



Regeneration of spent bleaching earth and its adsorption of copper (II) ions from aqueous solutions

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ABSTRACT

This study was designed to provide a comprehensive investigation into heat and acid reactivation of spent bleaching earth (SBE) and adsorption of Cu(II) ions from aqueous solutions. Heat treatment was the master variable in SBE regeneration. Dilute acid treatment did not constitute an effective SBE reactivation protocol for this purpose. Solvent extraction of residual oil using excess methylethyl ketone followed by heating at 370 °C was, therefore, the most effective reactivation procedure. Highly adsorptive materials with >98% removal of Cu(II) ions from solution were obtained. Thus, >80% Cu adsorption was reversible at SBE silicate sites because of their higher proportion in the adsorbent.

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1. Introduction

Adsorption technology has gained a lot of popularity in the recent years over traditional methods such as precipitation, coagulation, ion exchange; membrane technology and electro-dialysis in wastewater trace metal decontamination (Igwe et al., 2008; Tariq et al., 2009). This is because of its high aqueous metal removal efficiencies at low contamination levels among other merits. The main drawback of these adsorptive methods has been the high cost of conventional adsorbents such as activated carbons. Consequently, this field has attracted the interest of many researchers in an attempt to develop low cost adsorbents so as to make adsorption technology more affordable and accessible to small industries such as found in developing countries. Many investigations have involved low cost and waste material adsorbents such as biomass, industrial waste sludge and clay based geo-materials (Hefne et al., 2008). Use of industrial waste materials has become particularly attractive because of extra advantages such as waste elimination and cost reduction on the part of industrialists (Tumin et al., 2008).

The bulky nature, high residual oil content and increasing global production of spent bleaching earth (SBE), a clayey waste material from edible oil processing industries, pose major disposal problems (Weng et al., 2007). As a result, its regeneration and reuse has produced considerable interest among researchers in recent years. Heat treatment (Tsai et al., 2002), solvent cleansing (Folletto et al., 2002) and chemical treatment using acids (Low et al., 2003), bases (Mana et al., 2008) and

salt solutions (Tsai et al., 2003) have been used in SBE regeneration for adsorption of various adsorbates. The method of regeneration depends on the ultimate use for which the material is prepared (Folletto et al., 2002) because properties and performance of clay adsorbents depend on their mode of preparation (Hefne et al., 2008). In recent studies, Weng et al. (2007) who employed a method that involved washing with steam water to regenerate SBE for copper adsorption noted that alternative regeneration protocol could be explored to enhance its performance.

In this study, we report on alternative procedures of reactivation of SBE for adsorption of Cu(II) ions from aqueous solutions. Copper is one of the most widely used heavy metals. It is extensively discharged into the environment e.g. through several aqueous industrial waste flows (Tumin et al., 2008) and agro-chemicals application (Leeper, 1978). Because of its known environmental persistence, toxicity and non-biodegradability, the presence of copper in the environment continue to raise grave toxicological concerns around the world (Wong et al., 2000). Water and wastewater Cu remediation is for that reason of fundamental significance. The well known affinity of Cu(II) ions for soil and soil fractions adsorbents (Ulmuna et al., 2003) makes them an apt adsorbent for exploring new soil adsorbents.

2. Materials and methods

2.1. Preparation of the material

Spent bleaching earth (SBE) was collected at the point of disposal from edible oil processing industries in Industrial Area—near Nairobi, Kenya. It was air-dried and the residual oil was extracted with excess methylethyl ketone according to the procedure used by Folletto et al.

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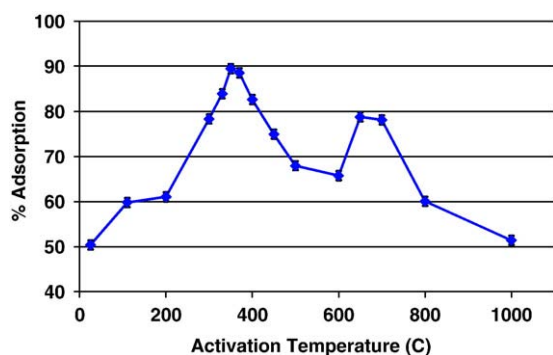


Fig. 1. Reactivation temperature and SBE-copper adsorption from 340 mg/L Cu(II) concentrations.

(2002). The material was then designated as solvent de-oiled SBE. Sub-samples of the solvent de-oiled SBE were separately heated in a muffle furnace for 12 h at pre-set temperatures of 50, 110, 200, 300, 330, 350, 370, 400, 450, 500, 600, 650, 700, 800, and 1000 °C respectively. Each of these samples was tested for Cu(II) ions uptake. The sub-sample with highest copper removal efficiency was designated heat regenerated spent bleaching earth (HRSBE).

Portions of solvent de-oiled SBE and HRSBE were independently stirred for 2 h in excess HCl (at 50 g per 200 mL) containing 0.0, 0.25, 0.5, 1.0, and 2.0 M concentrations. They were suction-filtered and washed thoroughly with excess distilled water before drying at 110 °C over-night. Other HRSBE sub-samples were exposed to a constant concentration of 1 M HCl for varying time intervals ranging from a half an hour to 12 h. All the sub-samples were tested for copper ion uptake and the results compared with those of solvent de-oiled and heat regenerated SBE.

2.2. Surface and chemical characterization of RSBE

Elemental analysis of the regenerated material was determined according to the method used by Wachira et al. (2005) and the amount of oxidizable organic matter determined according to the method described by Wilson (1994). The methodologies for evaluation of point of zero net charge (PZNC) and the cation exchange capacity (CEC) were adopted from Khoo et al. (1979) and Hesse (1971), respectively.

2.3. Initial tests for copper uptake from aqueous solution

Cu(II) uptake efficiency tests of pretreated samples were conducted at unbuffered initial pH of 3.3 ± 0.2 and ambient temperature of 22 ± 3 °C. Triplicate 1 g samples of the adsorbent were agitated for 12 h in 10 mL aliquots of solution containing 340 mg/L Cu(II) ions in 25 mL round-bottomed flasks on a reciprocating shaker. The supernatant solution was separated by centrifugation and its copper concentrations

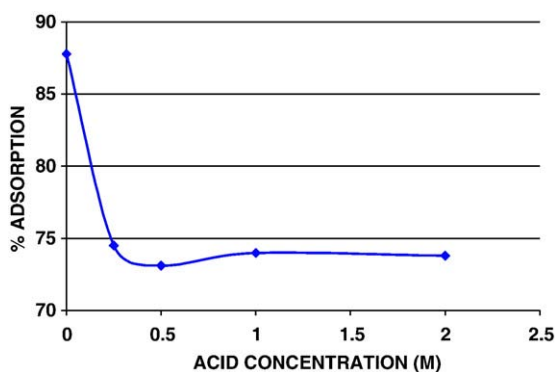


Fig. 2. Effect of concentration of hydrochloric acid at two-hour contact time on copper adsorption by SBE.

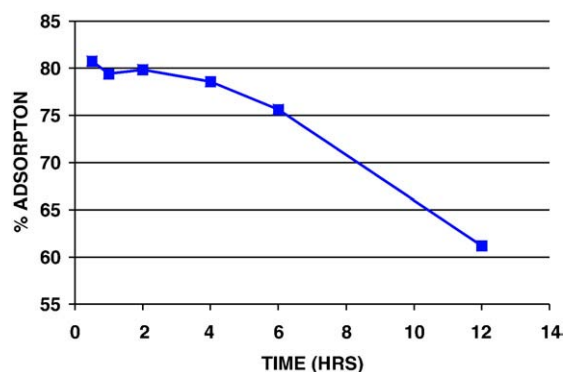


Fig. 3. SBE contact time in 1 M HCl and Cu²⁺ adsorption from aqueous solution.

determined by Anodic stripping differential pulse voltammetry (ASDPV) using an EG & G Princeton Applied Research Model 264 Polarographic Analyzer/Stripping Voltammeter in 0.1 M KCl. The Instrumental settings were adopted from Bard and Faulker (1980), and Hoyle et al. (1978). The copper uptake Q_{eq} (mg kg⁻¹) and percentage of copper removal were calculated according to the formula used by Tariq et al. (2009) and the sample with overall highest aqueous copper removal efficiency designated regenerated spent bleaching earth (RSBE).

2.4. Adsorption equilibrium analysis

Adsorption equilibrium studies were conducted as in Section 2.3 using constant contact time of 8 h (considering that in the previous tests, the initial equilibrium was established between 4 and 6 h) at varying initial Cu(II) concentration range of 0–544 mg/L and the adsorption characteristics evaluated using the Freundlich isotherm.

2.5. Desorption tests

Sub-samples of RSBE were reacted with Cu²⁺ at different initial concentrations as in Section 2.4. The copper concentration in solid phase was calculated as in Section 2.3 correcting for closed solution in the adsorbents. Desorption studies were then carried out by 1-hour agitation of 10 g of Cu-contaminated RSBE samples in 100 mL of extractant solution (0.5 M HCl, 0.25 M CaCl₂ or 0.25 M H₂SO₄ respectively). They were centrifuged and desorbed copper ions in the supernatant solution were determined by ASDPV. The percentage recovery of adsorbed Cu was calculated as shown below:

$$\% \text{ desorption} = C_d v / 10wC_s \quad (1)$$

where, C_d is desorbed copper concentration in the solution (mg/L), v is the volume of the solution used (mL); w is the mass of adsorbent

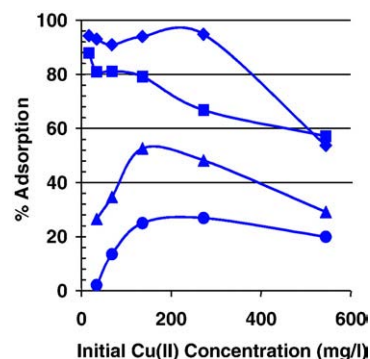


Fig. 4. Comparison of solvent, heat and dilute acid reactivation efficiency. Heat-treated SBE (◆), solvent de-oiled SBE (■), heat and acid treated BSE (▲) and acid treated SBE (●).

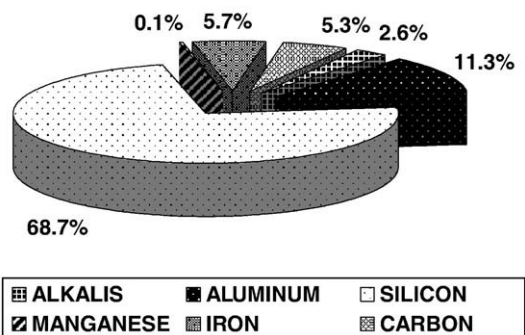


Fig. 5. Chemical composition of RSBE.

(kg) and C_s is initial concentration (mg kg^{-1}) of Cu in the solid phase of the adsorbent.

3. Results and discussion

3.1. Heat treatment of SBE

The results of these tests are shown in Fig. 1. The adsorption of Cu^{2+} by RSBE increased with reactivation temperatures up to between 350 and 370 °C for which about 90% of copper ions were adsorbed. The activity of the material then dropped to 65% copper uptake between 500 and 600 °C before rising to another pseudo-maximum between 650 and 700 °C.

The initial increase in the activity of the material when heated from room temperatures to 110 °C through 200 °C is attributable to the dehydration of physically adsorbed water and volatilization of low boiling point organic matter (OM) from the adsorbent opening it up for Cu(II) adsorption. Steady increase of the adsorption between 200 and 370 °C is due to heat-induced changes on surface functional groups in the materials and combustion of adsorbed organic matter. Development of new surface sites due to structural transformations and re-opening of existing ones increases the surface activity of the adsorbent. Specific heat-induced structural changes that occur in clay materials under thermo-treatments have been extensively reviewed in literature (Iler, 1979; Cook, 1986).

Since production of high temperatures is costly, heat treatment of SBE within 350–370 °C suffice to reactivate SBE for substantial removal of copper (II) ions from aqueous solutions. Low adsorption activity of the material dried below 50 °C indicates that solvent extraction of residual oil alone does not constitute effective reactivation of the materials for copper adsorption.

3.2. Effects of acid activation of SBE

Acid activation rapidly decreased the activity of the adsorbent from about 88% copper removal to about 74% when the acid concentration was increased from 0 to 0.5 M. (Fig. 2).

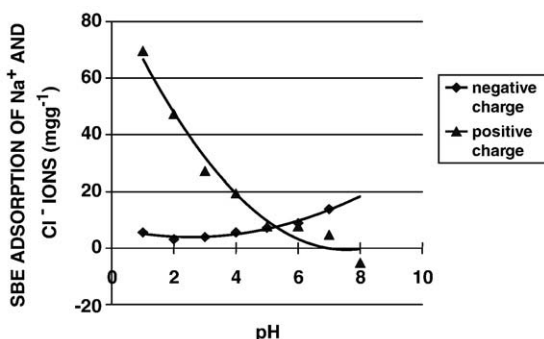


Fig. 6. pH dependence of RSBE surface charge showing the point of zero net charge (PZNC).

Table 1
Freundlich isotherm SBE–copper adsorption constants.

Sample activation temperature (°C)	Freundlich constant		
	K_F	n	R^2
25	100.70	1.6513	0.9819
110	411.56	1.9775	0.9003
300	29.89	0.8649	0.8423
370	5.92	0.3192	0.9883
400	132.35	1.6918	0.8883
700	320.38	1.9103	0.8853
800	218.25	2.2659	0.9221

Saturation with protons reduced the adsorption of copper ions strongly. When the time of SBE exposure to a constant concentration of $\text{HCl}_{(\text{aq})}$ was increased beyond 2 h, the adsorption activity rapidly decreased (Fig. 3).

This indicates that high acid concentrations ($\geq 0.5 \text{ M H}^+$) at prolonged time of exposure ($> 2 \text{ h}$) attacked the clay mineral structure (Onal et al., 2002). Acid treatment does not therefore constitute an effective SBE reactivation for Cu(II) uptake.

3.3. Comparison of reactivation efficiencies of various SBE treatment procedures

SBE reactivation efficiencies by solvent oil extraction, heat treatment and dilute acid treatment were compared across different concentrations of copper (II) ions in solution (Fig. 4). The activity of heat-treated material initially decreased with increasing copper concentration then rose to a maximum $> 98\%$ between 136 and 272 mg/L of initial Cu(II) ions. The trend of Cu adsorption on solvent de-oiled materials was similar except that it showed saturation at lower concentrations. For acid treated samples (before and after heat treatment), the copper uptake increased with concentration to a maximum.

Solvent oil extraction followed by heat treatment at 350–370 °C was the most effective SBE reactivation protocol for copper uptake. Highly adsorptive materials with up to 98% uptake (Fig. 4) at 272 mg/L Cu(II) ions were obtained. These materials were designated regenerated spent bleaching earth (RSBE).

3.4. Chemical compositions

Fig. 5 shows the results of X-ray fluorescence analysis of RSBE.

The average residual oil content of the SBE was 25% m/m. RSBE was found to be predominantly composed of aluminosilicates. This indicates that the variable charge sites provided by aluminum (hydr) oxides and the silicates play an important role in influencing the adsorption process. Such interactions may be the dominant mechanism in the copper adsorption process on RSBE.

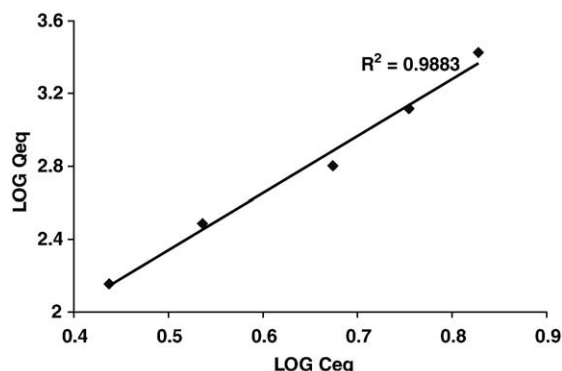


Fig. 7. Freundlich isotherm RSBE Cu(II) adsorption data fit.

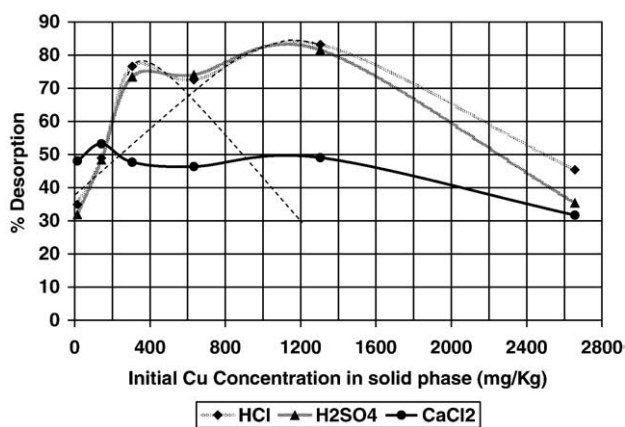


Fig. 8. Reversibility of Cu(II) adsorption onto RSBE in different extractant solutions.

3.5. Surface properties

PZNC and CEC of RSBE were estimated by saturation of the materials with Cl^- and Na^+ ions, respectively. Fig. 6 shows the variation of positive (adsorption of Cl^- ions) and negative (adsorption of Na^+ ions) surface charges on SBE surface with pH.

The PZNC was above the ambient surface pH of the material (3.3 ± 0.2). RSBE was therefore acidic with net positive surface charge due to the protons (Naidu et al., 1997). The CEC was determined as 6000 mg kg^{-1} of Na^+ equivalents; which was greater than the net surface negative charge. Therefore, cation adsorption onto RSBE must involve additional mechanisms such as inner sphere complex-formation, multilayer surface adsorptions and complexation with neutral groups on the surface of the material to account for the additional cation retention capacity.

3.6. Adsorption isotherm

The copper adsorption data was fitted to the linear Freundlich isotherm:

$$\log Q_{\text{eq}} = \log K_{\text{F}} + 1/n \log C_{\text{eq}} \quad (3)$$

where, Q_{eq} is the equilibrium concentration (mg kg^{-1}) of adsorbate in adsorbent, C_{eq} = equilibrium concentration (mg L^{-1}) of adsorbate in solution, and K_{F} and n are constants (Table 1, Fig. 7).

Both the affinity coefficient, K_{F} and the intensity parameter n indicated effective binding of Cu(II) species (Namasivayam and Yamuna, 1992). Saturation with Cu(II) ions is attained rapidly because of the high affinity ($K_{\text{F}} = 5\text{--}410 \text{ mg kg}^{-1}$) for the metal ions (Tariq et al., 2009). As Freundlich equation implies heterogeneity in the adsorbent surface, these results indicate that SBE heat treatment induces heterogeneous adsorption patches in the material.

3.7. Copper desorption from RSBE

The reversibility of copper adsorption onto RSBE was investigated at $22 \pm 3 \text{ }^\circ\text{C}$ (Fig. 8).

Recovery of adsorbed Cu(II) increased with increasing initial concentration of copper ions on the adsorbent and formed two pseudo-maxima. The first maximum was at about 300 mg kg^{-1} for dilute acids and at about 140 mg/g for CaCl_2 extraction while the second appeared within 1300 mg kg^{-1} in all the extractants. Above this concentration, recovery of Cu(II) ions declined steadily suggesting possible immobilization of the copper ions inside the mesoporous structure of the adsorbent. The two pseudo-maxima suggest that Cu (II) was initially adsorbed at different sites (and/or in different speciation). When the peaks were extrapolated (dashed lines) and the

area under each peak (representing relative Cu(II) recovery) calculated by counting-the-squares method, their relative proportions were found to be 24.8% and 75.2% respectively (for H_2SO_4). As can be seen from Fig. 5, proportions of desorbed Cu^{2+} in each peak (Fig. 8) match the extent of non-silicate and aluminosilicate components in the material. Apparently, $\approx 75\%$ Cu^{2+} was adsorbed at low affinity silicate sites which form the bulk of RSBE and a smaller proportion ($\approx 25\%$) was adsorbed at non-silicate sites provided by Fe_2O_3 , carbon and other components. At very low initial aqueous Cu^{2+} concentrations ($< 17 \text{ mg/L}$), close to 100% desorption occurred in the first peak alone, this indicated that copper ions were preferentially adsorbed at high affinity non-silicate sites before they filled up the silicate sites.

The dilute acids, 0.25 M H_2SO_4 and 0.5 M HCl gave comparable efficiencies of copper desorption but Cu desorption by 0.25 M CaCl_2 was much smaller. The proton exchange mechanisms were therefore more effective in Cu recovery from RSBE than the competitive effects of Ca^{2+} ions. Over 80% Cu was recovered from RSBE using acids. Thus, the largest part of Cu adsorption occurred reversibly at the SBE silicate sites because of their higher proportion in the adsorbent. This indicates that there is limited immobilization of Cu into the adsorbent pores.

4. Summary

Solvent residual oil extraction followed by heat treatment at $370 \text{ }^\circ\text{C}$ was the most effective SBE regenerating protocol for copper adsorption. The materials so obtained had large cation exchange capacities of 6000 mg kg^{-1} of Na^+ ions equivalents favorable for cation uptake. This value was higher than the net negative surface charge of RSBE indicating that additional copper adsorption mechanisms play a role in addition to electrostatic interaction. The pH of the dispersed RSBE was below PZNC indicating the net positive surface charge of this material. RSBE adsorption data were fitted by the Freundlich model. Desorption studies showed that Cu(II) ions preferentially adsorb at the high affinity non-silicate sites in RSBE but the silicate sites play a more significant role in Cu removal due to their higher proportion in the material. Consequently, most of adsorbed Cu ions were recovered indicating limited immobilization of Cu in the adsorbent pores. Thus, solvent residual oil extraction followed by heat reactivation is an effective alternative SBE regeneration protocol for removal of Cu(II) ions from aqueous solutions.

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