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

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Activated slag developed from blast furnace waste material has been used for the removal of copper and nickel. The effects of particle size distribution, contact time, and surface loading of these metal ions on the adsorbent for their removal have been studied at the optimum pH (5.0 for Cu^{2+} and 4.0 for Ni^{2+}). Kinetic studies were performed to decide the mechanistic steps 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. The bed-depth-service-time (BDST) model has successfully been applied to the sorptive removal of nickel and copper. Some feasibility experiments have been performed with a goal to recover adsorbate and chemical regeneration of the spent columns without dismantling the same.

Introduction

The presence of heavy metals in the environment has been of great concern because of their increased discharge, toxic nature, and other adverse effects on receiving waters. Elevated environmental levels of Cu^{2+} and Ni^{2+} come from a variety of sources. The potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paper and paper board mills, wood-pulp production, fertilizer industry, etc. Excessive intake of copper results in an accumulation in the liver. Chronic copper poisoning is related to hemochromatosis and produces gastrointestinal catarrh when present in large amounts. It is also toxic to aquatic organisms even at very small concentrations in natural waters. Ni^{2+} is present in small quantities (0.1−6.0 ppm) in plants and animals and also occurs in trace amounts of sea water, petroleum, and coal. Common nickel compounds, when present in large amounts, have produced toxic effects in humans and other animals. Ni^{2+} ions bind to nucleic acids and produce significant genetic effects. A commonly recognized local reaction to nickel is dermatitis.

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 (Weng and Huang, 1994). Various methods exist for the removal of toxic metal ions from aqueous solutions, viz., ion exchange, reverse osmosis, precipitation, and adsorption, among others. Adsorption is by far the most versatile and widely used process. Activated carbon has been the standard adsorbent for the reclamation of municipal and industrial wastewaters for potable use for almost 3 decades (Fornwalt and Hutchins, 1966). In spite of its large use in the water and waste industries, activated carbon is still an expensive material, and therefore the production of its low-cost alternatives has been the focus of researchers in the area for the last few years. Efforts made in this direction, for the removal of metals from aqueous solutions including natural and industrial wastewaters, are well documented (Pollard et al., 1992). The materials developed for this purpose range from industrial wastes to agricultural waste products, and the use of various substances such as fly ash (Viraraghaven and Rao, 1991; Panday et al., 1986), bagasse fly ash (Srivastava et al., 1995), carbonaceous material (Srivastava et al., 1989a, 1996; Srivastava and Tyagi, 1995), metal oxides (Koeppenkastrop and De Careo, 1993; Srivastava et al., 1988; Cowan et al., 1991), zeolites (Kesroul-Quke et al., 1993; Suzuki et al., 1994; Groffman et al., 1992), moss (Lee and Low, 1989; Low and Lee, 1991), hydroxides (Namasivayam and Ranganathan, 1994, 1995), lignin (Srivastava et al., 1994), clays (Srivastava et al., 1989b; Vishwakarma et al., 1989; Dias Filho et al., 1995), biomass (Rao et al., 1993), peanut hulls (Periasamy and Namasivayam, 1994), pyrite fines (Zouboulis et al., 1995), geothite (Rodda et al., 1993), Coral sand (Suzuki and Takeuchi, 1994), and so forth has been exploited.

Steel plants produce granular blast furnace slag as a byproduct which causes a disposal problem. It is being used as a filler or in the production of slag cement. Recently, it was converted into an effective adsorbent (Srivastava et al., 1997) and used for the removal of a dye (Gupta et al., 1997a) and metal ions (Srivastava et al., 1997; Gupta et al., 1997b) in this laboratory. Continuing the activities in this direction, activated slag has now been tried for the removal of nickel and copper, and the results are presented in this paper.

Material and Methods

All the reagents used were of AR grade. Stock solutions of the metal ions were prepared by dissolving $CuSO_4$ and $NiSO_4$ in doubly-distilled water.

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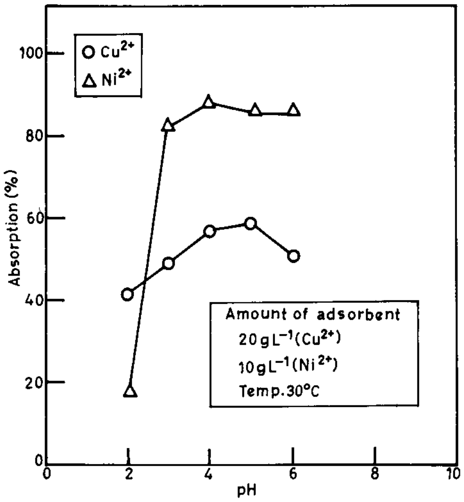


Figure 1. Effect of pH on the adsorption of metal ions.

Table 1. Chemical Composition and Characteristics of the Activated Slag

constituent	percentage by weight
CaO	30.47
SiO_2	30.77
S	0.85
MgO	9.85
MnO	0.59
Al_2O_3	23.30
FeO	0.54
loss on ignition	6.23
porosity (%)	67.5
surface area (m^2 g^{-1})	107
density (g/cm^3)	2.36
ZPC	2.8

(a) Equipments. Atomic absorption spectra were recorded using an atomic absorption/emission spectrophotometer (Perkin-Elmer Model 3100). pH measurements were made on a pH meter, (Model No. CL 46, CT, Toshniwal, India). The surface area of the sample was measured by a surface area analyzer (Quantasorb Model QS-7). 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 methods of chemical analysis (Vogel, 1989). Electrophoretic measurements for the determination of zero point of charge (ZPC) were carried out on a Lazer Z meter (Model 500, Penkem Inc., New York).

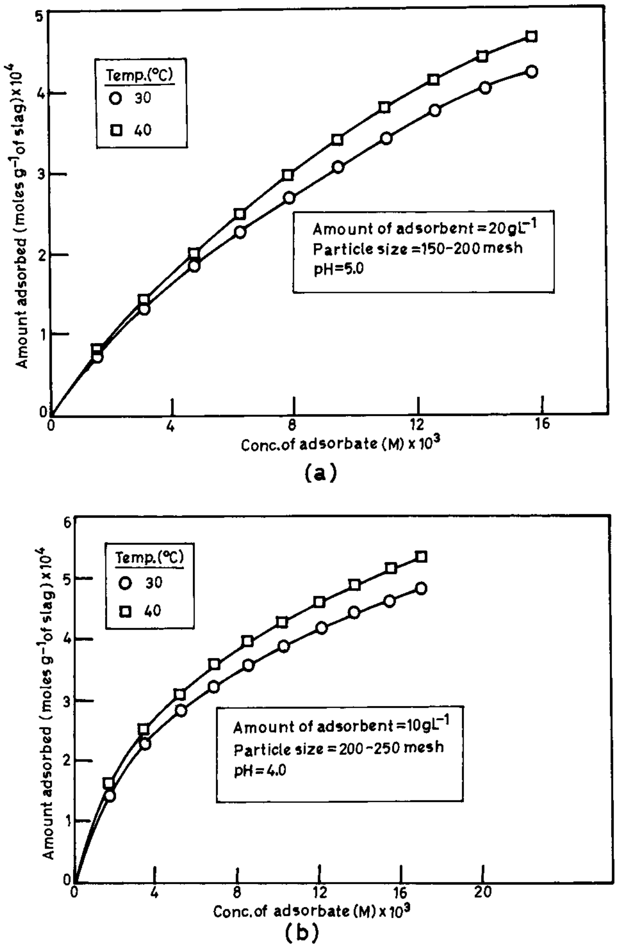
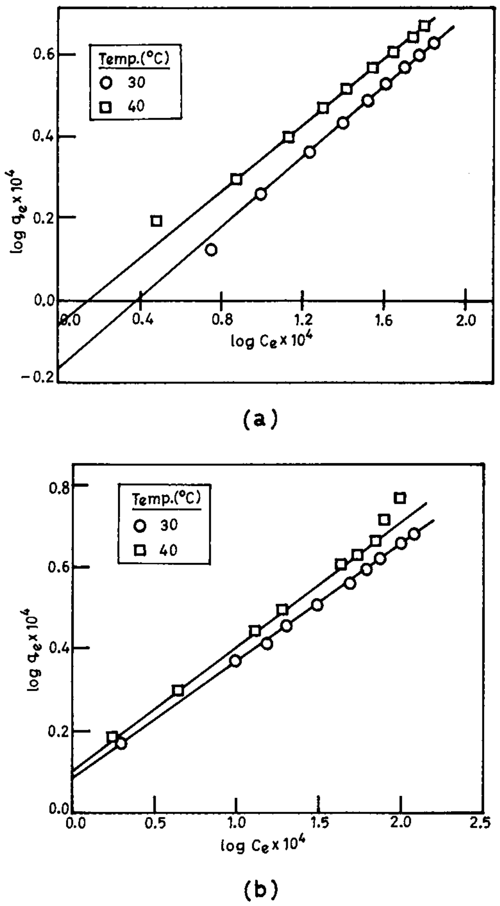


Figure 2. Adsorption isotherms of (a) Cu^{2+} and (b) Ni^{2+} at different temperatures.

(b) Material Development. Blast furnace slag obtained from Tata Iron and Steel Co., Ltd. (Jamshedpur, India) was in the form of small, spherical granules. The various steps involved in the treatment of the waste have already been given in detail in an earlier paper (Gupta et al., 1997a,b). The waste was washed with distilled water to remove the 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 h. The temperature and time were optimized by observing the surface properties of the activated product obtained by treating the raw material for different durations and temperatures. The conditions of activation were optimized to obtain samples exhibiting the best sorption capacity. It was observed that the product obtained on treatment of the waste at temperatures higher or lower than 600 °C exhibited poor adsorption capacity. The optimum temperature for the activation was, thus, 600 °C, and the product obtained from this process was sieved before use to obtain a desired particle size such as 100–150, 150–200, and 200–250 B.S.S. mesh. The studies were carried out with the slag of particle diameter 0.089 nm (mesh 150–200) unless stated otherwise. Finally, it was stored in a desiccator until used.

(c) Adsorption Studies. A batch method was used to obtain rate and equilibrium data. A series of 50 mL test tubes were employed. The procedure involved filling each test tube with 10 mL of metal ion solution of varying concentrations and adjusting to the desired pH and temperature. A known amount of adsorbent was then added into each test tube and agitated intermittently for 24 h. Preliminary investigations showed that equilibrium was attained in 6–8 h, with practically no significant change being observed even after 24 h of shaking. As such, all adsorption experiments were run after equilibrating 10 mL of adsorbate solution for 24 h. The solution was centrifuged and the supernatant in each case analyzed for aqueous metals. Initial sorbate concentrations ranged from 1.57×10^{-3} to 7.87×10^{-3} M for copper and 1.70×10^{-3} to 4.25×10^{-3} M for nickel. The effect of pH was studied over a range of 2–8, while the effect of temperature was assessed at 30, 40, and 50 °C. The influence of a cationic surfactant (cetyltrimethylammonium bromide) on the sorption was studied at the optimum pH (5.0 for Cu^{2+} and 4.0 for Ni^{2+}) as a function of concentration of the detergent. Stoppered glass tubes containing adsorbate solution along with the detergent and a fixed amount of adsorbent (10 g L^{-1} for Ni^{2+} and 20 g L^{-1} for Cu^{2+})



(a)

(b)

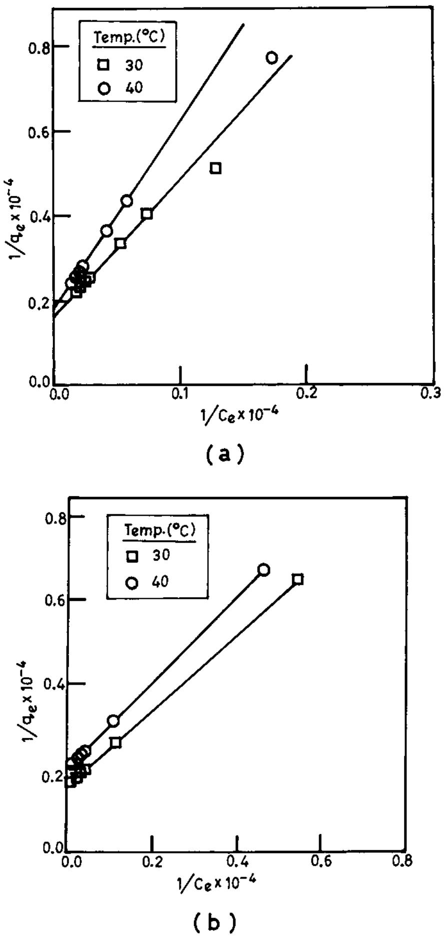
Figure 3. Freundlich adsorption isotherms of (a) Cu^{2+} and (b) Ni^{2+} at different temperatures.

were equilibrated for 24 h. The resulting solution was centrifuged and analyzed for aqueous metals.

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

(d) Kinetic Measurements. As in the case of adsorption studies, kinetics studies were also carried out using the batch method because of its simplicity and reliability. A number of 50-mL stoppered Pyrex glass tubes containing known volumes (10 mL) of metal ion solution, of known concentration, were brought to the desired temperature (±0.1 °C) with the help of a thermostat. A known amount of adsorbent (0.1 g) was added into each tube, and the solutions were agitated intermittently. At predecided intervals of time, the test solutions were centrifuged to separate the sorbent material from solution and the supernatant was analyzed for aqueous metal. The studies were carried out for a period of 6–8 h, i.e., until equilibrium was attained.

(e) Column Studies. Column operations are essential for industrial-scale designing of the technical systems. Moreover, the adsorption isotherms do not give accurate scale-up data in fixed-bed systems; therefore, the practical applicability of activated slag has also been ascertained in the column operations. A glass column (40 × 0.5 cm) filled with a known amount of slag (mesh size 200–250) was used for different metal ions. Investigations were carried out by feeding the columns with solutions of Cu^{2+} (3.9×10^{-3} M) and Ni^{2+} (4.25×10^{-3} M) at the desired flow rate by adjusting the same with a clip at the bottom of the column. The bed-depth-service-time (BDST) model proposed by Hutchins (1973) was successfully applied for the sorptive removal of Cu^{2+} and Ni^{2+}.



(a)

(b)

Figure 4. Langmuir adsorption isotherms of (a) Cu^{2+} and (b) Ni^{2+} at different temperatures.

(f) Regeneration. For any adsorption process, the most important factors are the recovery of the adsorbate material and regeneration capacity of the adsorbent. Consequently, experiments have been carried out in which a slag sample was loaded with adsorbate and subjected to elution of metal ions with a number of solvents. Simultaneous regeneration of adsorbent was also thought of.

Results and Discussion

Characterization of the Adsorbent Material. Chemical constituents of the activated slag as determined using standard methods of chemical analysis are given in Table 1. The characterization of the activated slag has already been reported (Gupta et al., 1997a,b). The material is amorphous in nature, with a surface area for the sample of 150–200 mesh size being 107 m^2 g^{-1}. It is quite stable in water, salt solutions, acids, and bases. One gram of the sample was stirred with 100 mL of deionized water (pH 6.8) for 2 h and left for 24 h in an airtight stoppered conical flask. Some enhancement in the pH was observed.

Adsorption Studies. Adsorption of the two metal ions was studied at varying pH values to determine the optimum pH range for their removal, and the results are shown in Figure 1. It is apparent that the uptake is quite low at lower pH; however, with an increase in pH, a significant enhancement in adsorption is recorded

Table 2. Freundlich and Langmuir Parameters

metal ion	Freundlich constant [$q_e = K_F C^{1/n}$]		Langmuir constant [$q_e = Q°b'c/(1 + b'c)$]			
			$Q° \times 10^4$ (mol g^{-1})		$b' \times 10^{-4}$ (L mol^{-1})	
	$K_F \times 10^4$	slope $1/n$	30 °C	40 °C	30 °C	40 °C
Cu^{2+}	0.68	0.43	5.55	6.06	0.04	0.05
Ni^{2+}	1.20	0.28	5.00	6.25	0.16	0.18

in both cases, with the optimum pH values for the removal of Cu^{2+} and Ni^{2+} being 5.0 and 4.0, respectively. This behavior can be explained by considering the surface charge of the activated slag which depends, to a large extent, upon the value of zero point of charge (ZPC) of silica (≈2.3) and alumina (≈8.2) (Panday et al., 1985). The composite ZPC of the adsorbent slag, as determined by electrophoretic measurements, was found to be 2.8 and as such the surface would have a high positive charge density in the low pH region. Under these conditions the uptake of metals would be quite low due to electrostatic repulsion. With increasing pH, i.e., beyond ZPC of the slag (>2.8) the negative charge density on the surface of the adsorbent increases, thereby resulting in a sudden enhancement in the removal. Further, it is also justified by considering the double layer at the SiO_2 and Al_2O_3 surfaces individually, which change in polarity from positive to negative as the concentration of hydrogen ions decreases.

The adsorption isotherms (Figure 2a,b) are regular, positive, and concave to the concentration axis. Initially the adsorption is quite rapid, which is followed by a slow approach to equilibrium at higher adsorbate concentrations. The uptake of metal ions is 75−90% at low concentrations and 28−55% at higher concentrations. These results reflect the efficiency of the slag for the removal of heavy metals from wastewaters in a wide concentration range. Further, the uptake of Cu^{2+} and Ni^{2+} increases by increasing the temperature. This may be due to the changes in the size of the pores of the adsorbent as well as to the increase in the number of adsorption sites due to the breaking of some internal bonds near the edge of the particle at higher temperatures (Bye et al., 1982; Panday et al., 1985; Yadava et al., 1988; Low and Lee, 1997). The increased rate of intraparticle diffusion of Cu^{2+} and Ni^{2+} into the pores of the adsorbent at higher temperature may also contribute to the increase in uptake because diffusion is an endothermic process (Knocke and Hemphill, 1981).

The data were fitted to Freundlich (Figure 3a,b) and Langmuir (Figure 4a,b) models. Values of Freundhlich and Langmuir constants are given in Table 2. The adsorption capacity K_F is less for the copper−slag system than for the nickel−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 almost the same for both nickel−slag and copper−slag systems.

The dimensionless separation factor, r (Weber and Chakraborti, 1974), in eq 1, calculated from the Langmuir isotherm, was found to be 0.14 and 0.03 for Cu^{2+} and Ni^{2+}, respectively. This indicates a highly favorable sorption ($r \ll 1$).

$$r = \frac{1}{1 + b'C_0} \tag{1}$$

Table 3. Thermodynamic Parameters for the Removal of Cu^{2+} and Ni^{2+} by Activated Slag

metal ion	$-\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ K^{-1} mol^{-1})
Cu^{2+}	15.02	17.99	0.108
Ni^{2+}	18.50	9.28	0.091

Thermodynamic parameters were also calculated using Langmuir isotherms and are given in Table 3. The changes in standard Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) for the process were obtained using expressions (2), (3), and (4), respectively, where

$$\Delta G° = -RT \ln b' \tag{2}$$

$$\ln\left(\frac{b'_1}{b'_2}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{3}$$

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

b', b'_1, and b'_2 are Langmuir constants at temperatures T, T_1, and T_2, respectively.

Negative $\Delta G°$ values confirm the feasibility of the process and spontaneous nature of the adsorption with a high preference of Cu^{2+} and Ni^{2+} for activated slag. Positive $\Delta H°$ values indicate the endothermic nature of the process, while positive values of entropy ($\Delta S°$) reflect the affinity of the adsorbent material for the metal ions and suggest some structural changes in adsorbate and adsorbent.

The discharge of wastewater from commercial and domestic sectors may cause the contamination of natural water by heavy metals, surfactants, and other substances. It is, therefore, necessary to examine the interference of other metal ions/surfactants, etc., for the removal of Cu^{2+} and Ni^{2+}. The effect of ionic interaction on the adsorption process may be interpreted, 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) (Tan et al., 1985) such that

$q_m/q_0 > 1$ adsorption is promoted by the presence of other metal ions

$q_m/q_0 = 1$ no observable net interaction effect

$q_m/q_0 < 1$ adsorption is suppressed by the presence of other metal ions

The competitive adsorption of Cu^{2+} and Ni^{2+} was studied in the presence of several metal ions and a surfactant. The removal of Cu^{2+} at 14.13×10^{-3} M concentration goes down by 6.60, 9.20, and 13.80% in the presence of Cd^{2+} (1.0×10^{-5} M), Ni^{2+} (1.0×10^{-5} M), and Zn^{2+} (1.0×10^{-5} M), respectively (Figure 5a). Similarly, the removal of Ni^{2+} at 15.40×10^{-3} M concentration is reduced by 4.30, 6.50, and 10.80% in the presence of Cd^{2+} (1.0×10^{-5} M), Zn^{2+} (1.0×10^{-5} M), and Cu^{2+} (1.0×10^{-5} M), respectively (Figure 5b). Interfering metal ions (M^{n+}) affect the uptake of primary ion by altering the surface charge density of the adsorbent. A decrease in the scavenging efficiency ($q_m/q_0 < 1$) of the adsorbent in the presence of 1.0×10^{-5} M cetyltrimethylammonium bromide is also evident (Figure 6a,b). It is found that the removal of Cu^{2+} and Ni^{2+} goes down by 1.76 and 1.42%, respectively.

Kinetic Studies. Studies on the rate of uptake of metal ions on activated slag indicated that the process

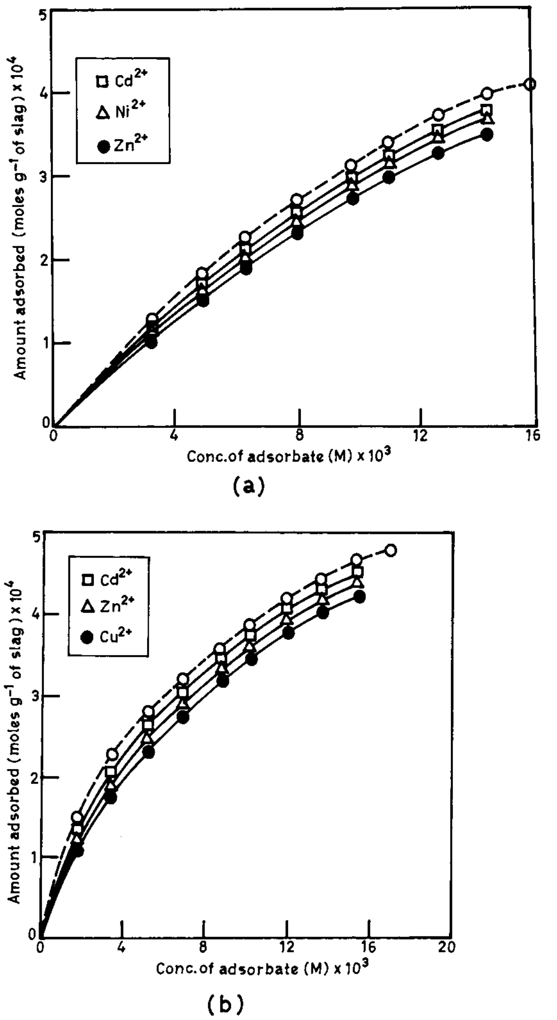


Figure 5. Competitive adsorption of (a) Cu^{2+} and (b) Ni^{2+} in the absence (- - -) and the presence (—) of interfering metal ions.

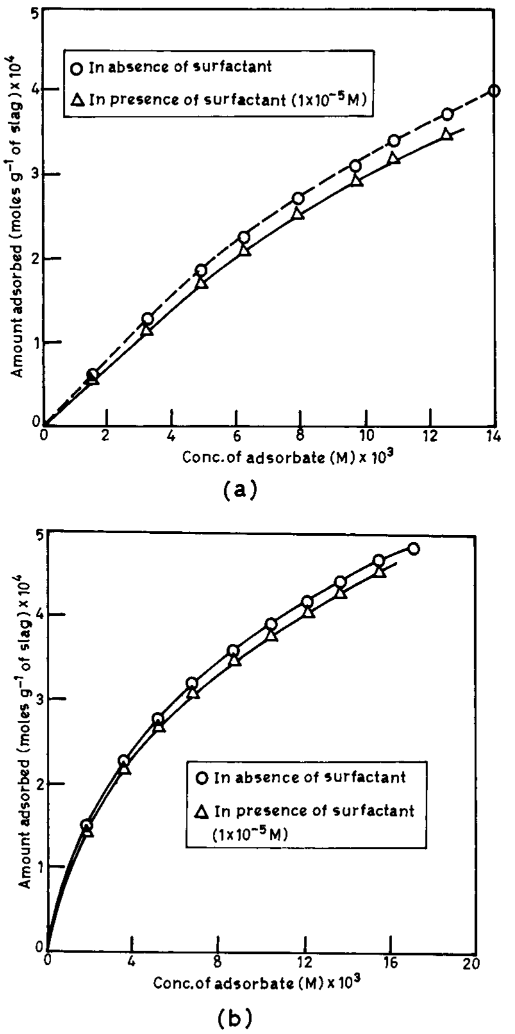


Figure 6. Effect of cationic surfactant on the adsorption of (a) Cu^{2+} and (b) Ni^{2+}.

is quite rapid, and typically 24–38% 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 h.

The effect of the amount of slag on the rate of uptake of copper and nickel is depicted in Figure 7a,b. It is seen that the rate of removal of metal ions increases with an increase in the amount of slag. For Cu^{2+}, there is a substantial increase (Figure 7a) in adsorption when the dose of slag is increased from 10.0 to 20.0 g L^{-1}, while the increase in removal efficiency is not so significant when the adsorbent amount is further increased from 20.0 to 30.0 g L^{-1}. Similarly, for Ni^{2+} (Figure 7b), the significant increase in uptake is observed when the slag amount increases from 5.0 to 10.0 g L^{-1} and an additional amount does not cause any significant change. Keeping this in mind, the amount of slag taken in all subsequent kinetic studies was 10.0 g L^{-1} for Ni^{2+} and 20.0 g L^{-1} for Cu^{2+} ions. The half-life of the process (t_{50}) decreases with an increase in the amount of the slag, thereby reflecting a dependence of the rate of adsorption on the amount of slag.

Rate of removal increases with an increase in temperature (Figure 8a,b), which is a usual phenomenon in the diffusion process. Further, 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, while the time required for 50% of the ultimate adsorption is independent of the initial adsorbate concentration (Figure 9a,b).

To interpret the experimental data, a quantitative treatment based on the model suggested by Helfferich (1962) has been applied. Various parameters were calculated by using the expressions (5–7), as given by Boyd et al. (1947).

$$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp[-D_i t\pi^2 n^2/r_0^2] \qquad (5)$$

or

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

and

$$B = \pi^2 D_i/r_0^2 \qquad (7)$$

Bt values as derived from eq 6 for the observed values of F were obtained from Reichenberg's Table (1953). The linearity test of Bt versus t plots is employed to distinguish between film and particle diffusion-con-

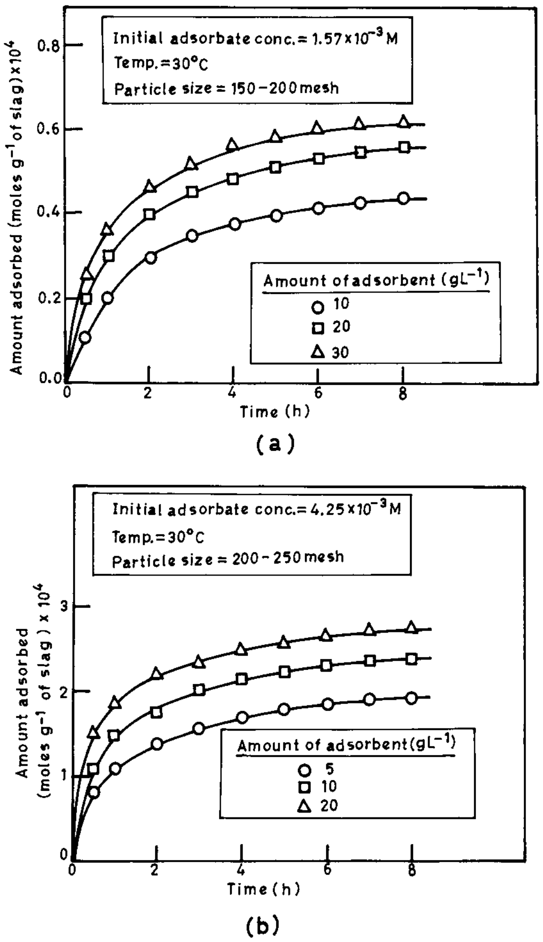


Figure 7. Effect of the amount of activated slag on the rate of removal of (a) Cu^{2+} and (b) Ni^{2+} by activated slag.

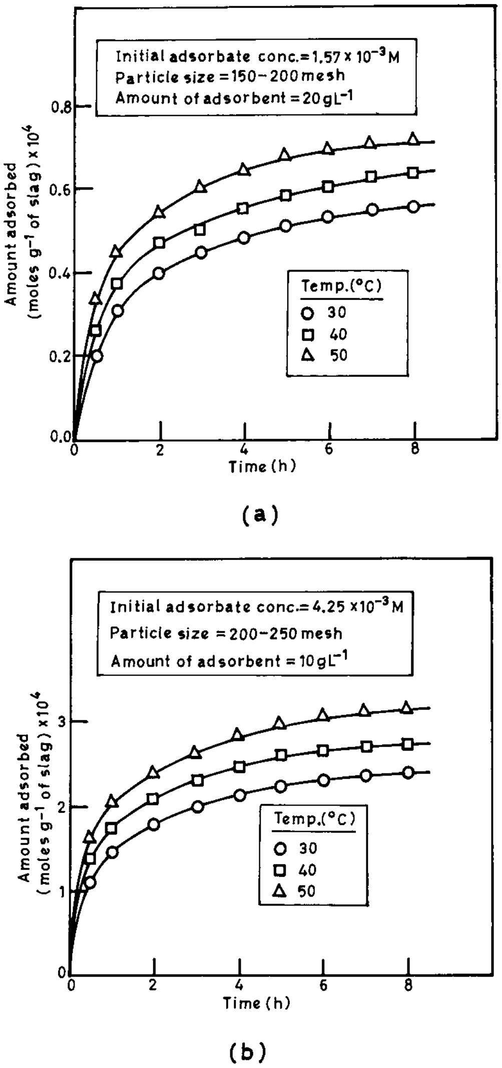


Figure 8. Effect of temperature on the rate of removal of (a) Cu^{2+} and (b) Ni^{2+} by activated slag.

trolled rates of adsorption. The *Bt* versus time plots for Cu^{2+} (Figure 10a) are linear at lower concentrations ($\leq 1.57 \times 10^{-3}$ M) and do not pass through the origin, indicating the process to be film diffusion, but at higher concentration ($\leq 7.87 \times 10^{-3}$ M), the plot is linear up to a certain time and passes through the origin, thereby indicating the process to be particle diffusion in nature. Similar plots for Ni^{2+} (Figure 10b) are linear and pass through the origin, reflecting the particle diffusion mechanism as the rate-controlling step. This was further confirmed by making McKay plots drawn for the same ions at different concentrations (Zogoroski et al., 1976).

D_i values increase with a rise in temperature (Table 4). The increase in mobility of ions and the decrease in the retarding forces acting on the diffusing ion result in the above behavior. Further, the D_i values for both the systems follow the same order in which these get adsorbed on activated slag.

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

$$D_i = D_0 \exp[-E_a/RT] \qquad (8)$$

$$D_0 = 2.72 d^2 (kT/h) \exp[\Delta S^{\ddagger}/R] \qquad (9)$$

The values of E_a, D_0, and $\Delta S^{\ddagger}$ for the diffusion of copper and nickel in slag are also given in Table 4. The D_0 values are greater than those reported in the case of hydrous ferric oxide and clay *montmorillonite* (Srivastava et al., 1988, 1989b) and lesser than those for minerals like iron(III) antimonate (Rawat and Singh, 1978). From these observations it can be inferred that the channels in the activated slag are wider than those of hydrous oxides and narrower compared to iron(III) antimonate. The negative values of entropy of activation obtained for the adsorption of Cu^{2+} and Ni^{2+} are not uncommon in ion-exchange processes. Such values normally reflect that no significant change occurs in the internal structure of adsorbent during the adsorption of metal ions.

The mass-transfer model (eq 10) suggested by McKay

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

(1982) and also by Periasamy and Namasivayam (1994) has been employed for the determination of the surface mass-transfer coefficient β_L, for the adsorption of Cu^{2+} and Ni^{2+} on activated slag.

Values of *m* and S_s can be calculated by using the expressions given in eqs 11 and 12.

$$m = W/V \qquad (11)$$

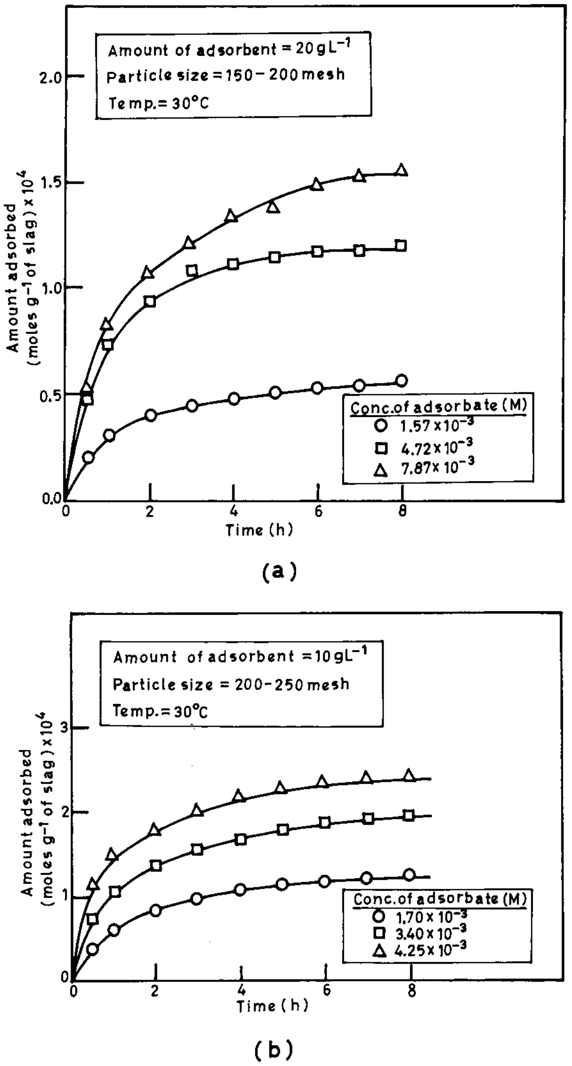


Figure 9. Effect of adsorbate concentrations on the rate of uptake of (a) Cu^{2+} and (b) Ni^{2+} by activated slag.

Values of β_L for the sorption of Cu^{2+} and Ni^{2+} on activated slag at 30 °C were calculated graphically (Figure 11) and are reported in Table 5. The linear nature of the plots for Cu^{2+} and Ni^{2+} suggests the applicability of the diffusion model. β_L values indicate that the velocity of the adsorbate transport from bulk to solid phase is quite rapid.

The adsorption of Cu^{2+} and Ni^{2+} from liquid to solid phase can be considered as a reversible process with an equilibrium established between two phases. The Lagergren first-order rate expression (eq 13),given by Periasamy and Namasivayam (1994), has been applied for the determination of a specific rate constant of adsorption for copper–slag and nickel–slag systems.

The linear plots of $\log(q_e - q)$ versus time at 30 °C (Figure 12) show the applicability of the rate expression mentioned above, and the values of K_{ad} evaluated from these plots are reported in Table 5.

Column Studies. Column operations were performed to evaluate the factual design parameters. 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 (1973) is adopted for the design of fixed-bed adsorbers. It deals with the movement of an adsorption wavefront through the adsorbent bed. The bed-depth-service-time has a linear relationship, and the curve can be described by eq 14 where t is the service time at breakthrough (min), x is the bed depth (cm), a

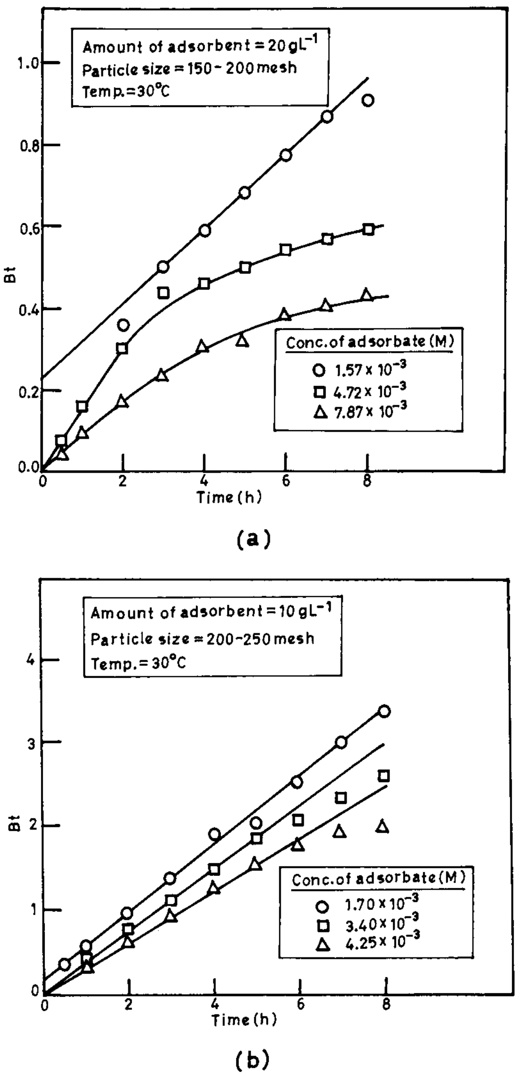


Figure 10. *Bt* versus time plots at various concentrations of (a) Cu^{2+} and (b) Ni^{2+}.

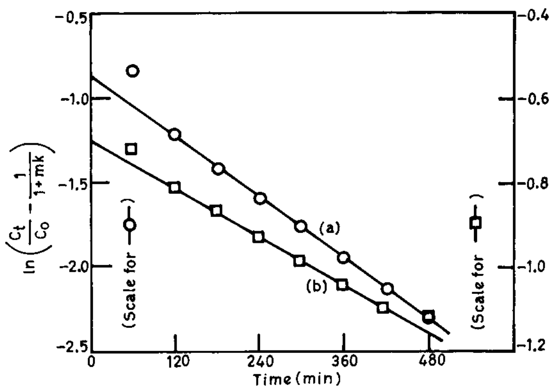


Figure 11. Plots of $\ln[C_t/C_0 - 1/(1 + mk)]$ versus time for the mass transfer of (a) Cu^{2+} and (b) Ni^{2+}.

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

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

Table 4. D_i, D_0, E_a, and $\Delta S^{\ddagger}$ Values for the Diffusion of Cu^{2+} and Ni^{2+} in Activated Slag

	D_i ($m^2\ s^{-1}$)					
metal ion	30 °C	40 °C	50 °C	D_0 ($m^2\ s^{-1}$)	E_a (kJ mol^{-1})	$-\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
Cu^{2+}	6.68×10^{-15}	9.69×10^{-15}	1.32×10^{-14}	1.82×10^{-14}	27.34	160.32
Ni^{2+}	3.51×10^{-15}	4.46×10^{-15}	5.46×10^{-15}	1.18×10^{-14}	14.79	163.88

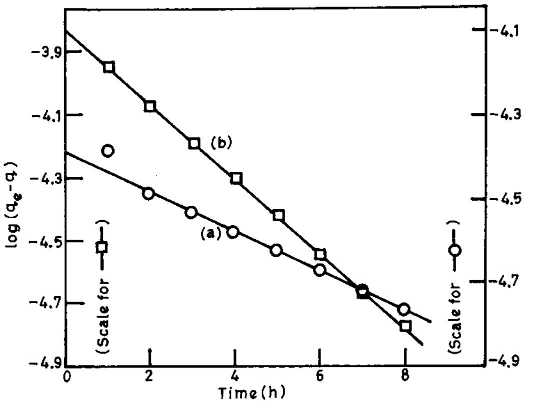


Figure 12. Lagergren plots for the adsorption of (a) Cu^{2+} and (b) Ni^{2+}.

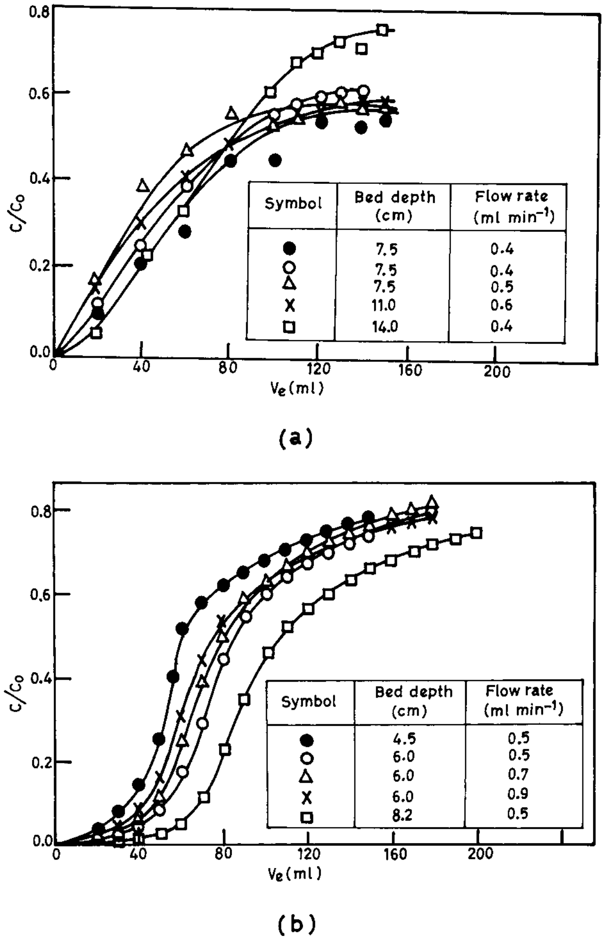


Figure 13. Breakthrough curves of (a) Cu^{2+} and (b) Ni^{2+} at varying bed depths and flow rates on activated slag.

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

is the slope (min cm^{-1}), and b is the intercept (min) which are given by the expressions

$$a = N_0/C_0V \tag{15}$$

$$b = -\frac{1}{LC_0}\ln\left[\frac{C_0}{C_B} - 1\right] \tag{16}$$

Vertical glass columns (dimension 40 × 0.5 cm) packed with known amounts of slag (mesh size 200–250) were used for the removal of Cu^{2+} and Ni^{2+}. Studies were performed by feeding the columns with a solution of Cu^{2+} (3.9×10^{-3} M) and Ni^{2+} (4.25×10^{-3} M) at controlled flow rate.

The data (Figure 13a,b) for different flow rates and bed depths are used to plot a BDST correlation. Figure 14a,b depicts the plots of BDST ($t_{1/2}$) at 50% breakthrough volume ($C/C_0 = 0.5$) against the bed depth at different flow rates. The nature of the plots indicates the applicability of the model to the bed system, and the BDST expressions for Cu^{2+} and Ni^{2+}, developed from the slope and intercepts of the plots of Figure 14 at a flow rate of 0.4 mL min^{-1}, are given in Table 6. After developing a BDST equation from column tests at one linear flow rate (0.4 mL min^{-1}), the expressions for other flow rates can be obtained with the help of eqs 17 and 18.

$$a_2 = a_1[Q_1/Q_2] \tag{17}$$

$$a_4 = a_3[C_1/C_2] \tag{18}$$

The capacity at complete exhaustion was determined by taking the total area at the point where the effluent plot joins the effluent in the breakthrough curve and dividing these values by the weight of adsorbent in the column. The column capacities of copper–slag (38.00 mg g^{-1}) and nickel–slag (66.0 mg g^{-1}) systems are found to be greater than their batch capacities, i.e., 30.00 and 29.35 mg g^{-1} for copper and nickel, respectively.

When the adsorbent gets exhausted or when the effluent from an adsorbed bed reaches the maximum allowable discharge level, the recovery of the adsorbed material as well as regeneration of the adsorbent becomes quite necessary. Thermal regeneration in a multiple-hearth furnace is the most common method used for this purpose in carbon columns. However, in this approach, some adsorbent is lost during each cycle and recovery of the adsorbate is not possible. Chemical regeneration by a suitable solvent is a definite alternative, and the same has been tried for Ni^{2+} desorption and column regeneration using various solvents. Almost quantitative recovery was observed with 1% HNO_3 as the eluent which has been used earlier also (Srivastava et al., 1997; Munaf and Zein, 1997; Low and Lee, 1997).

Figure 15 shows the results of the two consecutive adsorption–desorption curves for nickel. A total of 80 mL of 1% HNO_3 has been used. The first 40 mL of 1% HNO_3 leads to the elution of 58.8% nickel and the other 40 mL accounts for 27.05% nickel.

After desorption of metals, the column was washed with 10 mL fractions of distilled water at a fixed flow rate and was again loaded with various metal ions to check the sorption efficiency of the material during subsequent cycles. Figure 16 represents the amount of the adsorbate adsorbed as a function of the number of

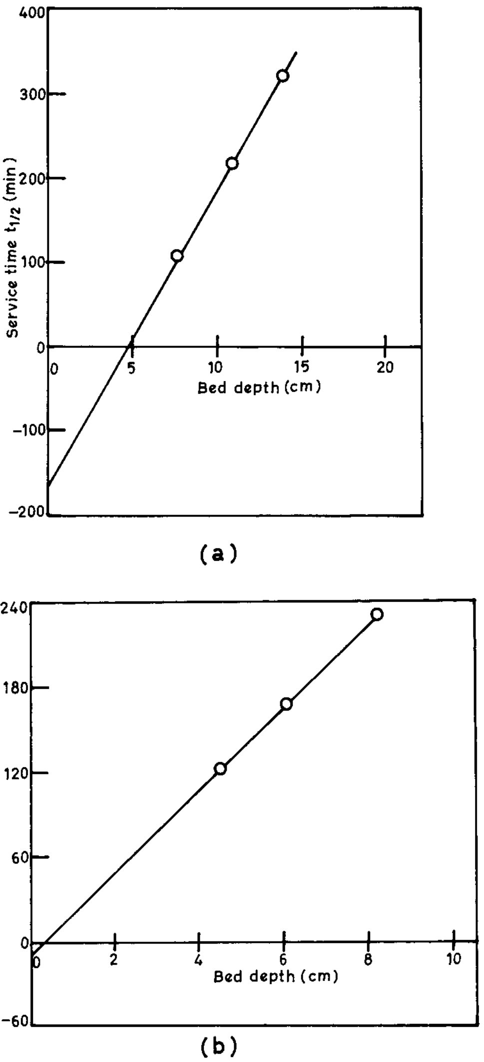


Figure 14. BDST (50% breakthrough) curves at different bed depths for (a) Cu^{2+} and (b) Ni^{2+}.

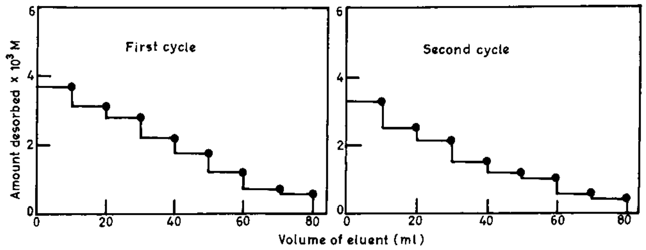


Figure 15. Desorption curve of Ni^{2+} with 1% HNO_3.

Table 5. Mass-Transfer Coefficient (β_L) and Rate Constant of Adsorption (K_{ad}) Values for Cu^{2+} and Ni^{2+}

metal ion	β_L (cm s^{-1})	K_{ad} (min^{-1})
Cu^{2+}	15.0×10^{-6}	0.18×10^{-2}
Ni^{2+}	6.05×10^{-6}	0.45×10^{-2}

Table 6. BDST Equations for Cu^{2+} and Ni^{2+}

metal ion	BDST equation
Cu^{2+}	$t_{1/2} = 1.73x + (-170)$
Ni^{2+}	$t_{1/2} = 32.0x + (-10)$

adsorption cycles for Ni^{2+}. The breakthrough capacities of Ni^{2+} in the first, second, and third cycles are 66, 54, and 52 mg g^{-1}. These values show a fall in the sorption capacity of the column.

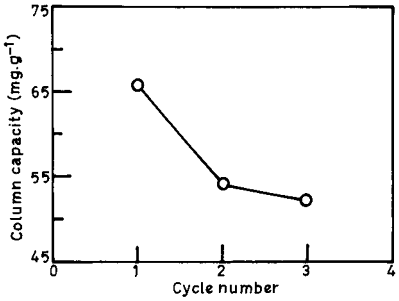


Figure 16. Variation of column capacity with the number of cycles for the nickel–slag system.

Applications

Activated slag was used for the treatment of an actual waste from a metal finishing plant bearing copper and nickel. Two typical runs containing Cu (10.0), Zn (3.0), Cd (4.0), Pb (12.0), and Ni (58.0 mg L^{-1}) and Cu (2.0), Zn (10.0), Cd (1.0), Pb (8.0), Ni (50 mg L^{-1}) were carried out with the adsorbent column (40 × 0.5 cm; 200–250 mesh) at a flow rate of 0.4 mL min^{-1}. The removal of Cu^{2+} and Ni^{2+} was found to be almost 90%.

Cost Estimation

The waste material is available for \$38.00 ton^{-1}, and adding the expenses for transport, chemicals, electrical energy, etc., the final product would cost approximately \$52.0 ton^{-1}. Further, recovery of adsorbates and regeneration of columns (without dismantling) will bring down the cost factor. This is in contrast to the commercially available carbons, the cheapest variety of which in India costs ≈\$1000 ton^{-1}.

Conclusions

The activated slag developed from the blast furnace waste material is an effective adsorbent for the removal of Cu^{2+} and Ni^{2+} from aqueous solution and wastewater which takes place via the particle diffusion mechanism. The thermodynamic parameters reflect the feasibility of the removal process. The results show that the waste material can be fruitfully employed for the removal of Cu^{2+} and Ni^{2+} in a wide range of concentrations. The column studies indicated that the product can be used on an industrial scale as well. It could be possible to quantitatively recover Ni^{2+} by 1% HNO_3, and the product has successfully been used for the removal of Ni^{2+} and Cu^{2+} from an effluent of a metal finishing plant.

Nomenclature

a_1 = slope at flow rate Q_1
a_2 = slope at flow rate Q_2
a_3 = slope at concentration C_1
a_4 = slope at concentration C_2
a = slope, min/cm
B = time constant
BSS = British standard size
b' = Langmuir constant
b'_1 = Langmuir constant at temperature T_1
b'_2 = Langmuir constant at temperature T_2
β_L = mass-transfer coefficient (cm s^{-1})
C_1 = concentration of adsorbate (mg L^{-1}) after time t
C_0 = initial concentration of adsorbate (mg L^{-1})
C = concentration in the bulk fluid phase
C_B = eluent concentration (mg L^{-1})

C_1 = old feed concentration
C_2 = new feed concentration
D_i = effective diffusion coefficient ($m^2\ s^{-1}$)
d = average distance between two successive sites of adsorbent (5 Å)
d_p = particle diameter (cm)
ϵ_p = percent porosity of adsorbent particles
F = fractional attainment of equilibrium at time t
h = Plank's constant
K_F = Freundlich constant
k = Boltzmann constant
K_{ad} = specific rate constant (min^{-1})
L = rate constant of adsorption ($mg^{-1}\ mL\ min^{-1}$)
m = mass of adsorbent per unit volume of particle free adsorbate solution ($g\ L^{-1}$)
n = integer defining the infinite series solution obtained for a Fourier type of analysis
N_0 = adsorption capacity (mg of adsorbate/cm^3 of adsorbent)-
$Q°$ = Langmuir monolayer capacity ($mol\ g^{-1}$)
Q_t = amount adsorbed at time t ($mol\ g^{-1}$)
q_m = adsorption capacity of ion in the presence of other metal ions
q_0 = adsorption capacity of ion in the absence of other metal ions
q_e = amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium
q = amount of adsorbate adsorbed per unit weight of adsorbent at any time t
R = gas constant
r_0 = radius of the adsorbent particle assumed to be spherical
ρ_p = density of the adsorbent ($g\ cm^{-3}$)
S_s = outer surface of the adsorbent per unit volume of particle free slurry (cm^{-1})
V = volume of particle free adsorbate solution
V_r = linear flow rate ($L\ min^{-1}\ cm^{-1}$)
W = weight of adsorbent (g)
ZPC = zero point of charge

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