A Comparative Adsorption Study of Copper on Various Industrial Solid Wastes

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The adsorption behavior of Cu on three solid waste materials—sea nodule residue (SNR), fly ash (FA), and red mud (RM)—was investigated. The effects of various parameters, such as pH of the feed solution, contact time, temperature, adsorbate and adsorbent concentration, and particle size of the adsorbent, were studied for optimization of the process parameters. Adsorption of copper increased with increasing time, temperature, pH, and adsorbate concentration, and decreased with increasing initial copper concentration. The equilibrium data fit well with the Langmuir and Freundlich isotherms in the case of SNR, but not on RM and FA, because there was no appreciable effect of temperature on the metal removal on these two adsorbents. The adsorption of copper on SNR followed first-order kinetics involving the surface complex formation mechanism on the charged surface. Under the optimized conditions the adsorption capacity for copper was found to be 19.65 mg/g of SNR, 1.98 mg/g of FA, and 2.28 mg/g of RM. Thus the adsorption capacity of SNR was found to be more than that of activated carbon, thus making it suitable for the treatment of industrial effluents to reduce the level of copper within the permissible limits for its land disposal (3 mg/L) according to ISI guidelines.
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Introduction

Nonferrous processing and metal-finishing industries produce large amounts of solid and liquid waste containing toxic radicals such as zinc, cadmium, copper, and nickel. Discharge of these industrial effluents onto land and into the river increases the level of heavy metals in the environment and aquatic systems, directly, or through percolation from the contaminated soil, thus posing adverse effects because of their toxic nature. Elevated levels of Cu^{2+} in the environment can be attributed to a variety of sources, such as industrial effluents from metal cleaning and plating baths, paper, paperboard mills, wood-pulp production, tire manufacture, and fertilizer industries. Excessive intake of copper results in its accumulation in the liver, leading to copper poisoning and gastrointestinal prob-

lems. It is also toxic to aquatic organisms, even at very low concentration. The tolerable limits for Cu^{2+} in the effluents onto the land according to ISI specifications is 3.0 mg/L (Trivedi, 1995); beyond this concentration the effluents must be treated before disposal.

There are various methods for wastewater treatment. In the conventional methods such as chemical precipitation, precipitation of copper as hydroxide in the pH range of 7–10 is the most common technique applied industrially to minimize its concentration in effluents (Anonymous, 1989). However, this leads to the production of solid wastes, often toxic, that may require safe disposal protocol or even further treatment to meet the stringent environmental regulations.

The solvent-extraction process treats a large volume of effluent and solvent losses and it is applicable to effluents having high content of metal ion (>1.0 g/L). Other options, such as cementation, electrodeposition, use of a membrane system, and activated carbon being used today for the treatment of large volumes of dilute metal ion solutions, are often unable to meet

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Table 1. Chemical Composition of the Solid Wastes Used in This Study

	Constituent (wt %)								
Adsorbent	Al_2O_3	SiO_2	Fe_2O_3	MnO	Na_2O	TiO_2	CaO	Zn	Mg
Sea nodule residue	1.58	19.04 (Si)	9.03 (Fe)	18.23	—	—	—	0.60	—
Red mud	14.8	6.4	62.78	1.1 (Mn)	4.8	3.7	0.23	0.02	0.06
Fly ash	28.23	59.72	5.37	0.08	1.23	2.01	1.39	—	0.83

the new and more stringent requirements and are also uneconomical (Weber, 1998). Thus, an innovative, new, and cost-effective method for removal of toxic metals from industrial waste streams or runoff constitutes a vital need for today: treatment of effluents by sorption (adsorption, ion exchange, and complexation), using low-cost filter media, could be an attractive option. Through the chemical and physical process of sorption a significant portion of the total metal concentration is reduced to a level that is less detrimental to the environment (McKay and Porter, 1997). Adsorption using naturally available solid waste is a cost-effective and viable option. Naturally occurring substances and solid wastes, such as zeolite, kyanite, activated slag, ferromanganese nodule, bentonite, chitosan, blast furnace slag, alginate, mixed fly ash, sea nodule residue, clay fraction of alluvial soil, and iron/cobalt oxide coated keramzite (Chen et al., 1997; de la Flor et al., 1995; Dimitrova, 1996; Gupta, 1998; Hequeta et al., 2001; Ke, 1992; Mohammad et al., 2001; Panayotova, 2001; Parida et al., 1996; Pesic et al., 1993; Sahoo et al., 2001; Stefanova 2001) have been investigated as scavengers of copper from synthetic solution/industrial effluents.

In this work systematic adsorption studies were carried out on red mud (RM) and fly ash (FA) obtained from NALCO (Bhubneshwar, India) and sea nodule residue (SNR) generated during the processing of sea nodules for the recovery of Cu, Ni, and Co by reduction roasting and an ammoniacal leaching process (Jana et al., 1999), developed at the National Metallurgical Laboratory (NML, Jamshedpur, India). The present study was undertaken to use them as potential adsorbents for the adsorption of copper from aqueous solution so that these wastes can be used as suitable substitutes of activated carbon.

Experimental

Instrumentation

Trace metal analysis was done by atomic absorption spectrophotometer [Thermol Jarrel Ash (TJA), SH-8000] in air–acetylene flame; pH measurements were done using a CL-46 Toshniwal pH meter. Sample shaking was done in a thermostatic shaker bath at 120 rpm for all the experiments. Surface area was determined by the BET method (Quantachrome, Boynton Beach, FL).

Chemicals

Stock solutions of 1000 mg/L copper were prepared by analytical-grade copper (II) nitrate from Sigma Chemicals (Mumbai, India). HNO_3 and NaOH, used to adjust the pH of the working solutions, were of LR grade (E. Merck, Mumbai, India). Distilled water was used for solution and sample preparation and dilution to make the copper solutions of different concentrations.

Adsorbents

Samples of about 2 kg, from each type of waste, were taken by the coning and quartering method. The samples of SNR and RM were treated with dilute HCl to reduce the pH to 6.5 and subsequently washed several times with distilled water to remove the excess of chloride ions. Fly ash was simply washed with distilled water before use. These washed samples were dried at 100°C for 24 h, sieved by using sieves of different BSS mesh sizes to obtain different size fractions, and stored in a desiccator over fused $CaCl_2$. The studies were carried out with materials of 150 to 104 μm size fraction, unless otherwise stated.

Adsorption experiments

The adsorption of copper was studied by batch technique. The initial pH of the feed solution of a known concentration was adjusted by adding dilute HNO_3/NaOH and a known amount of adsorbent was added to 100 mL of the solution in a 250-mL stoppered conical flask. The flasks were shaken in a thermostatic shaker bath at 120 rpm at 303 K. After equilibration the content of the flask was filtered and the residual concentration of copper was determined by atomic absorption spectrophotometry (AAS). The average of initial and final pH was reported. Percentage of Cu adsorbed was determined from the ratio of copper adsorbed by the adsorbent and the initial concentration of copper in the aqueous phase.

Results and Discussion

Sample characterization

Chemical analyses (Vogel, 1989) of all three adsorbents are detailed in Table 1. Phase identification by X-ray diffraction shows that in SNR mostly silica (SiO_2), manganese oxide (MnO_2 and MnO), and iron hydroxide are present with a minor amount of hematite (Fe_2O_3). Gibbsite (Al_2O_3·$2H_2O$) and hematite (Fe_2O_3) are the major phases in red mud along with minor amounts of quartz (SiO_2), kaolinite [$Al_2SiO_5(OH)_4$], anatase (TiO_2), and rutile (TiO_2). Fly ash contains alumina (Al_2O_3) and quartz (SiO_2) as major phases and hematite as a minor phase. Table 2 shows different size fractions present in the adsorbents. The major fraction in SNR and RM is in the

Table 2. Sieve Analysis of Sea Nodule Residue, Red Mud, and Fly Ash

Adsorbent	150 μm	150–104 μm	104–76 μm	<76 μm
Sea nodule residue (%)	10.8	54.3	11.6	23.4
Red mud (%)	27.1	60.4	—	12.5
Fly ash (%)	4.1	13.3	20.1	62.5
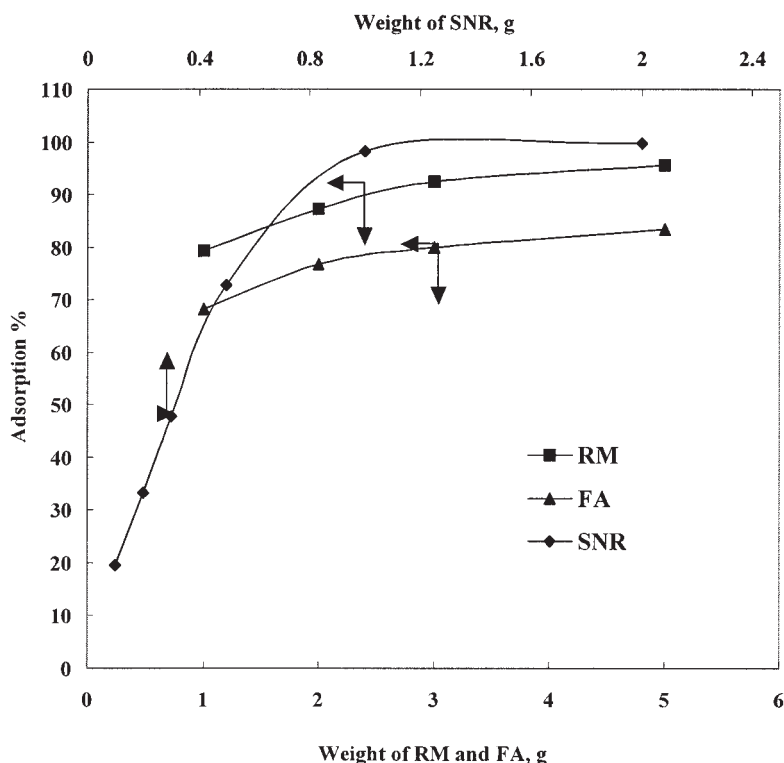
Figure 1. Effect of weight of adsorbent on SNR, RM, and FA.

Conditions: SNR: [Cu]: 200 ppm. FA and RM: [Cu]: 10 ppm; T: 303 K; Vol: 100 mL, PS: 150–104 μm; pH: 5.5.

range 150–104 μm and the major fraction in fly ash is <76 μm. Surface areas of these adsorbents, measured by BET apparatus, were found to be 138, 16, and 14 m^2/g for SNR, RM, and FA, respectively.

### Effect of weight of adsorbent on copper adsorption

The weight of SNR was varied from 0.1 to 2 g in 100 mL for 200 mg/L of copper and from 1 to 5 g in 100 mL for 10 mg/L of Cu adsorption on RM and FA (Figure 1), respectively. The adsorption of copper increased from 20 to 99.8% with increasing weight of SNR; this also decreased the equilibrium time from 8 to 2 h. Similarly, an increase in adsorbent weight from 1 to 5 g increased the metal removal from 79 to 96% in 8 h on RM and from 68 to 84% in 2 h on FA. Adsorption capacity of the adsorbent is in the order: SNR > RM > FA. The plot also reveals that the percentage adsorption of copper increases rapidly with increasing amount of adsorbents, attributed to the availability of a large surface area during the initial stage of adsorption. This is called the *capacity effect* and thus at a constant initial copper concentration the percentage adsorption on these adsorbents is determined by their adsorption capacity. Although adsorption within moderate coverage (up to 10%) may be governed by coulombic interaction of Cu^{2+} as an aquo-complex on the charged surface, higher coverage may involve complex formation with $CuOH^+$ species, thereby increasing the adsorption capacity (Subramaniam and Yiacoumi, 2001). The enhanced copper removal is thus possible because hydrolyzed species are larger and less hydrated than nonhydrolyzed species (Cu^{2+}) and coordinated hydroxide group of $CuOH^+$ favors adsorption (Stumm and Morgan, 1970).

Effect of initial copper concentration on adsorption

Copper (II) solutions (100 mL) of different concentrations, ranging from 50 to 500 mg/L, with 1 g of SNR, 5–25 mg/L with 2 g of RM, and 5–15 mg/L with 2 g of FA, were stirred at 303 K for a contact period of 24 h at pH 5.5. Percentage copper removal on SNR (Figure 2) decreased from 99.9 to 57.0% with increasing metal concentration. Also, the adsorption rate slowed down with the increase in initial copper concentration, thus increasing the equilibrium time from 2 to 8 h. In the case of red mud and fly ash the equilibrium was attained in 8 and 4 h, respectively, irrespective of the metal concentration. Figure 2 also shows a decrease in the percentage copper removal with increasing copper concentration on red mud and fly ash from 94.2 to 77.7% and 78 to 38%, respectively. The higher metal uptake at low concentration is attributed to the availability of greater surface area with active centers on the adsorbent for lesser amounts of adsorbate ions.

Effect of particle size and composition of the adsorbent

The influence of particle size of adsorbents was investigated at room temperature (303 K) using particle sizes ranging from 76 to 150 μm. A 200 mg/L Cu (II) solution was stirred with 1 g of SNR, whereas for 2 g of fly ash and red mud 10 mg/L of Cu (II) solution was taken. Maximum metal removal was found in 8 h on SNR at all particle sizes, and 99.9% copper adsorption was recorded for the size fraction of 150–104 μm on SNR; the solution, after adsorption, was found suitable (0.2 mg/L Cu) for disposal, thus fulfilling the ISI specification. Copper removal on SNR decreased with decreasing particle size to <76 μm,
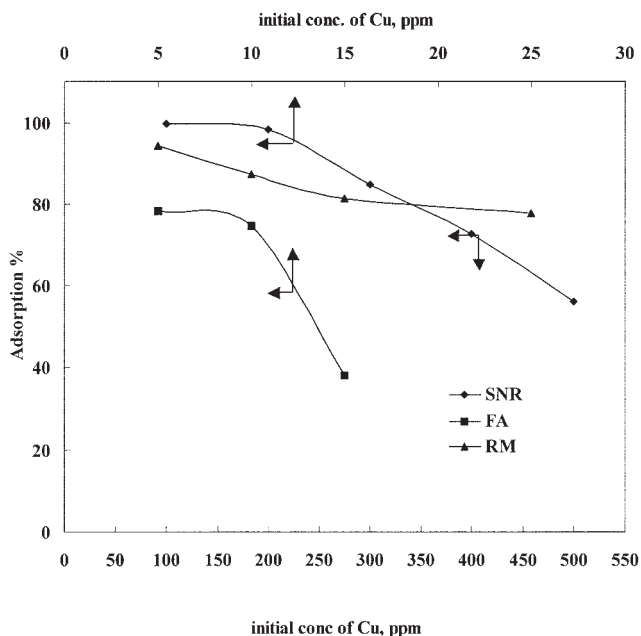
Figure 2. Effect of initial concentration of copper on adsorption on SNR, RM, and FA.

Conditions: SNR: S/L: 1/100. FA and RM: S/L: 1/50; pH: 5.5; T: 303 K; PS: 150–104 μm.
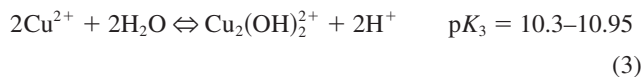
most likely attributable to the high porosity of the adsorbent promoting more adsorption sites on the coarser fraction, whereas in the finer fraction only the surface sites were available for adsorption. Practically, there was scarcely any effect of particle size on the adsorption of copper on red mud and fly ash, where maximum metal removal was 76 and 87%, respectively.

Here it will be worthwhile to take into account the compositional factors such as various phases of oxides/hydroxides of manganese and iron, alumina, and silica and chemical composition of each of the adsorbents responsible for the variation in adsorption capacity. The presence of major amounts of man-

ganese oxides/hydroxides, iron hydroxides, and silica in SNR is mainly responsible for such a high adsorption capacity compared to that of red mud, consisting of gibbsite and hematite constituting the major phase with quartz, kaolinite, anatase, and rutile constituting the minor constituent; and fly ash mainly consisting of alumina and quartz with hematite as the minor phase. Liu et al. (2002) studied the effect of manganese oxide morphology of Fe–Mn nodules from several Chinese soils on the adsorption of heavy metals. Surface area measurements of SNR (138 m^2/g), RM (14 m^2/g), and FA (16 m^2/g) also indicate that SNR has a greater effective area for adsorption compared to that of the other two adsorbents.

Effect of pH

The effect of pH on the adsorption of Cu(II) onto all three adsorbents was examined in the range 2.0–6.0, to optimize metal removal. Results presented in Figure 3 for the three adsorbents showed lower metal uptake at low pH, which significantly increased with increasing pH. A similar trend was reported for copper adsorption on activated carbon (Dastgheib and Rockstraw, 2001). This may be explained with formation of different species of copper

$$Cu^{2+} + H_2O \Leftrightarrow CuOH^+ + H^+ \qquad pK_1 = 7.2\text{–}8.1 \quad (1)$$

$$Cu^{2+} + 2H_2O \Leftrightarrow Cu(OH)_2 + 2H^+ \qquad pK_2 = 13.7\text{–}17.3 \quad (2)$$

$$2Cu^{2+} + 2H_2O \Leftrightarrow Cu_2(OH)_2^{2+} + 2H^+ \qquad pK_3 = 10.3\text{–}10.95 \quad (3)$$

The species of Cu^{2+} as an aquo-complex [Cu(H$_2$O)$_4$]$^{2+}$ and CuOH$^+$ up to 7.0 pH ($<$pK$_1$ value) are mainly involved in the adsorption process. The increase in adsorption of copper at higher pH may be attributed to the complex formation with CuOH$^+$ species accounting for electronic double layer on the charged oxide/hydroxide surface of the adsorbent (Leckie and Davis, 1979). This surface complexation approach to explain
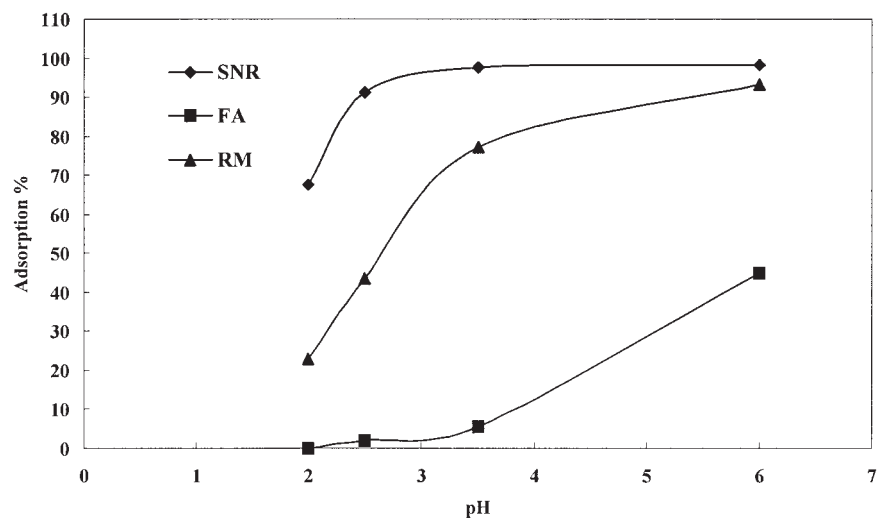
Figure 3. Effect of pH on Cu adsorption on SNR, RM, and FA.

Conditions: SNR: S/L: 1/100; [Cu]: 200 ppm. FA and RM: S/L: 1/50; [Cu]: 10 ppm; T: 303 K; PS: 150–104 μm.
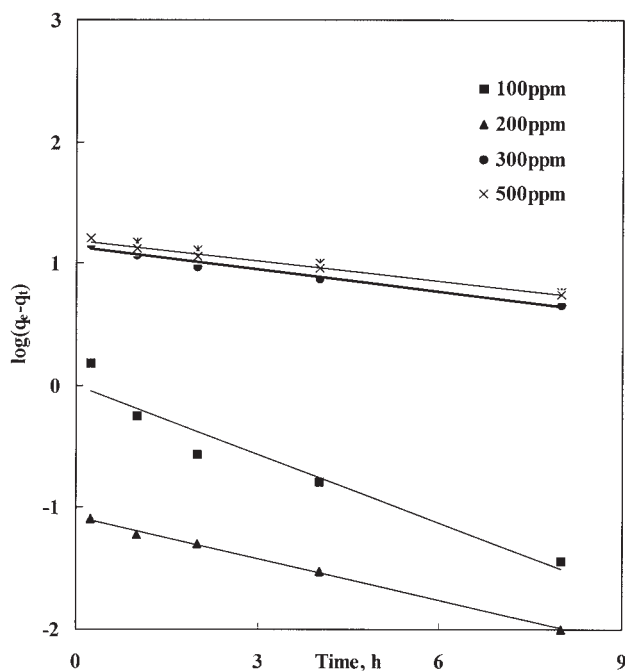
Figure 4. Lagergren plot for Cu adsorption on SNR.

Conditions: T: 303 K; S/L: 1/100; pH: 5.5; PS: 150–104 μm.

Cu adsorption on various adsorbents was also investigated by Runkel et al. (1999) and Wang et al. (1997). Although the adsorption of multinuclear species such as $Cu_2(OH)_2^{2+}$, based on spectroscopic evidence for its existence, was also considered by Subramaniam and Yiacoumi (2001), whereas an explanation of copper adsorption under high surface coverage conditions, using triple layer/continuum models (TLM/CM), was ignored in the present work. This stems from the insignificant amount of such species below 7.0 pH.

Adsorption was maximum at pH 5.5 for SNR–Cu and RM–Cu systems. At this pH, copper removal was 98.5% on SNR and 93% on RM. There was practically no adsorption on FA at low pH, but at a pH of 5.5 it was 45% from a solution containing 10 mg/L copper. This behavior can be explained on the basis of surface charge of the adsorbent, which is indicated by the PZC (point of zero charge) values and is measured by potentiometric titration of the adsorbent suspension at different ionic strengths of an electrolyte such as KNO_3 (Parida, 1988). The PZC values for SNR, RM, and FA were found to be 4.8, 3.8, and 4.0, respectively. Thus, at lower pH the surface of the adsorbent would have a high positive charge density and uptake of the metal would be quite low because of electrostatic repulsion. With increasing pH, the negative charge density on the surface of the adsorbent increases and, consequently, adsorption of $CuOH^+$ species takes place, thereby resulting in enhanced metal removal at pH 5.5. Thus, the mechanism of copper removal may be attributed to diffusion of Cu^{2+} from the bulk solution to the surface of the oxide/hydroxide component of the adsorbents, followed by hydrolysis, leading to the formation of the surface–metal complex SO–CuOH (Subramaniam and Yiacoumi, 2001).

Adsorption dynamics and isotherm studies

Two important facts for the evaluation of the parameter in metal adsorption are the kinetics and the equilibrium of adsorption. The adsorption of heavy metals from liquid phase to solid phase can be considered as a reversible reaction with equilibrium being established between the two phases (Hall et al., 1996). Because adsorption of copper on the adsorbent is a kinetic process, an increase in temperature from 303 to 333 K substantially increased the rate of removal of the metal on SNR, indicating the process to be endothermic (McKay et al., 1980). Details on Cu–RM and Cu–FA are not given because no major improvement in metal removal was observed at higher temperature.

The Lagergren equation representing a first-order kinetic model is given by the following equation

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}t}{2.303} \quad (4)$$

where q_e and q_t are the amount of copper adsorbed per unit weight of adsorbent under equilibrium and at time t, respectively, and k_{ad} is the rate constant for adsorption. Linear plots of $\log(q_e - q_t)$ vs. t (Figures 4–6) for copper adsorption on SNR indicated the applicability of the Lagergren equation. The k_{ad} values calculated from the slopes of the plots for different Cu(II) concentrations (100–500 mg/L) at different temperatures are presented in Table 3.

The activation energy for copper adsorption was calculated by the Arrhenius equation

$$k_{ad} = A \exp\left(-\frac{\Delta E_a}{RT}\right) \quad (5)$$
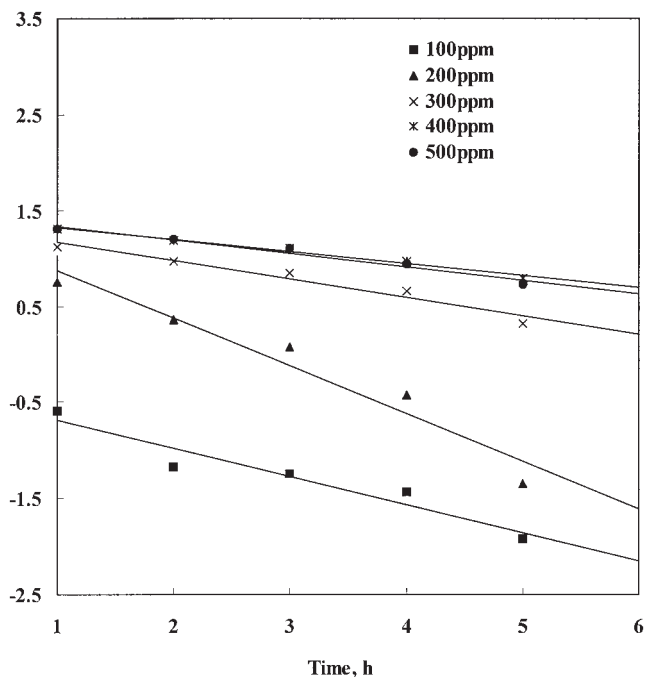
Figure 5. Lagergren plots for Cu adsorption on SNR.

Conditions: T: 318 K; S/L: 1/100; pH: 5.5; PS: 150–104 μm.
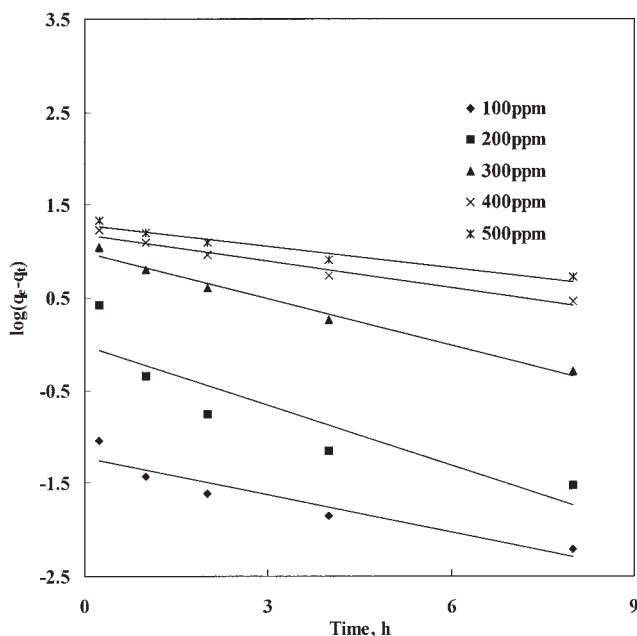
Figure 6. Lagergren plots for Cu adsorption on SNR.

Conditions: T: 333 K; S/L: 1/100; pH: 5.5; PS: 150–104 μm.

where ΔE_a is the activation energy (kJ mol^{-1}), T is the temperature (Kelvin), and R is the gas constant. From the plot of ln k_{ad} vs. $1/T \times 10^{-3}$ (Figure 7), the activation energy for the adsorption of 200 mg/L of Cu on 1 g of SNR was found to be 3.57 kJ mol^{-1}, indicating physical adsorption (Atkins, 1982), while showing the possibility of desorption and recovery of the adsorbed metal.

The equilibrium data were correlated by both Langmuir and Freundlich equations. The Langmuir treatment is based on the existence of an electronic double layer (Stumm and Morgan, 1970) on the charged adsorbent surface with the single species of copper as discussed earlier, with (1) negligible interaction between the adsorbed substances (Atkins, 1994), (2) constant heat of adsorption, and (3) no transmigration of adsorbate in the plane of the surface (Haggerty and Bowman, 1994). The linear form of the equation is expressed as

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \cdots \qquad (6)$$

where q_e represents the amount of copper adsorbed per unit weight of sample, C_e is the equilibrium concentration of the metal (mg/L), Q_0 is the adsorption capacity of the adsorbent, and b denotes an equilibrium constant related to the energy of

Table 3. Lagergren Constants for Cu Adsorption on SNR at Different Temperatures

	Rate constant, k_{ad} (min^{-1})		
Cu (ppm)	303 K	318 K	333 K
100	0.872	0.6731	0.3060
200	0.7619	0.6907	0.672
300	0.273	0.440	0.3829
400	—	0.2897	0.2204
500	0.2480	0.3254	0.1729
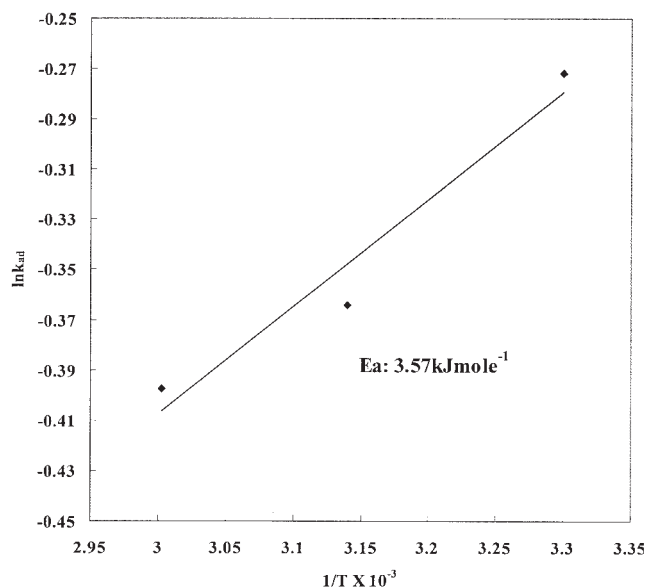
Figure 7. Arrhenius plot for Cu adsorption on SNR.

Conditions: S/L: 1/100; [Cu]: 200 ppm; pH: 5.5; PS: 150–104 μm.

adsorption. Linear plots of $1/q_e$ vs. $1/C_e$ (Figure 8) indicate that the adsorption obeyed the Langmuir isotherm model. The values of Q_0 and b, calculated from Figure 8, are listed in Table 4. An increase in the value of Q_0 with increasing temperature indicated the endothermic nature of the adsorption process, which may be attributed to the change in size of the pores of the adsorbent as well as to an increase in the number of adsorption sites resulting from the breaking of some internal bonds near the edge of the particles at higher temperatures. The apparent equilibrium constant K_a can be assumed to be a relative indicator of the SNR's affinity for copper (Prades et al., 1994) and
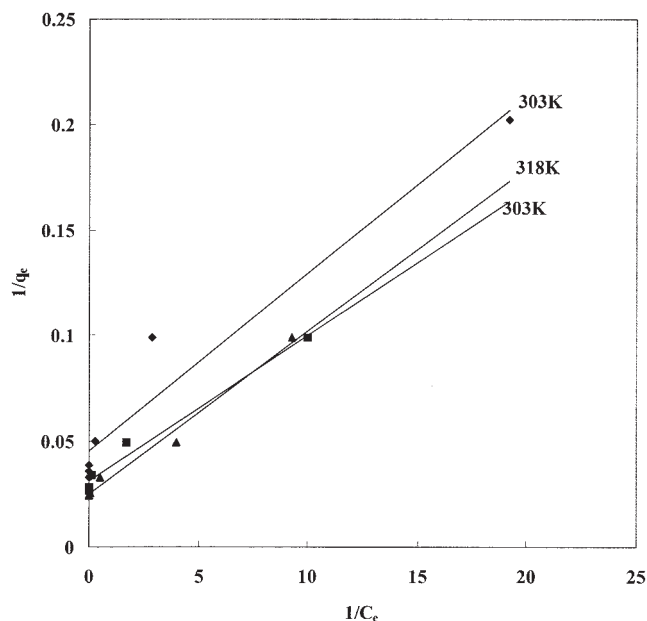
Figure 8. Langmuir isotherms for the adsorption of Cu on SNR at different temperatures.

Table 4. Langmuir and Freundlich Constants for Cu Adsorption on SNR

Temp. (K)	Langmuir Constants				Freundlich Constants		
	Q_0 (mg/g)	b	K_a	R^2	n	K_f	R^2
303	22.07	5.39	118.95	0.945	4.88	11.39	0.923
318	31.94	4.53	144.68	0.977	5.86	17.78	0.895
333	40.00	3.35	134.0	0.982	5.41	21.02	0.832

is calculated as a product of Langmuir parameters b and Q_0. Thus, the values of K_a (Table 4) showed a great affinity of SNR for copper ions in the solutions. The Langmuir adsorption capacity for SNR was found to be 22.07 mg Cu/g of SNR at 303 K, which was very close to the adsorption capacity under optimized experimental conditions (19.65 mg/g of SNR). Table 5 gives a comparative value of Q_0 for Cu adsorption on various adsorbents.

The data for copper adsorption on SNR were also fitted to the Freundlich model, expressed as

$$\log q_e = \log K_f + 1/n \log C_e \qquad (7)$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), and K_f and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively (McKay et al., 1993). Plots of $\log q_e$ vs. $\log C_e$ (Figure 9), with the slopes and the intercepts corresponding to the value of n and K_f (Table 4), showed that the adsorption of copper on SNR also followed the Freundlich isotherm.

Thermodynamic parameters (Gupta et al., 2000), calculated using Eqs. 8–10, are given in Table 6

$$\Delta G^\circ = -RT \ln b_1 \qquad (8)$$

$$\Delta H^\circ = -R\left(\frac{T_2 T_1}{T_2 - T_1}\right) \ln \frac{b_2}{b_1} \qquad (9)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \qquad (10)$$

where b_1 and b_2 are the Langmuir constants corresponding to the temperatures 303 and 318 K, respectively. Negative values of ΔG° (Table 6) indicated the feasibility of the process and spontaneous nature of adsorption. A similar trend was observed for Cr(VI) adsorption on BRS (Namasivayam and Yamuna, 1995) and copper adsorption on blast furnace slag (Gupta,

Table 5. Comparison of the Equilibrium Capacities of Copper on Various Adsorbents

Adsorbent	Q_0 (mg/g)	pH	Temperature	Reference
Zeolite	6.74	5.0	Room temp.	Panayotova
Coir-pith carbon	39.7	5.0	Room temp.	Namahsivayam et al.
Bentonite	13	n.a.	30 ± 2°C	Ke et al.
Blast-furnace slag	34	4.2	20°C	Dimitrova
Sea nodule	25.4	4.0	30 ± 2°C	Parida et al.
Activated charcoal	11	4–5	30°C	Sahoo et al.
SNR	22.07	5.5	30 ± 1°C	Present study
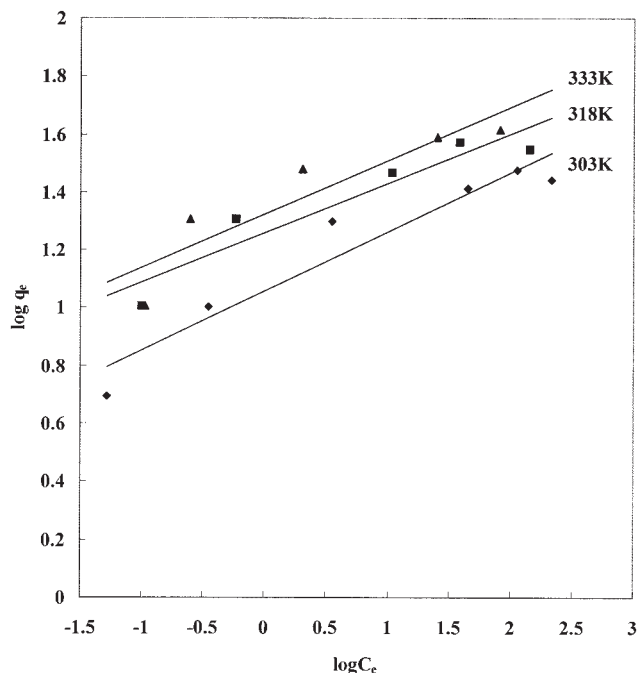
Figure 9. Freundlich isotherms for Cu adsorption on SNR at different temperatures.

1998). The positive value of ΔH° confirmed the endothermic adsorption of copper and the positive ΔS° suggested the affinity of the adsorbent and increased randomness at the solid–solution interface. In the adsorption of copper, the adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions, thus promoting the prevalence of randomness in the system (Namasivayam and Ranganathan, 1995)
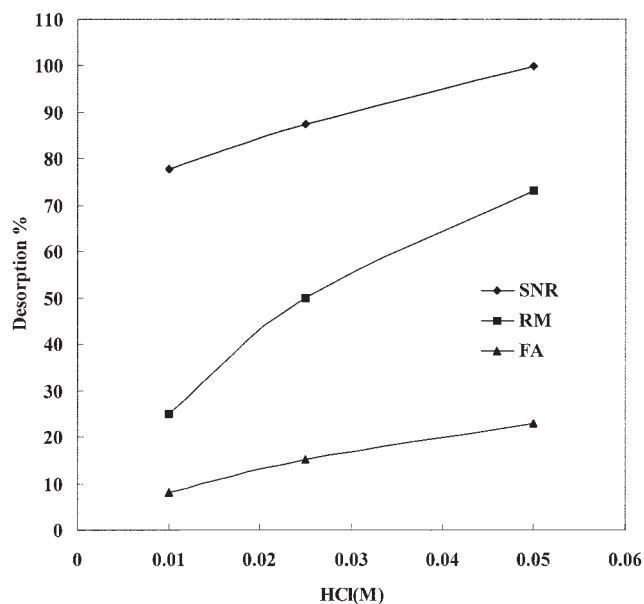
Desorption studies

Because adsorption of copper on SNR is pH dependent, its desorption is possible by controlling the pH of the eluent. Figure 10 shows the percentage desorption of copper from the sorbed SNR, RM, and FA. To desorb the adsorbed metal 2 g of the loaded material was treated with 0.01–0.05 M HCl for a reaction time of 4 h. The results presented in Figure 10 show the increase in desorption with increasing acid concentration. Almost complete copper desorption (99.9%) could be achieved with 0.05 M HCl from SNR, about 73% from RM, and about 23% from FA.

Conclusions

Sea nodule residue, red mud, and fly ash were examined for their potential use as low-cost materials for the removal of

Table 6. Thermodynamic Parameter for the Adsorption of Cu (200 mg/L) on SNR

Temperature (K)	$-\Delta G^\circ$ (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J mol^{-1} K^{-1})
303	4.24	19.49	49.14
318	3.99		
333	3.36		

Figure 10. Desorption of copper from loaded SNR, RM, FA by HCl.

Conditions: SNR: S/L: 1/100; [Cu]: 200 ppm. RM and FA: S/L: 1/50; [Cu]: 10 ppm; *T*: 303 K; PS: 150–104 μm.

copper from wastewaters. The results were very encouraging in the case of sea nodule residue. The presence of manganese oxides, iron hydroxide, and oxides/hydroxides of silicon, aluminum, and so forth were mainly responsible for the high adsorption property of SNR. The parameters under investigation showed a wide difference in the adsorption capacity of copper on all three adsorbents. Adsorbents exhibited variable response to different concentrations of copper in the aqueous feed. Thus SNR was very effective for a solution containing 200 mg/L copper, whereas red mud and fly ash worked well in very dilute solutions, containing 10–25 mg/L copper. Under optimized experimental conditions, the adsorption capacity for copper was 19.65 mg/g of SNR, 1.98 mg/g of fly ash, and 2.28 mg/g of red mud. Because the effect of temperature was marginal in red mud and fly ash, all the adsorption models were restricted to SNR. Data for copper adsorption on SNR were fitted to the Langmuir equation and the adsorption capacity (Q_0) for SNR was found to be 22.07 mg/g of adsorbent, which was higher than that of activated carbon (11 mg/g of adsorbent). The data were also fitted to the Freundlich model. Copper uptake followed first-order kinetics in SNR. The calculated thermodynamic parameters showed that the sorption was endothermic and spontaneous. The adsorption of copper may be explained by the electronic double layer on the charged SNR surface through formation of a surface complex involving $CuOH^+$ species at higher pH (5.5). Sea nodule residue can be used effectively for the removal of copper up to 200 mg/L, whereas red mud and fly ash can work well for copper concentrations up to 25 mg/L from wastewaters, reducing the copper level within the permissible limit for disposal according to ISI standards.

Acknowledgments

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