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Process Development for the Removal of Zinc and Cadmium from Wastewater Using Slag—A Blast Furnace Waste Material

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ABSTRACT

Blast furnace slag, a waste generated in steel plants in India, has been converted into a low cost potential adsorbent. The resulting product has been characterized and used for the removal of zinc and cadmium. The effect of particle size, contact time, and surface loading of zinc and cadmium on the adsorbent for their removal have been studied at the optimum pH (6.0 for Zn^{2+} and 5.0 for Cd^{2+}). Kinetic studies were undertaken to show the mechanistic aspects of the process and to obtain the thermodynamic parameters. Sorption data have been correlated with both Langmuir and Freundlich adsorption models. Column operations were also performed in an attempt to simulate industrial conditions. Some feasibility experiments have been performed with a view to recovering Zn^{2+} and Cd^{2+} and for the chemical regeneration of the spent columns without dismantling them.

Key Words. Blast furnace slag; Adsorption; Wastewater treatment; Adsorbent; Zinc and cadmium

INTRODUCTION

The presence of heavy metals in the aquatic ecosystem has been of increasing concern because of an increase in discharge, their toxic properties, and other adverse effects on receiving water use. Elevated environmental levels of Zn^{2+} and Cd^{2+} come from a variety of sources. Cadmium finds its way to water bodies through wastewater from metal plating industries, cadmium nickel batteries, phosphate fertilizer, mining, pigments, stabilizers, and alloys (1). The effects of acute cadmium poisoning in humans are high blood pressure, kidney damage, and destruction of testicular tissue and red blood cells (2). Even small amounts of Cd^{2+} are believed to be associated with hypertension diseases. The permissible limits of cadmium discharge in wastewater and drinking water are 0.1 and 0.05 $mg \cdot L^{-1}$ respectively.

Zinc is present in most foods, especially those high in protein. The average human body contains about 2 g zinc. The inhalation of zinc fumes from galvanizing baths and the like sometimes produces "zinc fever," characterized by chills and fevers. Edema of the lungs from fumes of zinc chloride ($ZnCl_2$ smoke) is sometimes fatal. Soluble and astringent acid salts, such as $ZnSO_4$ in large doses (about 10 g), have caused internal organ damage and death.

A number of technologies have been suggested to remove metal pollution of surface water. These include ion exchange, chemical precipitation, membrane separation, solvent extraction, sedimentation chemical oxidation, ultrafiltration, electrodialysis, foam separation, adsorption, etc.

Adsorption on activated carbon and separation by ion-exchange resins are well-known techniques for the removal of heavy metals, but the high cost of these materials and some other limitations restrict their large-scale use for the abatement of heavy metal pollution. On account of this, investigations were initiated to identify other cheap commercially available materials as potential adsorbents.

Contributions in this regard have been made by many workers who have exploited substances like flyash (3), metal oxides (4–6), zeolites (7), moss (1), biomass (8), goethite (9), pyrite fines (10), hydroxides (11), clays (12–14), peanut hulls (15), coral sand (16), etc. Numerous other efforts made in this regard are compiled in a review article by Pollard et al. (17). The adsorption of inorganic compounds on hydrous solids (18, 19) is an electrostatic process where specific interaction between the ionic species and the surface of the solid are established.

Work on the treatment and utilization of solid waste materials being generated in some prime industries has been going on here for quite some time (20–23). Continuing efforts have been made to convert granular blast furnace waste material generated in the steel industry into an adsorbent slag for the removal of Cd^{2+} and Zn^{2+} from wastewater.

MATERIAL AND METHODS

All the reagents used were of AR grade. Stock solutions of the test sorbates were made by dissolving $ZnCl_2$ and $CdCl_2$ in doubly distilled water.

Equipments

pH measurements were made using a pH meter (Model CT No. CL 46, Toshniwal, India). Atomic absorption spectra were recorded on an atomic absorption/emission spectrophotometer (Model Perkin-Elmer 3100). IR spectra of the sample were recorded on an infrared spectrophotometer [Model (FTIR) Perkin-Elmer 1600]. X-ray measurements were done with a Phillips X-ray Diffractometer employing nickel-filtered CuK_α radiation. The surface area of the sample was measured by a surface area analyzer (Model QS-7 Quantasorb Surface Area Analyser). The porosity and density of the adsorbent were determined by mercury porosimetry and by specific gravity bottles, respectively. The constituents of slag were analyzed following the standard routine methods of chemical analysis (24). Zero point charge (ZPC) of the slag was determined from potentiometric titration data, following the general procedure of Parks and de Bruyn (25).

Material Development

Waste material obtained from Tata Iron and Steel Company Limited, Jamshedpur (India), was in the form of small, spherical granules of average diameter 0.098 nm. As reported earlier (26), the waste was washed with distilled water to remove any adhering impurities and dried at 200°C. The heated product was cooled and activated in air in a Muffle furnace at 600°C for 1 hour. The temperature and time were optimized by observing the surface properties of the activated product obtained by treating the raw material for different time durations and temperatures. The conditions of activation were optimized to obtain samples exhibiting the best sorption capacity. Treatment at a temperature higher or lower than 600°C (optimum) provided material having poor adsorption capacity. The product so obtained was sieved before use to obtain such desired particle sizes as 100–150, 150–200, and 200–250 mesh. The studies were carried out with slag of particle diameter 0.089 nm (150–200 mesh) unless otherwise stated. Finally, the slag was stored in a dessicator until it was used.

Adsorption Studies

Sorption studies were mainly performed by the batch technique to obtain rate and equilibrium data, and for these investigations a series of 50-mL test tubes was employed. Each test tube was filled with 10 mL of metal ion solution of varying concentrations and adjusted to the desired pH and temperature. A known amount of adsorbent was added into each test tube and then agitated intermittently for 24 hours. Preliminary investigations showed that equilibrium was attained in 6–8 hours. Shaking for any time between 8 to 24 hours gave practically the same uptake. Beyond this time the adsorption of metal ions on the adsorbent material remains almost constant. Therefore, all adsorption experiments were run after equilibrating a 10-mL adsorbate solution for 24 hours. After this period the supernatant solution was centrifuged and analyzed for aqueous metals. Initial sorbate concentrations ranged from 7.64×10^{-4} to 3.05×10^{-3} M for zinc and from 4.44×10^{-4} to 8.89×10^{-4} M for cadmium. The effect of pH was studied over a range of 2 to 8. Sorption studies were carried out at 30, 40, and 50°C to assess the effect of temperature. The influence of a cationic surfactant (cetyltrimethyl ammonium bromide) on sorption was studied at optimum pH (6.0 for Zn^{2+} and 5.0 for Cd^{2+}) as a function of the concentration of detergent. Stoppered glass tubes containing adsorbate solution along with the detergent and a fixed amount of adsorbent ($10\,g{\cdot}L^{-1}$ for Cd^{2+} and $20\,g{\cdot}L^{-1}$ for Zn^{2+}) were equilibriated for 24 hours. The supernatant was centrifuged and analyzed for aqueous metals.

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

Kinetic Measurements

The batch technique was selected for kinetic investigations because of its simplicity. A number of 50-mL stoppered Pyrex glass tubes containing known volume (10 mL) solutions of metal ions of known concentration (1.52×10^{-3} M for Zn^{2+} and 8.89×10^{-4} M for Cd^{2+}) were placed in a temperature-controlled mechanical shaker. When the desired temperature was reached, a known amount of adsorbent (0.1 g) was added into each tube and the solutions were mechanically agitated. At predicted intervals of time, the test solutions were centrifuged to separate the sorbent material from solution, and the supernatant was analyzed for aqueous metal. Kinetic studies were also performed at different adsorbate (7.64×10^{-4} to 3.05×10^{-3} M for Zn^{2+} and 4.44×10^{-4} to 8.89×10^{-4} M for Cd^{2+})

and adsorbent (10 to 30 $g \cdot L^{-1}$ for Zn^{2+} and 5 to 20 $g \cdot L^{-1}$ for Cd^{2+}) concentrations. Equilibrium was attained in about 6–8 hours.

Column Studies

Adsorption isotherms have traditionally been used for preliminary investigations and fixing the operational parameters, but in practice the final technical systems normally use column-type operations. Moreover, the isotherms cannot give accurate scale-up data in fixed-bed systems, and so the practical applicability of the product in column operations has also been determined. A glass column (40 × 0.5 cm) filled with a known amount of slag (mesh size 200–250) was used for different metal ions. Effluent flow was adjusted with a clip at the bottom of the column. Investigations were carried out by feeding the columns with solutions of Zn^{2+} (1.5×10^{-3} M) and Cd^{2+} (8.86×10^{-4} M). The bed-depth-service-time (BDST) model proposed by Hutchins (32) was successfully applied for the sorptive removal of Zn^{2+} and Cd^{2+}.

Regeneration

Regeneration of adsorbent as well as the recovery of adsorbate material is quite an important process in wastewater treatment. Consequently, experiments have been carried out in which a slag sample was loaded with adsorbate and subjected to elution of metal ions with 1% HNO_3. Simultaneous regeneration of adsorbent was also considered.

RESULTS AND DISCUSSION

Characterization of the Adsorbent Material

Different constituents of the slag were determined using standard methods of chemical analysis (24) as described earlier (26), and they are given in Table 1. The x-ray spectra of the adsorbent material did not show any peak, thereby indicating its amorphous nature. The surface area of the sample (150–200 mesh) as determined by the BET method was 107 $m^2 \cdot g^{-1}$. IR spectra indicated the presence of nordstrandite, brucite, bochmite, diaspore, braunite, goethite, and γ-FeOOH. Activated slag is quite stable in water, salts solutions, acids, and bases. One gram of the sample 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. Some pH enhancement was observed.

TABLE 1
Chemical Constituents and Characteristics of Activated Slag

Constituents	Percentage by weight
CaO	30.47
SiO_2	30.77
S	0.85
MgO	9.85
MnO	0.59
Al_2O_1	23.30
FeO	0.54
Loss on ignition	6.23%
Porosity	67.5%
Surface area	107 $m^2 \cdot g^{-1}$
Density	2.36 g/cm^3
ZPC	2.8

Adsorption Studies

Experiments were conducted at various pH values to determine the optimum pH range for maximum metal adsorption by slag. The results are shown in Fig. 1. The uptake of various metal ions is quite low at higher $[H^+]$. A significant enhancement in adsorption is recorded with an increase in pH in both cases.

The optimum pH values for the removal of Cd^{2+} and Zn^{2+} are 5.0 and 6.0, respectively. The variation in the removal of Zn^{2+} and Cd^{2+} with pH can be explained by considering the surface charge of the adsorbent material, i.e., the slag. The surface charge on slag very much depends upon the ZPC value of silica (≈ 2.3) and alumina (≈ 8.2). The composite ZPC of the adsorbent slag was found to be 2.8, and as such the surface would have a high positive charge density in the low pH (<2.8) region. The uptake of metals would be quite low under these conditions due to electrostatic repulsion. With increasing pH, i.e., beyond the ZPC of the slag (>2.8), the negative charge density on the surface of adsorbent would increase, resulting in a sudden enhancement in metal adsorption. Also, the double layers at the SiO_2 and Al_2O_3 surfaces change in polarity from positive to negative as the $[H^+]$ changes from the acidic to the basic region. It is worth mentioning that Cd^{2+} behavior is different from that reported on other adsorbents and is probably due to the ZPC of slag. Isotherms and other kinetic runs were therefore made at pH 5.0 and 6.0 for

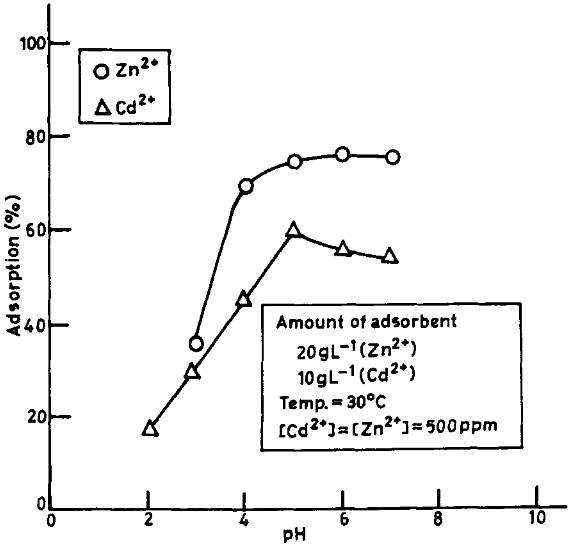


FIG. 1 Effect of pH on the adsorption of metal ions on activated slag.

Cd^{2+} and Zn^{2+}, respectively. Adjustment of pH was made in adsorbate solutions of various concentrations, and a very slight (i.e., insignificant) rise in final equilibrium pH was recorded. This does not disturb the process as the uptake is almost constant from 5 to 7 pH.

Adsorption isotherms of the two metal ions on slag are depicted in (Fig. 2a–b). The isotherms are regular, positive, and concave to the concentration axis. The initial rapid adsorption gives way to a slow approach to equilibrium at higher adsorbate concentrations. The uptake of metal ions is 75 to 90% at low concentrations and 28 to 55% at higher concentrations. These results reflect the scavenging efficiency of slag for the removal of heavy metals from wastewaters in a wide range of concentration. The uptake of Zn^{2+} and Cd^{2+} increases with an increase in temperature thereby indicating the process to be endothermic in nature. The concentration of adsorption sites may increase with rising temperature due to the breaking of some internal bonds near the edge of the particle.

The sorption data were fitted to Freundlich (Fig. 3a–b) and Langmuir (Fig. 4a–b) isotherms. The values of Freundlich and Langmuir constants are given in Table 2.

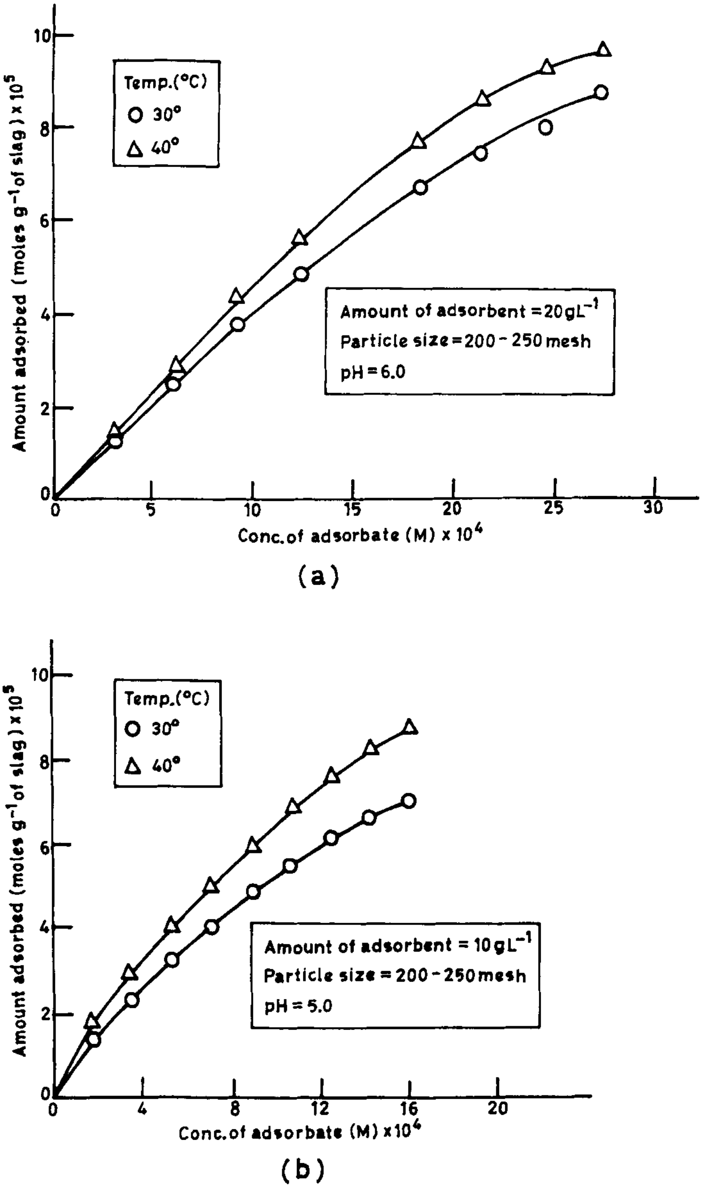


FIG. 2 Adsorption isotherms of (a) Zn^{2+} and (b) Cd^{2+} on activated slag at different temperatures.

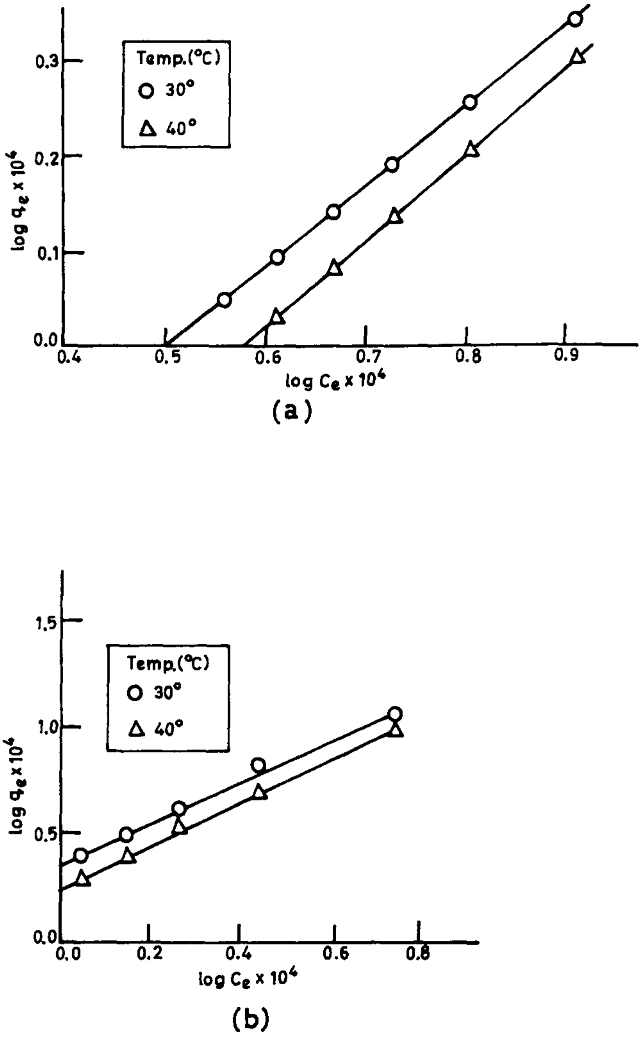


FIG. 3 Freundlich isotherms of (a) Zn^{2+} and (b) Cd^{2+} on activated slag at different temperatures.

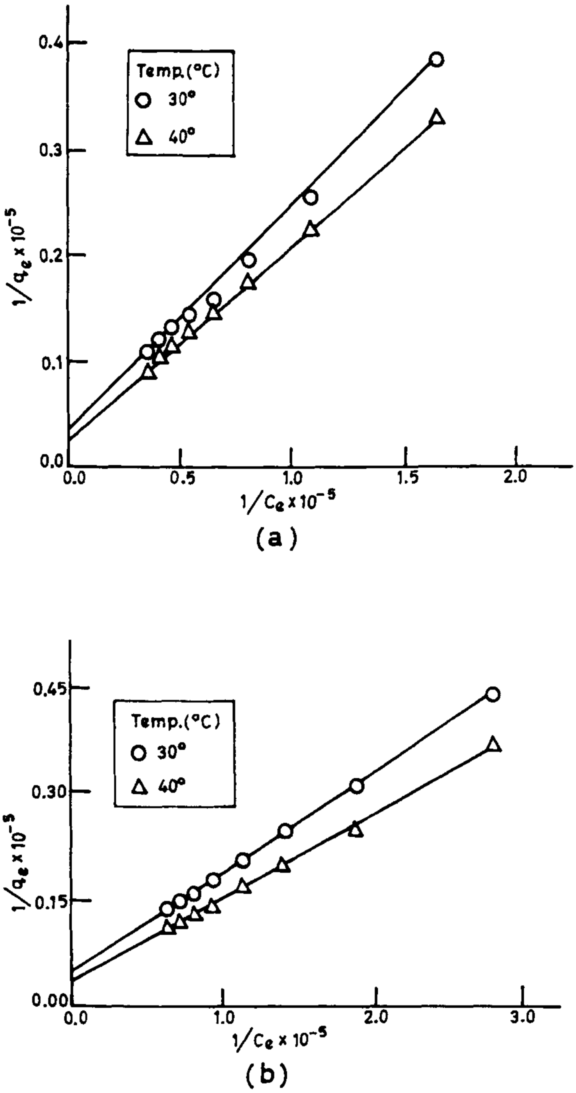


FIG. 4 Langmuir isotherms of (a) Zn^{2+} and (b) Cd^{2+} on activated slag at different temperatures.

TABLE 2
Freundlich and Langmuir Constants

			Langmuir constants $\left[q_e = \frac{Q_0 bc}{1 + bc}\right]$			
	Freundlich constants $[q_e = K_F C^{1/n}]$		$Q^\circ \times 10^4$ ($\mathrm{mol \cdot g^{-1}}$)		$b \times 10^{-4}$ ($\mathrm{L \cdot mol^{-1}}$)	
Metal ions	$K_F \times 10^4$	Slope $1/n$	30°C	40°C	30°C	40°C
Zn^{2+}	0.45	0.59	2.70	3.63	0.16	0.17
Cd^{2+}	1.84	0.86	1.66	2.35	0.42	0.40

The adsorption capacity, K_F, is less for the zinc–slag system than that for the cadmium–slag system. The slope, $1/n$, which reflects the intensity of adsorption, presents the same trend. The Langmuir constant, Q°, increases with an increase in temperature, thereby indicating the process to be endothermic in nature. The value of Q° (i.e., maximum uptake) appears to be significantly higher for the zinc–slag system in comparison to the uptake of cadmium on the same adsorbent.

The dimensionless separation factor, R (27) in Eq. (1), calculated from the Langmuir isotherm, was found to be 0.18 and 0.13 for Zn^{2+} and Cd^{2+}, respectively. This indicates a highly favorable sorption ($R \ll 1$).

$$R = \frac{1}{1 + bC_0} \tag{1}$$

Thermodynamic parameters were also calculated using the Langmuir isotherm and are given in Table 3. The changes in standard Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) for the process were obtained using Expressions (2), (3), and (4).

$$\Delta G^\circ = -RT \ln K_1 \tag{2}$$

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{3}$$

where k_1 and k_2 are Langmuir constants at temperatures T_1 and T_2.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{4}$$

The negative free energy values shown in Table 3 further indicate the feasibility of the process and its spontaneous nature. Positive ΔH° and

TABLE 3
Thermodynamic Parameters for the Uptake of Zn^{2+} and Cd^{2+} on Activated Slag

Metal ions	$-\Delta G^\circ$ ($kJ \cdot mol^{-1}$)	ΔH° ($kJ \cdot mol^{-1}$)	ΔS° ($J \cdot K^{-1} \cdot mol^{-1}$)
Zn^{2+}	24.40	2.57	89.0
Cd^{2+}	26.80	3.82	75.0

ΔS° values show the process to be endothermic and the affinity of the adsorbent material for the metal ions under consideration.

Natural water bodies can be contaminated by heavy metals, surfactants, and other substances due to the discharge of wastewater from commercial and domestic sources. It is therefore necessary to examine the interference of other metal ions/surfactants etc. when the adsorbent is used for the removal of the above-mentioned metal ions. The effect of ionic interaction on the adsorption process may be interpreted by using the ratio of the adsorption capacity of the ion in a single component system (q_0) to that in a multicomponent system (q_m) (28) such that

$\frac{q_m}{q_0} > 1$: adsorption is promoted by the presence of other metal ions

$\frac{q_m}{q_0} = 1$: no observable net interaction effect

$\frac{q_m}{q_0} < 1$: adsorption is suppressed by the presence of other metal ions

The competitive adsorption of Zn^{2+} and Cd^{2+} was studied in the presence of several metal ions and surfactants. The removal of Zn^{2+} at 27.53×10^{-4} M is reduced by 4.50, 7.41, and 11.04% in the presence of Ni^{2+} (1.0×10^{-5} M), Cu^{2+} (1.0×10^{-5} M), and Cd^{2+} (1.0×10^{-5} M), respectively (Fig. 5a). Similarly, the removal of Cd^{2+} at 16.01×10^{-4} M is reduced by 1.56, 3.90, and 6.24% in the presence of Ni^{2+} (1.0×10^{-5} M), Cu^{2+} (1.0×10^{-5} M), and Zn^{2+} (1.0×10^{-5} M), respectively (Fig. 5b). Interfering metal ions (M^{n+}) affect the uptake of the primary ion by altering the surface charge density of the adsorbent material. A decrease in the scavenging efficiency ($q_m/q_0 < 1$) of the adsorbent in the presence of a cationic detergent was also observed. These findings suggest a nonselective utility of the adsorbent during the uptake of metal ions in the presence of various other ingredients.

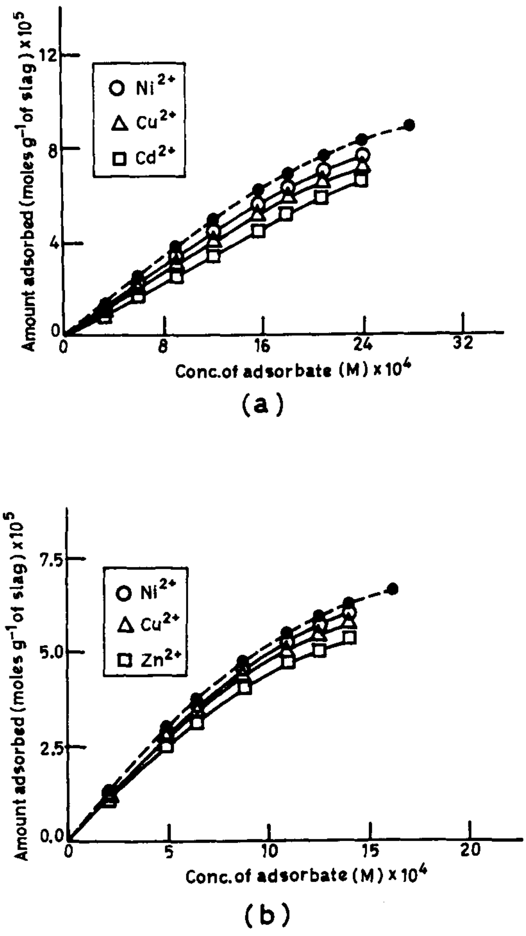


FIG. 5 Competitive adsorption of (a) Zn^{2+} and (b) Cd^{2+} in the absence and in the presence (——) of interfering metal ions on activated slag.

Kinetic Studies

Preliminary investigations on the rate of uptake on the activated slag under consideration indicated that the process is quite rapid; typically 24 to 38% of the ultimate adsorption occurs within the first hour of contact. This initial rapid adsorption subsequently gives way to a very slow approach to equilibrium, and saturation is reached in 6–8 hours.

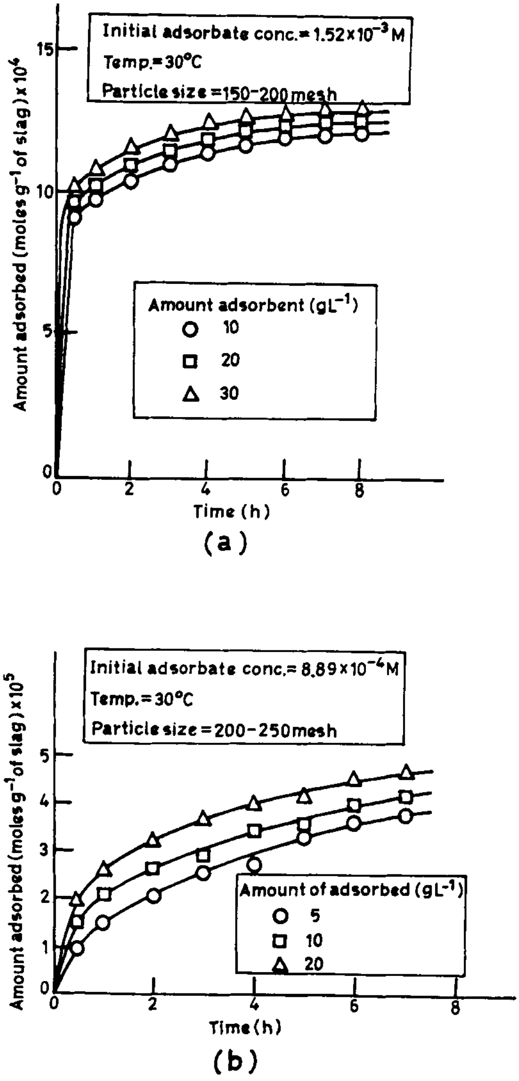


FIG. 6 Effect of amount of activated slag on the rate of uptake of (a) Zn^{2+} and (b) Cd^{2+}.

Figure 6(a–b) depicts the effect of the amount of slag on the rate of uptake of zinc and cadmium. It is found that the rate of removal of metal ions increases with an increasing amount of slag. For Zn^{2+}, there is an increase (Fig. 6a) in adsorption when the amount of slag is enhanced from

10.0 to 20.0 g·L^{-1}, while the increase in removal efficiency is not as significant when the amount of adsorbent is increased further from 20.0 to 30.0 g·L^{-1}. Similarly, for Cd^{2+} (Fig. 6b) a significant increase in uptake is observed when the amount of slag is increased from 5.0 to 10.0 g·L^{-1}. Any additional amount of slag does not cause any significant change. Taking into account both the handling problems associated with large quantities of slag and the relatively smaller solute removal with smaller amounts of adsorbent, the amount of slag taken in all subsequent kinetic studies was 10.0 g·L^{-1} for Cd^{2+} and 20.0 g·L^{-1} for Zn^{2+} ions. The half-life of the process (t_{50}) decreases with an increasing amount of slag, thereby reflecting a dependence of the rate of adsorption on the amount of slag.

The rate of removal of metal ions increases with increasing temperature (Fig. 7a–b), thereby showing the process to be endothermic. It is observed that the half-life (t_{50}) of the total adsorption decreases with an increase in temperature.

The rate of uptake of adsorbate in the first hour of contact increases with an increase in the concentration of adsorbate. Also, the time required for 50% of the ultimate adsorption to occur is independent of the initial adsorbate concentration (Fig. 8a–b).

For a proper interpretation of the experimental findings, a quantitative treatment of the data based on the model suggested by Helfferich (29) has been applied. Various parameters were calculated by using Expressions (5)–(7) as given by Boyd et al. (30).

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[\frac{D_i t \pi^2 n^2}{r_0^2}\right] \tag{5}$$

or

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

and

$$B = \frac{\pi^2 D_i}{r_0^2} \tag{7}$$

where F is the fractional attainment of equilibrium at time t, B is the time constant, D_i is the effective diffusion coefficient of ion in the 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.

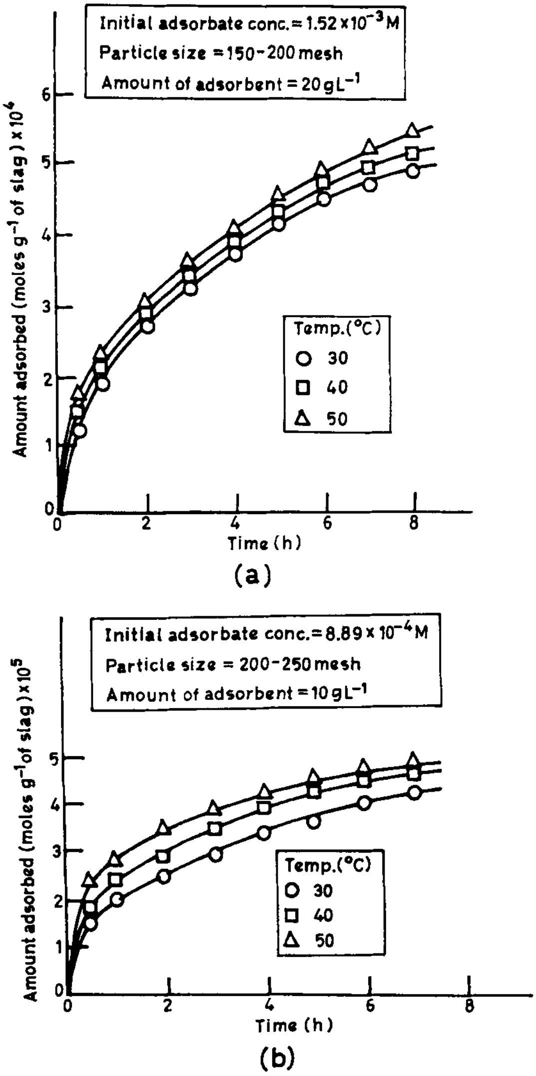


FIG. 7 Effect of temperature on the rate of uptake of (a) Zn^{2+} and (b) Cd^{2+} on activated slag.

Bt values as derived from Eq. (6) for the observed values of *F* were obtained from Reichenberg's table (31). The linearity test of *Bt* versus *t* plots is employed to distinguish between the film and particle diffusion-controlled rates of adsorption. The *Bt* versus time plots for Zn^{2+} are linear

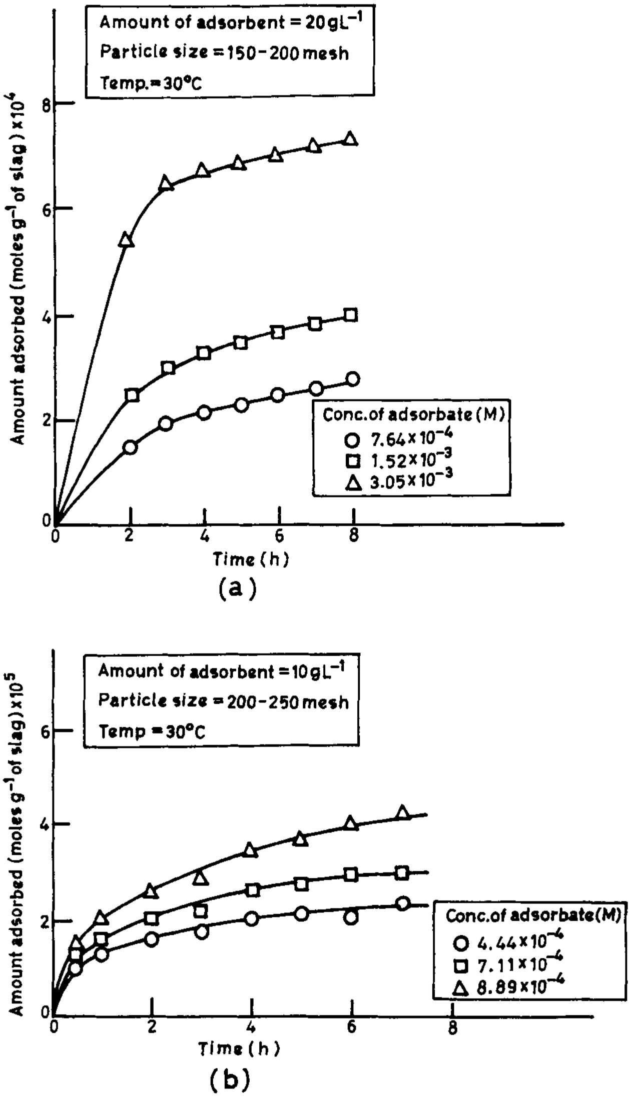


FIG. 8 Effect of adsorbate concentrations on the rate of uptake of (a) Zn^{2+} and (b) Cd^{2+} on activated slag.

at lower concentrations ($\leq 1.52 \times 10^{-3}$ M) and pass through the origin, indicating the process to be particle diffusion, but at higher concentrations ($\geq 3.0 \times 10^{-3}$ M) the plot is linear but does not pass through the origin, thereby indicating the process to be film diffusion (Fig. 9a). Similar plots

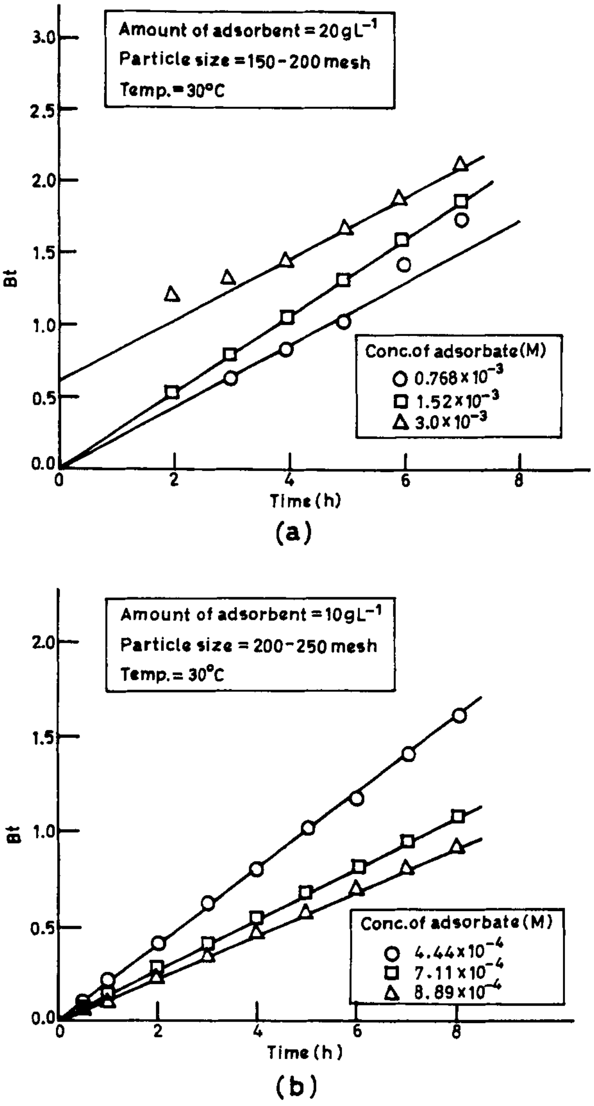


FIG. 9 *Bt* versus time plots at various concentration of (a) Zn^{2+} and (b) Cd^{2+} on activated slag.

(Fig. 9b) for Cd^{2+} are linear and pass through the origin, indicating the process to be particle diffusion at different concentrations. This was further confirmed by observing Mckay plots drawn for the same ions.

The values of D_i calculated at 30, 40, and 50°C are presented in Table 4. The increase in mobility of ions and a decrease in the retarding forces acting on the diffusing ion results in an enhancement of D_i with temperature. Diffusion coefficient values for the two systems follow the same order in which the ions are adsorbed on the prepared adsorbent.

The energy of activation E_a, entropy of activation $\Delta S^{\ddagger}$, and preexponential constant D_0 (analogous to Arrhenius frequency factor) were evaluated by using the following equations.

$$D_i = D_0 \exp\left[\frac{-E_a}{RT}\right] \tag{8}$$

and

$$D_0 = 2.72d^2 \frac{kT}{h} \exp\left[\frac{\Delta S^{\ddagger}}{R}\right] \tag{9}$$

The values of E_a, D_0, and $\Delta S^{\ddagger}$ for the diffusion of zinc and cadmium in slag are also listed in Table 4. The effective diffusion coefficient (D_f) values obtained in the present investigations are greater than those reported for hydrous ferric oxide and clay montmorillonite (5, 13) and lesser than those reported for minerals like iron(III) antimonate (31). This leads to the conclusion that the channels developed in slag from blast-furnace waste are wider than those of hydrous oxides and narrower than those of the mineral mentioned above. The activation energy (E_a) values are higher for Cd^{2+} than for Zn^{2+}. The negative entropy of activation values obtained for the adsorption of Zn^{2+} and Cd^{2+} are not uncommon for an ion-exchange process. Such values normally indicate that no significant

TABLE 4

D_i, D_0, E_a, and $\Delta S^{\ddagger}$ Values for the Diffusion of Zn^{21} and Cd^{2+} in Activated Slag

Metal ions	D_i ($m^2 \cdot s^{-1}$) 30°C	40°C	50°C	D_0 ($m^2 \cdot s^{-1}$)	E_a ($kJ \cdot mol^{-1}$)	$-\Delta S^{\ddagger}$ ($J \cdot K^{-1} \cdot mol^{-1}$)
Zn^{2+}	5.86×10^{-14}	6.83×10^{-14}	7.49×10^{-14}	5.88×10^{-14}	10.27	150.48
Cd^{2+}	7.21×10^{-15}	8.76×10^{-15}	10.20×10^{-14}	6.60×10^{-15}	17.14	168.76

change occurs in the internal structure of an adsorbent during the adsorption of metal ions.

The following mathematical mass transfer model (Eqs. 10–12), suggested by Mckay and also by Periasamy and Namasivayam (15), has been employed for the determination of the surface mass transfer coefficient β_L for the adsorption of Zn^{2+} and Cd^{2+} on activated slag.

$$\ln\left[\frac{C_t}{C_0} - \frac{1}{mk}\right] = \ln\frac{mk}{1 + mk} - \frac{1 + mk}{mk}\beta_L S_s t \tag{10}$$

where

$$m = W/V \tag{11}$$

and

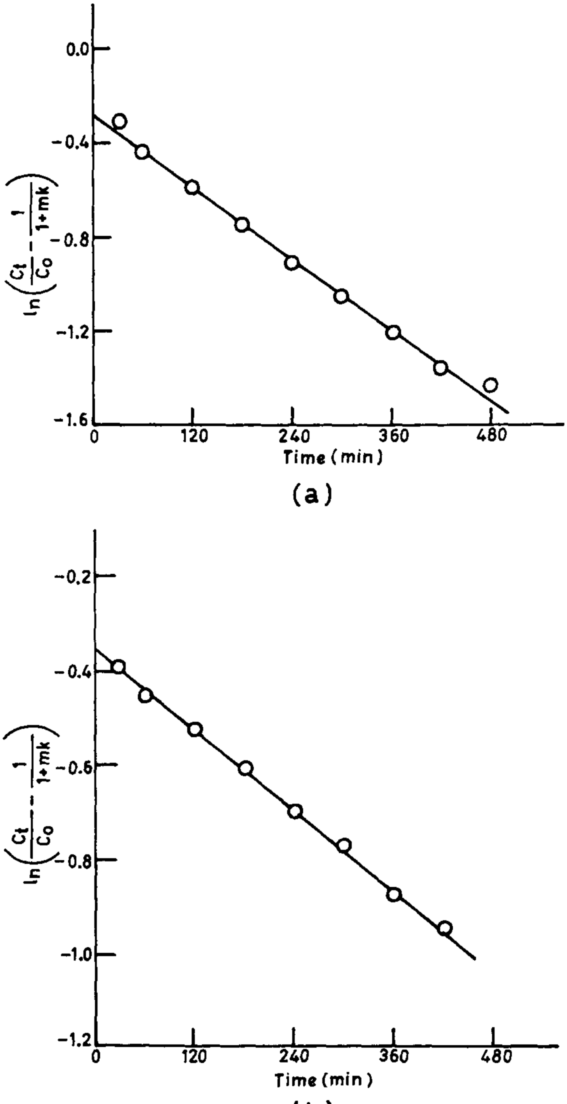
$$S_s = \frac{6m}{(1 - \epsilon_p)d_p\rho_p} \tag{12}$$

where C_t is the concentration of adsorbate ($mg{\cdot}L^{-1}$) after time t, C_0 is the initial concentration of adsorbate ($mg{\cdot}L^{-1}$), m is the mass of adsorbent per unit volume of particle free adsorbate solution ($g{\cdot}L^{-1}$), k ($L{\cdot}g^{-1}$) is a constant obtained by multiplying adsorption capacity Q° and adsorption energy (b), β_L is the mass transfer coefficient ($cm{\cdot}s^{-1}$), and S_s is the outer surface of the adsorbent per unit volume of particle-free slurry (cm^{-1}). The value of m and S_s can be calculated using Expressions (11) and (12) where W is the weight of adsorbent (g), V is the volume of particle-free adsorbate solution (L), d_p is the particle diameter (cm), ρ_p is the density of adsorbent ($g{\cdot}cm^{-3}$), and ϵ_p (%) is the porosity of adsorbent material.

Values of β_L for the sorption of Zn^{2+} and Cd^{2+} on slag at 30°C were calculated graphically (Fig. 10) and are reported in Table 5. The linear nature of the plots for Zn^{2+} and Cd^{2+} suggests the applicability of the diffusion model. The values of the mass transfer coefficient indicate that the velocity of adsorbate transport from the bulk to the solid phase is quite rapid.

The adsorption of Zn^{2+} and Cd^{2+} from the liquid to the solid phase can be considered to be a reversible reaction with an equilibrium established between the two phases. The Lagergren first-order rate Expression (13), given by Periasamy and Namasivayam (15), has been applied for the determination of specific rate constants of adsorption for zinc–slag and cadmium–slag systems.

$$\log(q_e - q) = \log q_e - \frac{K_{ad}}{2.303}t \tag{13}$$



(b)

FIG. 10 Plots of $\ln\left[\frac{C_t}{C_0} - \frac{1}{1 + mk}\right]$ versus time for the mass transfer of (a) Zn^{2+} and (b) Cd^{2+} on activated slag.

TABLE 5
Mass Transfer Coefficient (β_L) and Rate Constant of Adsorption (K_{ad}) for Various Metal Ions

Metal ions	β_L (cm·s^{-1})	K_{ad} (min^{-1})
Zn^{2+}	8.12×10^{-6}	0.29×10^{-2}
Cd^{21}	7.90×10^{-6}	0.32×10^{-2}

where q_c and q are the amounts of adsorbate species adsorbed by 1 gram of adsorbent (mol·g^{-1}) at equilibrium and at any time t, respectively, and K_{ad} is the specific rate constant of adsorption (min^{-1}). The linear plots of log ($q_c - q$) versus time at 30°C (Fig. 11) show the applicability of the rate expression mentioned above, and the K_{ad} values are reported in Table 5.

Column Studies

A number of models for the design of fixed-bed adsorbers have been developed. These are based on mathematical analysis and prediction of the shape of breakthrough curves. The bed-depth-service-time (BDST) model proposed by Hutchins (32) is adopted for the design of fixed-bed adsorbers. It deals with the movement of an adsorption wave front through the adsorbent bed. The BDST has a linear relationship, and the curve can be described by Eq. (14).

$$t = ax + b \tag{14}$$

where

$$a = \frac{N_0}{C_0 V} \tag{15}$$

and

$$b = -\frac{1}{KC_0}\ln\left[\frac{C_0}{C_B} - 1\right] \tag{16}$$

where t is the service time at breakthrough (minutes), x is the bed depth (cm), a is the slope (min·cm^{-1}), N_0 is the adsorption capacity (mg adsorbate per cm^3 of adsorbent), C_0 is the initial concentration (mg·L^{-1}), V is the linear flow rate (L·min^{-1}·cm^{-1}), b is the ordinate intercept (minutes), K is the rate constant of adsorption (mL·mg^{-1}·min^{-1}), C_B is the eluent concentration (mg·L^{-1}), and C_o is the initial concentration (mg·L^{-1}).

Vertical glass columns (dimension 40 × 0.5 cm) packed with known

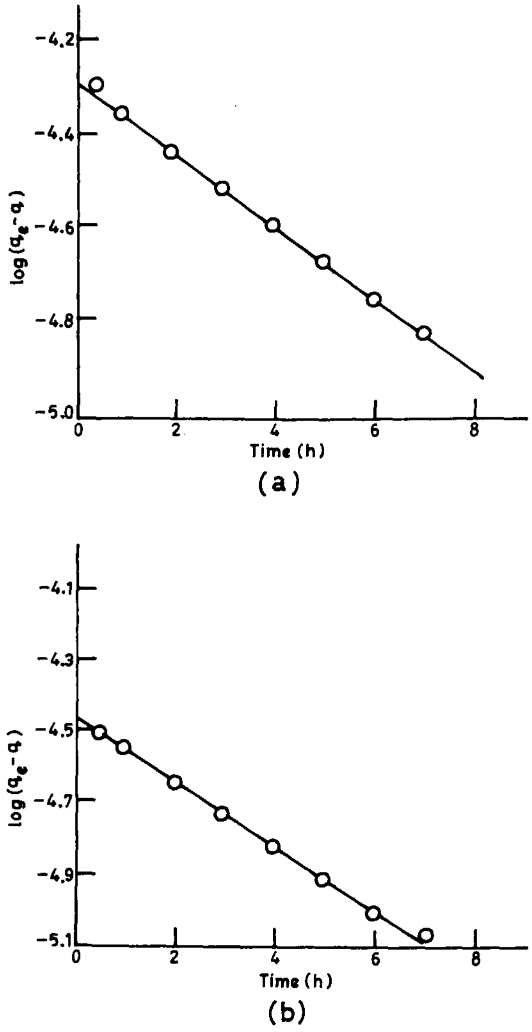


FIG. 11 Lagergren plots for the adsorption of (a) Zn^{2+} and (b) Cd^{2+} on activated slag.

amounts of slag (mesh size 200–250) were used for the removal of Zn^{2+} and Cd^{2+}. Flow of the effluent was regulated. Studies were performed by feeding the columns with a solution of Zn^{2+} (1.5×10^{-3} M) and Cd^{2+} (8.86×10^{-4} M).

The data (Fig. 12) for different flow rates and bed depths are used to plot a BDST correlation. Figure 13 (a–b) depicts the plots of BDST

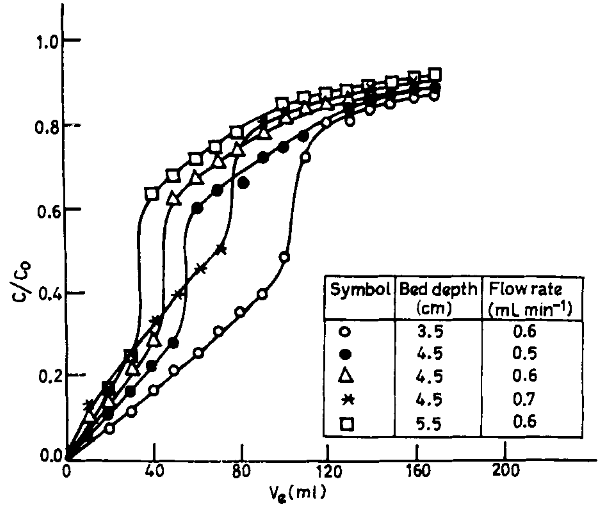


FIG. 12 Breakthrough curves of Zn^{2+} at varying bed depths and flow rates on activated slag.

($t_{1/2}$) at 50% breakthrough volume ($C/C_0 = 0.5$) against the bed depth at different flow rates. The linear plots indicate the applicability of the model to the bed system under investigation. After developing a BDST equation from column tests at one linear flow rate (0.4 mL·min^{-1}), expressions for the other flow rates were obtained with the help of the Eqs. (17) and (18).

$$a_2 = a_1\left[\frac{Q_1}{Q_2}\right] \tag{17}$$

$$a_4 = a_3\left[\frac{C_1}{C_2}\right] \tag{18}$$

where a_1 = slope at flow rate Q_1, a_2 = slope at flow rate Q_2, and a_3 and a_4 are slopes at concentrations C_1 and C_2.

The BDST expressions for Cd^{2+} and Zn^{2+} at a flow rate of 0.4 mL·min^{-1} are given in Table 6.

The breakthrough curves (Fig. 12) were used to calculate the column capacity at complete exhaustion by taking the total area at the point where the effluent plot joins the effluent volume (V_e) and dividing this value by the weight of adsorbent in the column. The column capacity of zinc slag (37.98 mg·g^{-1}) and cadmium-slag (33.0 mg·g^{-1}) systems is found to be

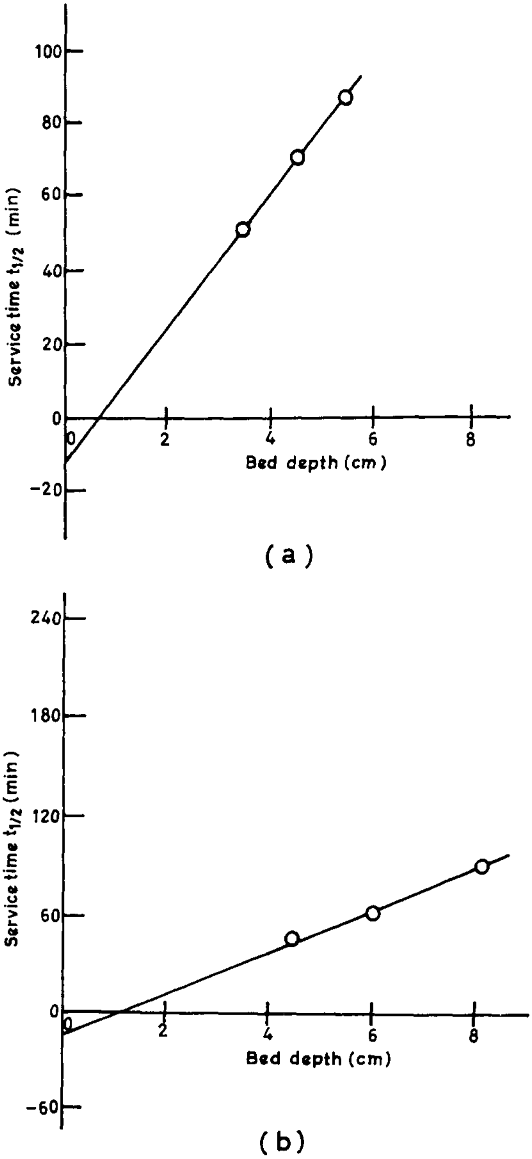


FIG. 13 BDST (50% breakthrough) curves at different bed depths for (a) Zn^{2+} and (b) Cd^{2+}.

TABLE 6
BDST Equations for Zn^{2+} and Cd^{2+}

Metal ions	BDST equations
Cd^{2+}	$t_{1/2} = 15.79x + (-11)$
Zn^{2+}	$t_{1/2} = 14.54x + (-14)$

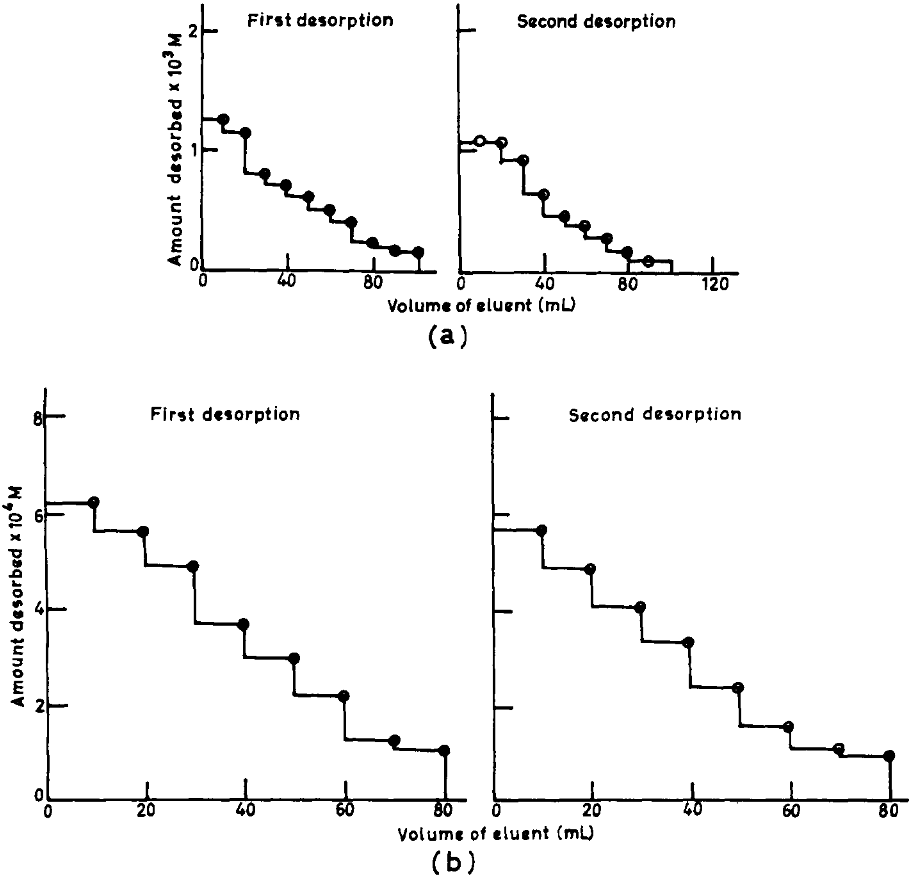


FIG. 14 Desorption curve of (a) Zn^{2+} and (b) Cd^{2+} with 1% HNO, for activated slag.

greater than the batch capacity (i.e., 17.66 and 18.72 mg·g^{-1} for zinc and cadmium, respectively). This is due to the inherent difference in the nature of continuous and batch operations.

When the adsorbent becomes exhausted or when the effluent from an adsorbed bed reaches the maximum allowable discharge level, recovery of the adsorbed material as well as regeneration of the adsorbent becomes necessary. Thermal regeneration in a multiple hearth furnace is the most common method used for this purpose in carbon columns. However, some

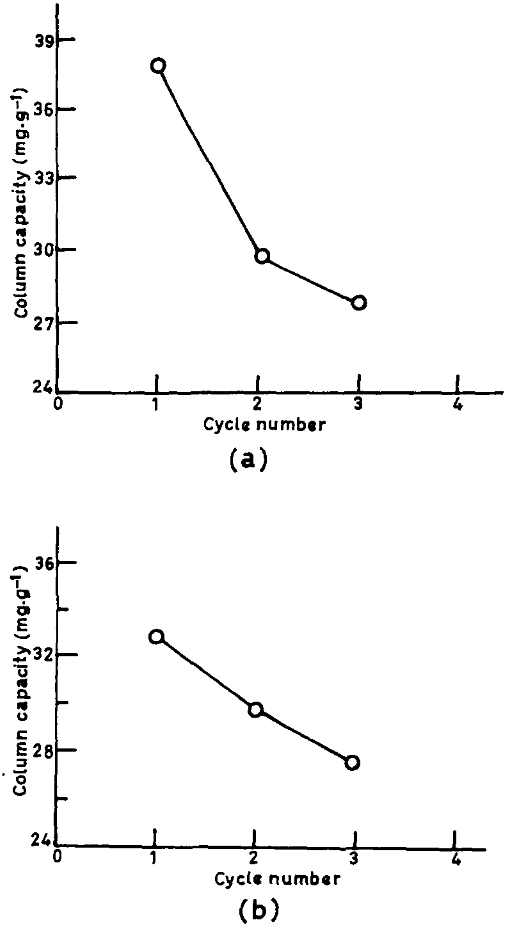


FIG. 15 Variation of column capacity with number of cycles for (a) zinc–slag and (b) cadmium–slag systems.

adsorbent is lost during each cycle in this approach, and recovery of the adsorbate is not possible. Chemical regeneration by a suitable solvent is a possible alternative method. Consequently, experiments were carried out for the desorption of Zn^{2+} and Cd^{2+} by 1% HNO_3. Simultaneous regeneration of adsorbent was also considered.

Figure 14 (a–b) shows the results of the two consecutive adsorption–desorption curves for Zn^{2+} and Cd^{2+}. For zinc, 100 mL of 1% HNO_3 was used. The first 40 mL of acid accounted for 53.3% elution of zinc while the next 40 mL removed 28.83% and the last 20 mL took out 15.86% of zinc in the column. For cadmium, 80 mL of 1% HNO_3 was used. The first 40 mL of 1% HNO_3 led to the elution of 66.2% cadmium and last 40 mL took out 21.37% cadmium.

After the desorption of metals, the column was washed with 10-mL fractions of distilled water at a fixed flow rate for each metal. The column was again loaded with various metal ions to check the sorption efficiency of the material during subsequent cycles.

Figure 15 (a–b) represents the amount of the adsorbate adsorbed as a function of the number of adsorption cycles. The breakthrough capacities of Zn^{2+} in the first, second, and third cycles are 38, 30, and 28 $mg \cdot g^{-1}$; for Cd^{2+} they are 33, 30, and 28 $mg \cdot g^{-1}$. These values for the two metal ions show a fall in sorption capacity of the column, i.e., some loss in their adsorption efficiencies during repeated cycles. Loss of column capacity is a normal phenomenon which may be overcome to some extent by the use of some redox reagents.

APPLICATIONS

The findings mentioned above show the possibility of using activated slag for the treatment of zinc and cadmium-bearing waste. Experiments with actual waste from a metal finishing plant provided some fruitful results. Two typical runs (Cu = 10.0, Zn = 3.0, Cd = 4.0, Pb = 12.0, Ni = 58.0 $mg \cdot L^{-1}$; Cu = 2.0, Zn = 10.0, Cd = 1.0, Pb = 8.0, Ni = 50 $mg \cdot L^{-1}$) were carried with an adsorbent column (40 × 0.5 cm; 200–250 mesh) at a flow rate of 0.4 $mL \cdot min^{-1}$. The removal of Zn^{2+} and Cd^{2+} was found to be almost 98%.

COST ESTIMATION

In India the cheapest variety of commercially available carbon costs Rs.10,000 ton^{-1}. Blast furnace waste is available at Rs.38.00 ton^{-1}. Considering the total expenses for transport, chemicals, electrical energy, etc., the finished product would cost approximately Rs.52.00 ton^{-1}. Recovery of metal ions and the chemical regeneration of columns (without dismantling) may further bring down the cost factor.

CONCLUSIONS

Slag developed from blast furnace waste material is an effective adsorbent for the removal of Zn^{2+} and Cd^{2+} from aqueous solution and wastewater. The removal of these two metal ions by the adsorbent material takes place via a particle diffusion mechanism, and the thermodynamic parameters reflect the feasibility of the process. The sorption of Zn^{2+} and Cd^{2+} is an endothermic process. The results show that the waste material can be fruitfully employed for the removal of Zn^{2+} and Cd^{2+} in a wide range of concentrations. The results of column operations indicate that the product can also be used on an industrial scale. It has been possible to recover Zn^{2+} and Cd^{2+} quantitatively from the effluent of a metal-finishing plant.

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