1.315	Hematite

[a] Adopted from References 18 and 19.

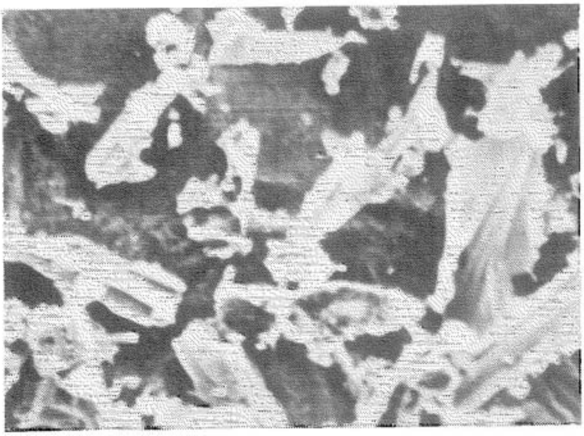

FIG. 1 SEM photograph of bagasse fly ash at 320×.

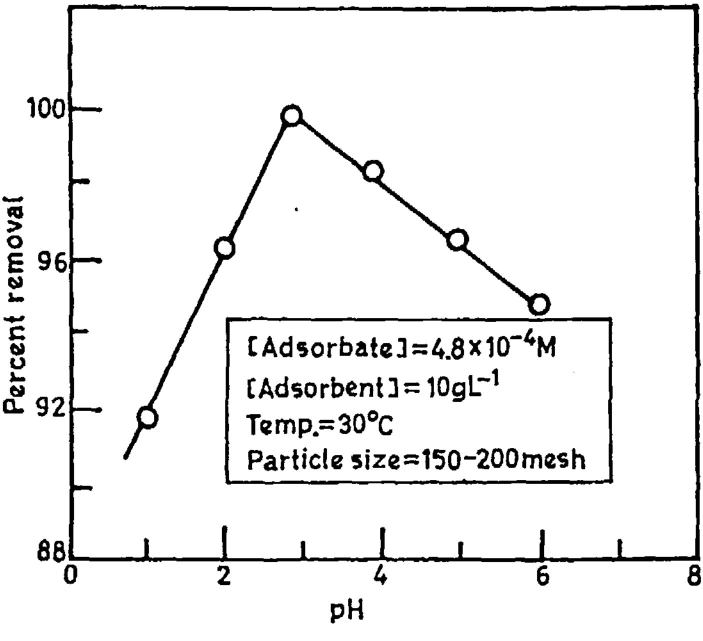

FIG. 2 Effect of pH on the adsorption of Pb^{2+} on bagasse fly ash.

TABLE 3
Effect of Initial Concentration and Temperature on Pb(II) Adsorption

Pb(II) concentration (M)	% Adsorption		
	30°C	40°C	50°C
4.80×10^{-4}	100	87.3	50.0
2.41×10^{-3}	87.1	59.1	51.0
3.86×10^{-3}	63.4	39.3	34.0
4.83×10^{-3}	53.2	32.0	27.3

the studies were made at pH 3.0. The pH of the solutions was monitored before and after adsorption, and no noticeable change was observed.

Adsorption decreased with a rise in temperature, indicating the process is exothermic in nature (Table 3). The sorption data were fitted to Freundlich and Langmuir adsorption isotherms (Figs. 3 and 4), and the values of

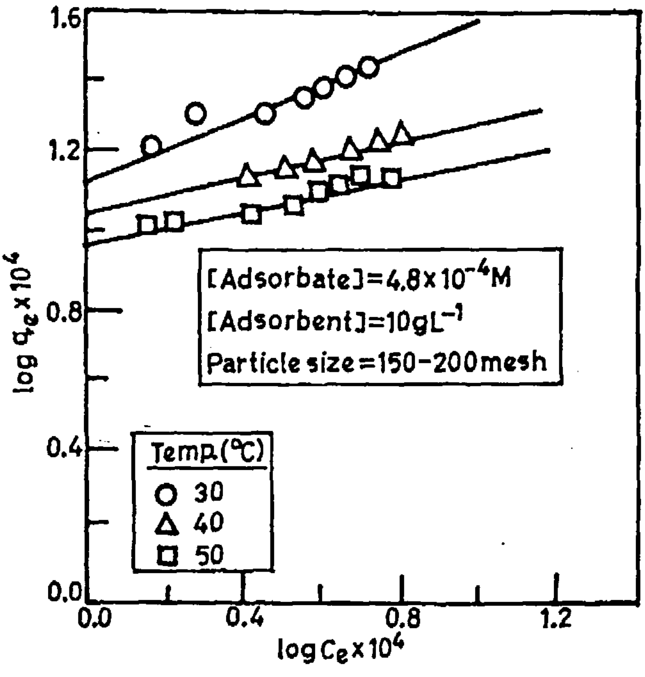

FIG. 3 Freundlich adsorption isotherms of Pb^{2+} at various temperatures on bagasse fly ash.

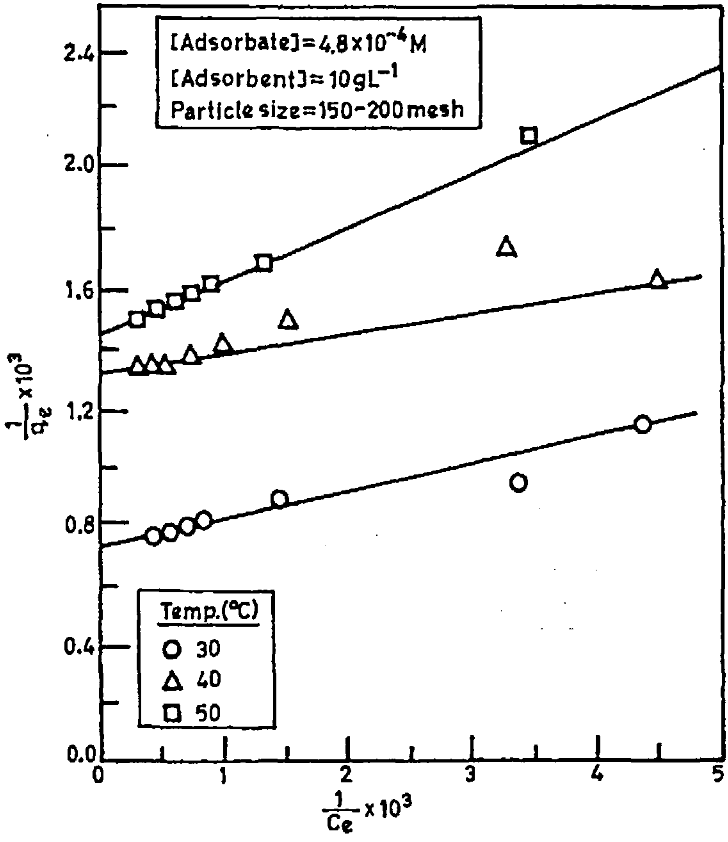

FIG. 4 Langmuir adsorption isotherms of Pb^{2+} at various temperatures on bagasse fly ash.

Freundlich and Langmuir constants are given in Table 4. The adsorption capacity, K_F, decreases as the temperature of the system increases. Besides, the Q° values obtained theoretically are larger than the experimentally observed ones (Table 4).

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 (25, 26) and is defined by

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

where b is the Langmuir constant and C_0 is the initial concentration of Pb(II).

TABLE 4
Freundlich and Langmuir Constants

Temperature (°C)	Freundlich constants $[q_e = K_F C^{1/n}]$ K_F	Slope $1/n$	Langmuir constants $\left[q_e = \frac{Q^\circ bC}{1 + bc}\right]$ $Q^\circ \times 10^3$ (m·g^{-1})	$b \times 10^5$ (L·mol^{-1})
30	13.77	1.07	2.73 (2.60)[a]	3.51
40	11.75	0.21	1.54 (1.51)[a]	2.67
50	9.66	0.07	1.38 (1.30)[a]	0.63

[a] Experimentally observed values.

The values of R_L calculated were between 0 and 1, indicating favorable adsorption of Pb^{2+} on bagasse fly ash at all the temperatures studied. The thermodynamic parameters calculated using Langmuir isotherms are given in Table 5. The negative free energy (ΔG°) values further indicate the feasibility of the process. The negative enthalpy change (ΔH°) reflects the exothermic nature of the process while the negative entropy (ΔS°) value suggests the probability of favorable adsorption.

The competitive adsorption of Pb^{2+} was studied in the presence of several metal ions and an anionic detergent (Manoxol-IB) (which are the major contaminants in natural water) at the optimum pH of uptake of the primary metal ion (Fig. 5). The effect of ionic interaction has been interpreted using the ratio of adsorption capacity of the ion in a single component system (q_0) to that in a multicomponent system (q_m) (27). The presence of interfering metal ions would reduce the uptake ($q_m/q_0 < 1$) of Pb^{2+} (Table 6). Similarly, a decrease in the scavenging efficiency ($q_m/q_0 < 1$) of the adsorbent in the presence of an anionic detergent takes place. These findings suggest a nonselective utility of the adsorbent for the uptake of Pb^{2+} in the presence of various other ingredients.

TABLE 5
Thermodynamic Parameters for the Uptake of Pb^{2+} on Bagasse Fly Ash

$-\Delta G^\circ$ (kJ·mol^{-1}) 30°C	40°C	$-\Delta H^\circ$ (kJ·mol^{-1})	$-\Delta S^\circ$ (J·K^{-1}·mol^{-1})
26.36 ± 0.50	26.52 ± 0.50	70.76 ± 1.0	145.80 ± 2.0

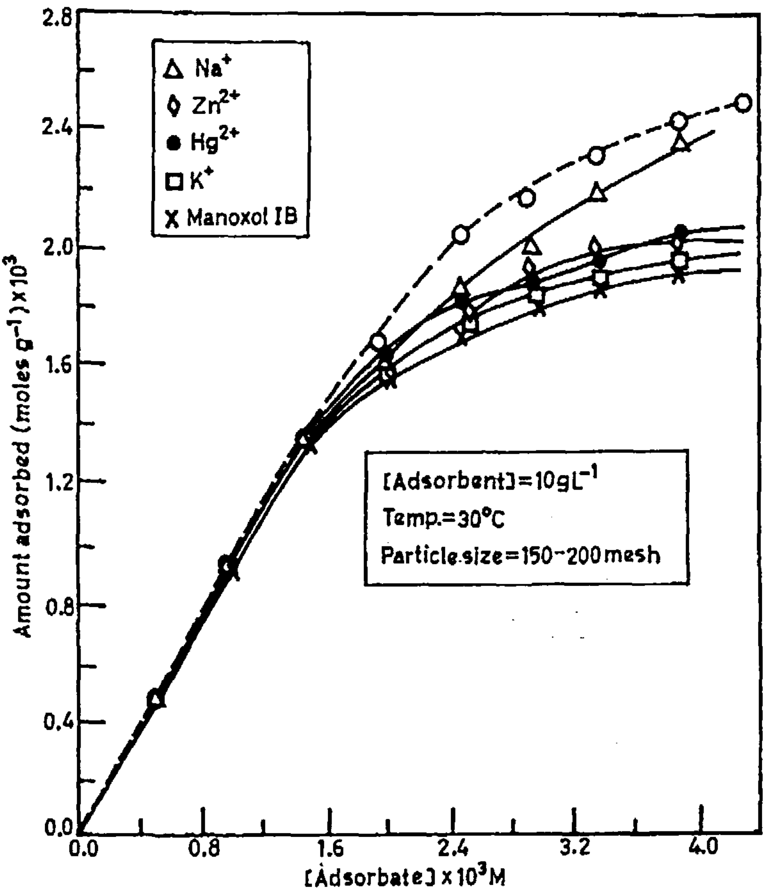

FIG. 5 Competitive adsorption of Pb^{2+} in the absence (- - -) and in the presence (——) of interfering metal ions and surfactant.

Preliminary investigations on the removal of Pb^{2+} with time on bagasse fly ash (at optimum pH 3.0) indicated the process to be quite rapid. Typically, 50–65% of the sorption capacity is realized within the first hour of contact. The initial rapid adsorption gives way to a very slow approach to equilibrium (reached in 6–8 hours). It is pertinent to mention that the pH of the solution does not change during the adsorption process. The effect of particle size and the concentration of adsorbent and adsorbate were also studied and the data are presented in Table 7. It is seen that 10 $g{\cdot}L^{-1}$ of the adsorbent (particle

TABLE 6
Effect of Interfering Metal Ions on the Uptake of Pb^{2+} by Bagasse Fly Ash

Interfering metal ions/anionic surfactant	Percent reduction in the uptake of Pb(II) $[Pb^{2+}] = 4.80 \times 10^{-4}$ M
Na^+	1.80
K^+	9.00
Zn^{2+}	9.60
Hg^{2+}	11.41
Manoxol-1B	14.20

size 150–200 mesh) gave the maximum removal. Pb^{2+} is 100% removed at lower concentrations and about 50–70% at higher concentrations.

Kinetic data have been treated by Eq. (2) [given by Boyd et al. (28)] which is valid under the experimental conditions employed. This is in accordance with the observations of Reichenberg (29) and has also been used earlier (16, 17).

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

where $B = \pi^2 D_i / r_0^2$, F is the fractional attainment of equlibrium at time t, D_i is the effective diffusion coefficient of the ion, r_0 is the radius of the adsorbent particle, and n is an integer. F is given by

$$F = Q_t/Q_\infty \tag{3}$$

where Q_t and Q_∞ are the amounts adsorbed after time t and infinite time (at equilibrium), respectively.

TABLE 7
Effect of Particle Size, Adsorbent Concentration, and Adsorbate Concentration on the Removal of Pb^{2+}: Temperature 30 ± 1°C, pH 3.0

Metal ion concentration (M)	Amount of adsorbent ($g \cdot L^{-1}$)	Particle size (BSS mesh)	Amount adsorbed (M)
4.80×10^{-4}	5	150–200	2.30×10^{-4}
4.80×10^{-4}	10	150–200	4.80×10^{-4}
4.80×10^{-4}	20	150–200	4.80×10^{-4}
4.80×10^{-4}	10	100–150	3.50×10^{-4}
4.80×10^{-4}	10	200–250	4.70×10^{-4}
9.60×10^{-4}	10	150–200	9.60×10^{-4}
1.44×10^{-3}	10	150–200	1.43×10^{-3}
2.89×10^{-3}	10	150–200	2.20×10^{-3}
3.86×10^{-3}	10	150–200	2.45×10^{-3}

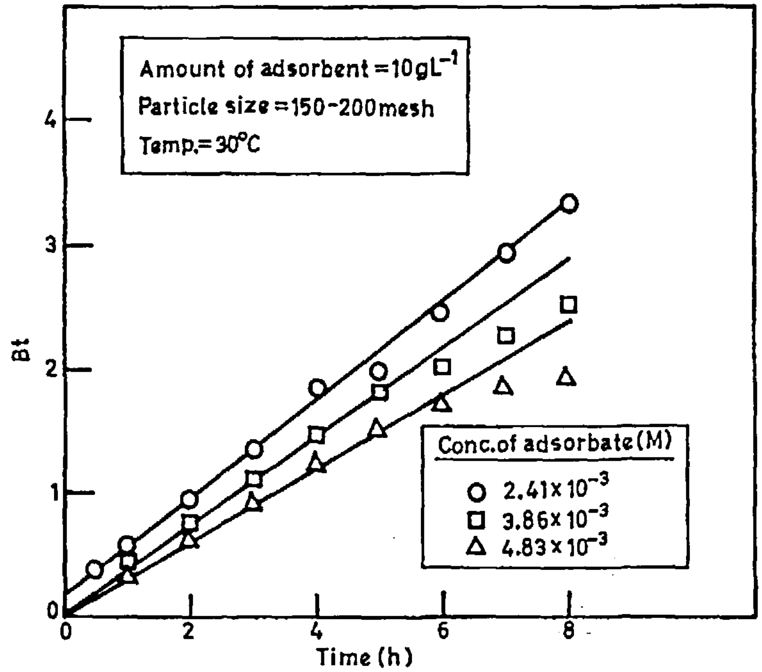

FIG. 6 *Bt* vs time plots at various adsorbate concentrations.

For every observed value of *F*, corresponding *Bt* values as derived from Eq. (3) are obtained from Reichenberg's (29) table.

The linearity test of *Bt* versus *t* plots (Fig. 6) are employed to distinguish between film and particle diffusion-controlled mechanisms. At lower concentrations ($\leq 2.41 \times 10^{-3}$ M) the linear *Bt* versus time plot does not pass through the origin, signifying the adsorption to be film diffusion, while at higher concentrations ($\geq 2.41 \times 10^{-3}$ M) the plot has a break, dividing it into two linear parts with different slopes, thereby indicating a change in mechanism at this concentration. The initial portion passes through the origin, reflecting that particle diffusion is the rate-limiting step, whereas in the later course of the process the D_i changes and the line does not pass through the origin. At this stage the process may not be purely particle diffusion controlled, and electrokinetic interaction and molecular diffusion may also be effective (30). Besides this, the decrease in diffusion with an increase in metal ion concentration also reflects that less surface is accessible for the sorbate in the internal sorbent layers. These findings were substantiated further by drawing McKay plots (21) at different adsorbate concentrations (plots not given). The effective diffusion coefficient (D_i) values at 30, 40, and 50°C are 4.80×10^{-10}, 2.96×10^{-10}, and 2.90×10^{-10} $cm^2 \cdot s^{-1}$, respectively. Diffusion coefficient values follow the same order in which Pb^{2+} is adsorbed on the developed adsorbent.

COST ESTIMATION

In India, the cheapest variety of commercially available carbon costs ~US\$285 ton^{-1}. Waste bagasse fly ash is available for US\$2 ton^{-1}, and considering the cost of transport, chemicals, electrical energy, etc. used in the process, the finished product would cost ~US\$12 ton^{-1}. Hence, the developed adsorbent would be a good replacement for commercially available carbons based on its low cost and good efficiency.

TREATMENT OF EFFLUENT

Experiments with actual wastewater from a metal-finishing plant provided some fruitful results. The characteristics of the wastewater were pH 3.7, total solids = 5320 $mg \cdot L^{-1}$, COD = 721 $mg \cdot L^{-1}$, chloride = 173 $mg \cdot L^{-1}$, Cu = 10.0 $mg \cdot L^{-1}$, sulfate = 180 $mg \cdot L^{-1}$, and Pb = 17.0 $mg \cdot L^{-1}$. A typical run was carried out using bagasse fly ash. Increasing the adsorbent concentration enhanced the removal of Pb(II) from wastewater. Almost complete removal of Pb(II) from 50 mL of wastewater at pH 3.2 was possible with 4.0 $g \cdot L^{-1}$ of the adsorbent.

CONCLUSIONS

Bagasse fly ash is an effective and low cost adsorbent for the removal of Pb^{2+} from aqueous solutions and wastewater. The removal of Pb^{2+} by this adsorbent is an exothermic process and takes place via film diffusion mechanism at lower concentrations ($\leq 2.41 \times 10^{-3}$ M) and through particle diffusion at higher concentrations ($\geq 2.41 \times 10^{-3}$ M). The process follows both Freundlich and Langmuir adsorption models.

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