Kinetics of Copper Desorption from Regenerated Spent Bleaching Earth

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Abstract: Recent studies have shown that spent bleaching earth (SBE), a clayey waste from edible oil refineries, could be used to remove Cu from aqueous solutions. This could result in copper-laden material whose continual disposal into the environment may lead to bioaccumulation of toxic metal ions in the ecosystems. To assess the reversibility of copper uptake by spent bleaching earth, the kinetics of copper recovery from regenerated spent bleaching earth (RSBE) was studied on a batch basis in H_2SO_4, and $CaCl_2$. The acid showed superior desorption efficiency than competitive effects of Ca^{2+} ions. The initial solid-phase Cu concentration and desorption resident time were most important factors affecting copper release from RSBE. Up to 80% copper recovery was realized in 1-hour agitation period but longer contact time reduced the fraction of metal recovery from the adsorbent. The desorption process was consistent with the parabolic diffusion kinetics in both desorbants although it was also correlated to the first order and second order models in H_2SO_4 and to the modified Freundlich model in $CaCl_2$ respectively.

Key words: Copper Desorption Kinetics · Regenerated Spent Bleaching Earth

INTRODUCTION

Inorganic copper is extensively used as a broad-spectrum fungicide in coffee plantations in Kenya [1]. After application, copper accumulates in the upper 20 cm of soil resulting in high levels of copper contamination of water sources in these areas [2]. This poses serious threat to the surrounding ecosystems [3]. Excessive intake of Cu results in its accumulation in the liver and it is toxic to the ecosystem even at low contamination levels [4].

Use of low cost adsorbents to remove heavy metals from aqueous solutions has been extensively studied in the recent years [4-7]. Latest studies have demonstrated that spent bleaching earthextensively produced by edible oil processing industries in Nairobi and resulting in serious disposal problems [8], could be efficiently utilized as a low-cost adsorbent for the removal of Cu (II) ions from aqueous solutions [9]. Unfortunately these adsorptive methods concentrate metal ions in the materials. Continued utilization and environmental dumping of such contaminated adsorbents may lead to accrual of poisonous materials in the ecosystems and create point-source of Cu pollution in future [10].

The recovery of adsorbed metal ions from used up adsorbents would be important to avert such a discharge of toxic matter to the environment. Besides cleansing used-up adsorbents, desorption studies provide useful insights into the nature and reversibility of the adsorption process [11]. They are useful in predicting the consequences of incorporation of used-up adsorbents into the ecosystems [4] and therefore critical in the design of remediation strategies.

Desorption experiments often consist of column, batch or stirred flow washing of spent adsorbent with excess desorbing agent. Dilute acids [12], dilute salt solutions [13], bases [14] and complexing agents [6] have been proposed for extracting potentially available metals ions from soil adsorbents. The soil solution pH is often the main factor controlling solubility of heavy metals in soil solutions [11] whereas presence of other cations increases solubility of exchangeable metal ions from the soil surfaces by enhancing competition for surface complexation [14, 15]. Consequently, dilute acids and salt solutions have become particularly popular because they are often readily available, non-polluting and can be incorporated into the ecosystems with relative ease and safety [6].

Although adsorption studies on spent bleaching earth has attracted considerable interest in the recent past, the corresponding desorption studies are sparse. The current experiments were initiated to (i) study Cu desorption patterns and (ii) determine the suitability of different models for description of the kinetics of Cu recovery from heat regenerated spent bleaching earth. This paper reports on the results of such tests.

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Table 1: Different kinetic Models used in this study

Model	Equation	Parameters
First order kinetics [6]	$\ln q_t = \ln q - k_1 t$	k_1 = First order rate constant (s^{-1})
Second order kinetics [6]	$1/q_t = 1/q - k_2 t$	K_2, is second-order rate constant (g/mg/s)
Parabolic Diffusion [15]	$q_t = a_p + k_d t^{1/2}$	a_p = a constant and k_d = apparent diffusion rate constant (min^{-1})
Elovich kinetics [5]	$q_t = (1/\alpha_e)\ln(a_e\alpha_e) + (1/\alpha_e)\ln(t)$	a_e is a constant, $\acute{a}_e$ = Elovich initial rate constant
Modified Freundlich [15]	$q_t = k_f C_0 t^{1/m}$	k_f is rate coefficient (min^{-1}), m is a constant

[1]C_0 is initial Cu concentration (mg/L), q_t = desorbed Cu (mg/g) at time t (min), q = solid phase Cu concentration (mg/g)

MATERIALS AND METHODS

Preparations of Materials: Spent bleaching earth was collected at the point of its disposal from edible oil refineries in Industrial Area- Nairobi, Kenya. The material was air-dried and residual oil extracted by repeated washing in excess methyl ethyl ketone to a constant mass and until the extract liquor was clear. It was suction-filtered using 0.45 µm membrane and dried at room temperature for two days. The samples were heated in a muffle furnace for 12 hours at 643 K and designated regenerated spent bleaching earth (RSBE).

Adsorption Experiments: RSBE samples were treated with aqueous Cu(NO$_3$)$_2$ at 295±3 K and unbuffered pH of 3.2±0.3 by adding 10 g of the materials to 100 ml of adsorbate solutions containing 17, 34, 68, 136, 272 and 545 mgl^{-1} Cu(II) ions in 250 ml Erlen Meyer flasks according to the procedure described by Wambu *et al.* [9]. The resulting solid phases were designated Cu-contaminated RSBE and preserved for subsequent tests.

Desorption Experiments: Desorption studies were carried out at 295±3 K as follows: 10 g of Cu-contaminated RSBE samples were placed in 100 ml of CaCl$_2$ or 0.25 M H$_2$SO$_4$ respectively. They were agitated on a reciprocating shaker for one hour, centrifuged and desorbed Cu determined using ASDPV. Percentage Cu recovery was calculated as follows:

$$\%Desorption = \frac{C_f v}{10 w C_s} \qquad (1)$$

where, C_f is final copper concentration in the solution (mg/L), v is the volume of the solution used (ml), w is the mass of adsorbent (g) and C_s is initial concentration (mg/g) of copper in the solid phase of the adsorbent.

Desorption Kinetics: The desorption kinetic experiments were conducted by agitating 10 g of Cu-saturated RSBE samples in 100 ml of extractant solutions (0.25 M CaCl$_2$ and 0.25 M H$_2$SO$_4$) at 295±3 K. Aliquots of 10 ml were drawn from the mixture at selected time intervals of 0.1, 0.25, 0.5, 1.0, 2.0, 4.0 and 8.0 hours respectively. They were centrifuged and analyzed for desorbed Cu as in previous sections. To understand the resident time requirement of the metal desorption, five kinetics models (Table 1) [6] were applied to the desorption data and their respective parameters determined.

RESULTS AND DISCUSSION

Copper Adsorption: The shapes of adsorption isotherms depend on the dominant adsorption mechanism of the system. They can therefore be used to clarify the nature of the adsorption process [17]. The results of initial Cu uptake by RSBE are presented in Figure 1 and 2.

The amount of Cu uptake by RSBE increased linearly with the amount of Cu in solution (Fig. 1) from about 0.08 mg/g to saturation at about 2.8 mg/g when the initial Cu concentration was increased from of 17 to 272 mg/L. Figure 2 shows that Cu adsorption isotherm on RSBE may be classified as an L2 type of the Giles classification of solution adsorption isotherms [17]. Type L2 isotherms describe a system of average affinity of adsorbent for the adsorbate and little competition from the solvent for sorption sites. It means that adsorption of Cu proceeds until a monolayer is established and formation of further layers is not possible in this case [17]. The semblance of the isotherm to the S-type, based on the initial section of the curve being convex to the concentration axis at initial concentration below 68 mg/L indicates an apparent tendency for adsorbed copper species to associate at low surface concentration rather than remain as isolated units on the adsorbent surface [7]. This suggests that copper is adsorbed as ligand complexes or as hydrolysis products which enhance inter-particular interactions between the adsorbed particles through H-bonding.
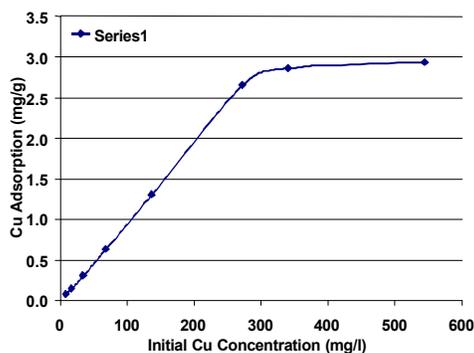
Fig. 1: Variation of Cu (II) ions removal from solution with change in initial adsorbate concentration (Experimental Conditions: 0-545 mg/L initial adsorbate concentration; Temperature of 295 ±3K; un-buffered initial pH of RSBE 3.2±0.3)
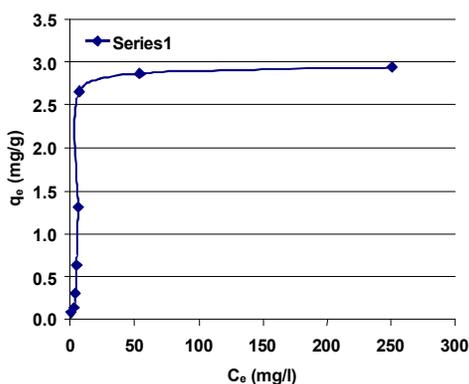

Fig. 2: Adsorption isotherm of Cu (II) ions on regenerated spent bleaching earth (RSBE) (Experimental Conditions: 0-545 mg/L initial adsorbate concentration; Temperature of 295 ±3K; un-buffered initial pH of RSBE 3.2±0.3)

Fig. 3: Desorption efficacies of various desorbing agents for copper recovery RSBE (Experimental Conditions: Extracting solutions 0.25 M H_2SO_4, 0.5 M HCl and 0.25 M $CaCl_2$ Temperature conditions of 295 ±3 K; un-buffered initial pH of RSBE 3.2±0.3)

Fig. 4: Effect of contact time on copper desorption from RSBE (Experimental Conditions: Extracting solutions 0.25 M H_2SO_4, 0.5 M HCl and 0.25 M $CaCl_2$; Temperature = 295±3 K; un-buffered initial pH of RSBE in water = 3.2±0.3)

Copper Desorption: Copper was adsorbed from aqueous $Cu(NO_3)_2$ solution at different initial concentrations between 0 and 445 mg/L prior to its desorption. From the initial results obtained for H_2SO_4 and $CaCl_2$, it was necessary to conduct Cu desorption tests in 0.5 M HCl to clarify the effect of H^+, Ca^{2+}, Cl^- and SO_4^{2-} in the desorption process. Figure 3 illustrates the desorption efficiencies of H_2SO_4, HCl and $CaCl_2$.

The dilute acids, 0.25 M H_2SO_4 and 0.5 M HCl had comparable effectiveness of copper desorption. Their copper desorption formed two pseudo-maxima of about 80% and 90% efficiencies at initial Cu concentration of 68 and 272 mg/L respectively. This indicates that Cu (II) ions were initially adsorbed on different types of sites and/or in different speciation in the clay. The efficacy of 0.25 M $CaCl_2$ to desorb Cu from
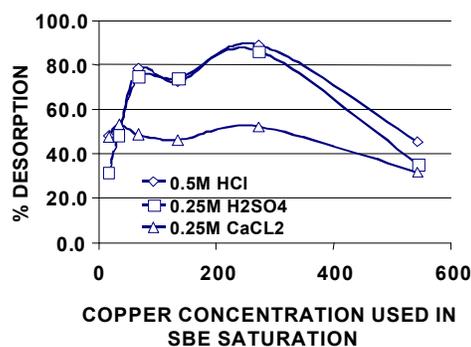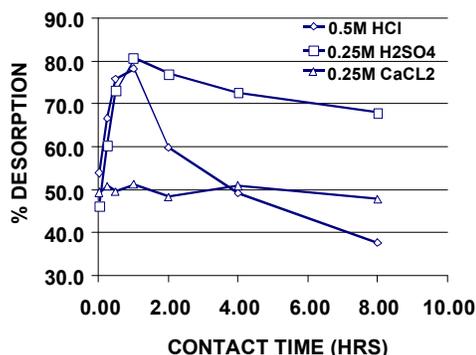
RSBE was much lower. Cao *et al*. [16] found that copper desorption from soil samples increased with decrease in pH of extracting solution. This may explain why the metal was more readily released from RSBE in acid desorbants than in the neutral salt solution. It also means that adsorbed copper could be in form of pH-susceptible speciation such as hydrolysis products. The inefficiency of calcium salts to recover adsorbed Cu from soil samples has been reported [14]. Casgrande *et al*. [18] using $CaCl_2$ reported that soil bound Cu did not show selectivity to Ca^{2+} ions. They concluded that adsorbed Cu was more strongly bound to the soil surfaces in a more complex process than a simple ion-exchange mechanism.

Copper Desorption Time Profile: Figure 4 illustrates the effect of change in contact time on release of Cu (II) ions by RSBE into an aqueous media.

The percentage of Cu desorption in acids increased rapidly and reached a maximum of 80% within an hour. It then declined steadily with agitation time. This gradual decline in desorbed copper has been reported in the literature [12]. The nature of the slow reactions that lead to this decrease is not well understood, but a number of studies have attributed it to migration of desorbed metal ions into inner adsorptive sites of the clay [13,17]. McBride [19], on the other hand, has pointed out that such migratory mechanisms would be very slow. This is because in presence of ligands, metal ions form ligand complexes often with larger spatial radius and greater viscous drag in solution than the corresponding hexaaquo species.

The larger radius of such complexes would slow down Cu diffusion through the aqueous matrix and into adsorbent mesopores. This drop in acid desorbed metal (which was notably lacking in $CaCl_2$ (Fig. 4) despite $CaCl_2$ having similar ligand as HCl) could therefore be attributed to ligand-aided re-adsorption of aqueous Cu complexes onto protonated surface groups in RSBE. The apparent lack of these re-adsorptions in $CaCl_2$ suggests that ion-exchange reaction between Cu^{2+} and H^+ ions could be the underpinning process in Cu release from RSBE in acidic desorbants.

The rapid re-adsorption of the metal ions results from this protonation of the adsorbent surface which increases the positive surface charge density and the re-adsorption potential of negative-ligand enclosed Cu species. Barrow [20] indicated that such re-adsorption may be followed by slow transformations such as surface precipitation [15] that would immobilize re-adsorbed copper in the adsorbent. This appears to be the case in the current study. As would be expected, Cu-Chloride complexes with smaller spatial radius adsorb more rapidly and afford closer packing on adsorbent than more sterically hindered sulfate species. Hence, faster and greater re-adsorption of desorbed Cu in HCl than in H_2SO_4 (Fig. 4).

Similar discrepancy in soil Cu desorption by different mineral acids has been reported in the literature [12]. In general, Cu desorption efficiency in acid media increased in presence of a more sterically hindered ligand. These results indicate that optimized contact time and ligand effects would afford higher efficiency of copper removal and that extended time of contact would result in more stable forms of Cu-RSBE complexes in the adsorbent surface limiting the desorption efficiency of the desorbants.

Copper Desorption Kinetics: Kinetic models are often used for qualitative comparison of adsorption-desorption data [5]. Time and again, different models fit the same set of data [4] because each model is based on independent kinetic assumptions for the different chemical and physical properties of the system to which it applies. Five kinetic models (Table 1) were used to investigate the efficacy and Cu desorption trends of RSBE in 0.25 M H_2SO and 0.25 M $CaCl_2$. The kinetics of Cu release in HCl was not tested. Figure 5 and Table 2 shows the resulting linear plots and their corresponding kinetic parameters of different models as employed in this work respectively.

Table 2: Values of copper desorption kinetic parameters of various kinetic models used in this study

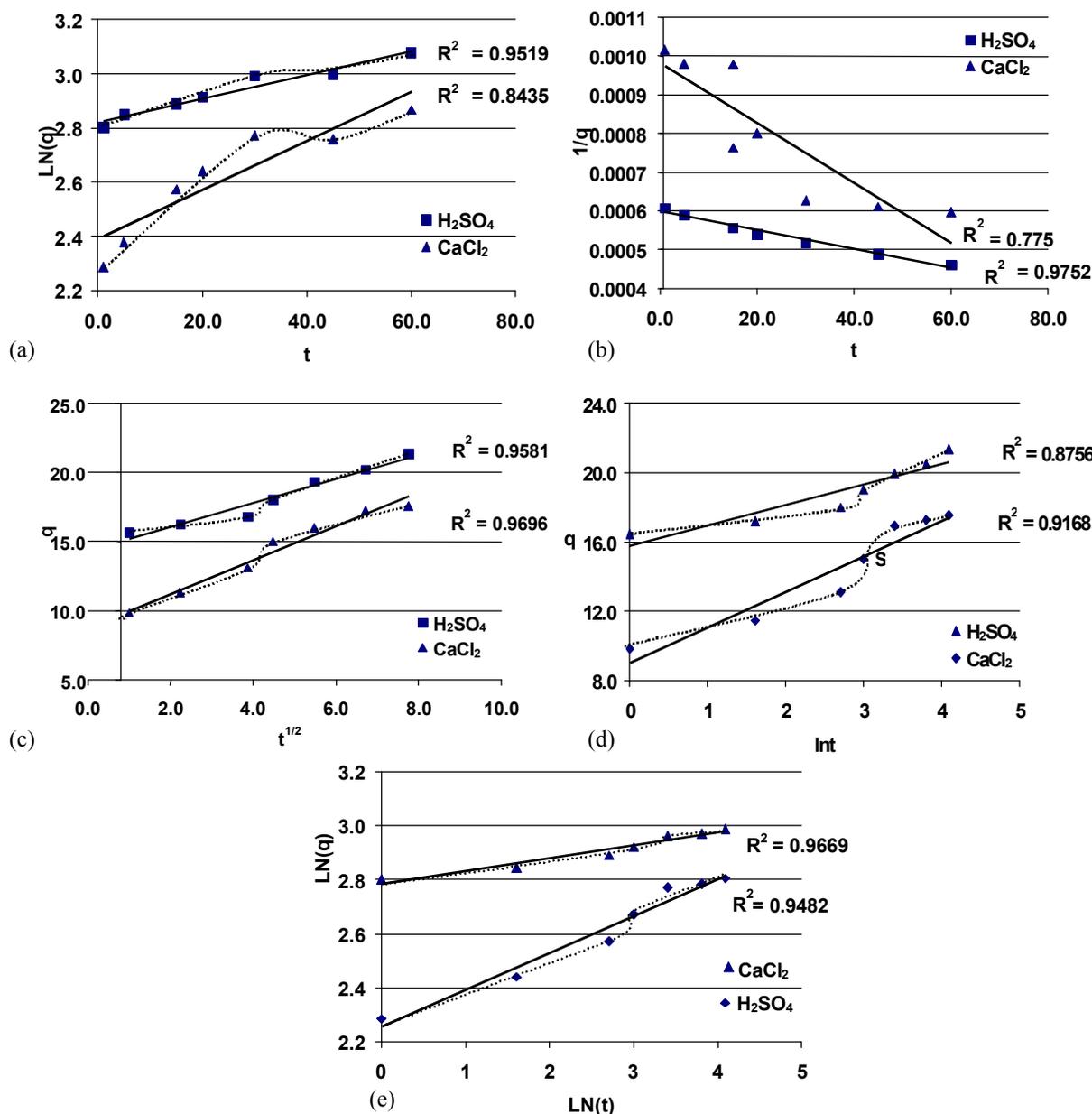| First Order Model		
Extracting Solution	k_1	R^2
H_2SO_4	0.0044	0.9519
$CaCl_2$	0.0093	0.8435
Second Order		
	k_2	R^2
H_2SO_4	2.57×10^{-6}	0.9752
$CaCl_2$	7.24×10^{-6}	0.7714
Parabolic Diffusion Model		
	a_p	k_d	R^2
H_2SO_4	14.9	0.8791	0.9581
$CaCl_2$	9.7	1.2261	0.9696
Elovich Kinetics Model		
	a_e	$á_e$	R^2
H_2SO_4	8.0×10^5	0.8506	0.8756
$CaCl_2$	3.1×10^2	0.4883	0.9186
Modified Freundlich Model		
	k_f	m_f	R^2
H_2SO_4	9.5574	0.0473	0.9482
$CaCl_2$	16.1965	0.1358	0.9669

Fig. 5: Test of the (a) First Order, (b) the second Order, (c) the parabolic Diffusion, (d) the Elovich and (e) the Modified Freundlich Equation for Cu recovery from RSBE in $CaCl_2$ and H_2SO_4 at $295\pm3K$

Desorption data in H_2SO_4 was correlated to the kinetics models in the order; second order > first order > parabolic diffusion > modified Freundlich > Elovich. In $CaCl_2$ the order followed; parabolic diffusion > modified Freundlich > Elovich > first order > second order. Kinetics of copper recovery was best simulated by one-constant models (First order and Second order) in H_2SO_4 and by two-constant model (Modified Freundlich) in $CaCl_2$. The parabolic diffusion equation

fitted copper recoveries with $R^2 = 0.96$ in both H_2SO_4 and $CaCl_2$. This indicates that RSBE copper desorption from RSBE (in acid and in neutral salt solutions) could be described by this model. The apparent parabolic diffusion rate constant k_d and the coefficient of determination R^2 were higher in $CaCl_2$ than in H_2SO_4. This suggests that whereas diffusion processes could be rate determining in both cases, they were more significant in $CaCl_2$ than in H_2SO_4 [15].

Copper recovery from RSBE in H_2SO_4 was also sufficiently consistent with both First Order ($R^2 = 0.9519$) and Second Order ($R^2 = 0.9752$) equations. Conformity of experimental data to the First order model indicates that the rate of Cu release in H_2SO_4 is proportional to the concentration of exchangeable Cu in the adsorbent surface and that film diffusion and break down of the adsorbate-adsorbent complex could be rate determining steps [15].

The second order kinetics is based on the assumption that the rate limiting step could be chemical in nature involving valence sharing or exchange of electrons. The second order correlation coefficients of the desorption data indicate that surface reactions could be more significant in recovery of RSBE adsorbed Cu in acid than in the salt solution. Such surface interactions depend on migration of desorbant particles in solution to the adsorbent surface and so, H+ ions with higher solution diffusivity than Ca+ ions showed greater influence on the reaction kinetics than the latter ions.

In $CaCl_2$, copper recovery was correlated to both the parabolic diffusion and modified Freundlich kinetics with goodness of fit, $R^2 > 0.966$. The modified Freundlich model has been used to describe an initially rapid desorption reaction and decreasing rate of reaction at prolonged time [15]. It suggests that the energy of the process decreases exponentially with depletion of adsorbed particles from the soil surface. Correlation of desorption data to the modified Freundlich model means that copper release from RSBE in these desorbants is characterized by an initial fast reaction which decreases with time. This may imply that the adsorptive surface of RSBE consisted of heterogeneous patches with different adsorption energies and that RSBE copper desorption in $CaCl_2$ could be more surface concentration-dependent in $CaCl_2$ than in H_2SO_4.

In general, copper desorption in H_2SO_4 was best described by second order kinetics whereas in $CaCl_2$ the parabolic diffusion kinetics were more significant. The Elovich equation did not sufficiently describe Cu release f rom RSBE in both desorbants (R2 < 0.92 in both acidic and salt desorbants). However, in all models, kinetic linear plots showed discontinuity in the slopes (dotted lines Fig. 5) resulting in lower coefficients of determination than those reported for similar systems [6, 23]. This suggests that copper desorbed from a heterogeneous surface with two distinct kinds of adsorptive sites which have different adsorptive properties.

CONCLUSSION

Copper was more effectively desorbed from RSBE in 0.25M H_2SO_4 (as well as 0.5 M HCl) than in 0.25 M $CaCl_2$. The Cu desorption patterns in 0.25 M H_2SO_4 and the kinetic linear plots for various models indicated that Cu desorbed from a heterogeneous surface consisting two kinds of sites resulting in two distinct desorption pseudo-maxima. It seems that surface reactions involving H+ was most significant in Cu recovery. The concentration in the solid phase and the contact time were the two most important variables affecting copper desorption from RSBE. One-hour equilibration was adequate for > 80% copper recovery form RSBE in dilute H_2SO_4. It was plain that prolonged contact time above an hour reduced the efficacy of the desorbants causing re-adsorption of metal ions into the material. The results indicate that Cu (II) ions can significantly be recovered from the material after adsorption process before the material is ultimately disposed of into the environment. This is important to ensure that regenerated spent bleaching could be used to removed copper metal from water sources without the threat of the adsorbent becoming another point source of copper pollution of the environment.

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