

KINETICS AND THERMODYNAMICS OF AQUEOUS Cu(II) ADSORPTION ON HEAT REGENERATED SPENT BLEACHING EARTH

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ABSTRACT. This study investigated the kinetics and thermodynamics of copper(II) removal from aqueous solutions using spent bleaching earth (SBE). The spent bleaching earth, a waste material from edible oil processing industries, was reactivated by heat treatment at 370 °C after residual oil extraction in excess methyl-ethyl ketone. Copper adsorption tests were carried out at room temperature (22±3 °C) using 5.4 x 10⁻³ M metal concentrations. More than 70% metal removal was recorded in the first four hours although adsorption continued to rise to within 90% at 42 hours. The pH, adsorbent dosage and initial concentrations were master variables affecting RSBE adsorption of Cu(II) ions. The adsorption equilibrium was adequately described by the Dubinin-Radushkevich (D-R) and the Temkin isotherms and the maximum sorption capacity derived from the D-R isotherm was compared with those of some other low cost adsorbents. The adsorption process was found to follow Lagergren Pseudo-second order kinetics complimented by intra-particle diffusion kinetics at prolonged periods of equilibration. Based on the D-R isotherm adsorption energy and the thermodynamic adsorption free energy ΔG, it was suggested that the process is spontaneous and based on electrostatic interactions between the metal ions and exposed active sites in the adsorbent surface.

KEY WORDS: Kinetics, Thermodynamics, Copper adsorption isotherms, Spent bleaching earth

INTRODUCTION

The removal of toxic heavy metals from aqueous solutions by sorption has been extensively studied in recent years. The common adsorbents used include activated carbons, synthetic resins, activated alumina, and silica [1]. Activated carbons, alumina and silica are dear to produce and regenerate for reuse. On the other hand, many synthetic resins are resistant to biodegradation and pose serious disposal problems. Exploitations have therefore; recently focused on the use of non-conventional agricultural by-products and other naturally derived waste geo-material adsorbents because they are easily obtainable, relatively low-priced and can easily be incorporated in the ecosystems if they are appropriately cleansed of the adsorbates. Examples of low cost adsorbents which have been used in the adsorptive removal of heavy metals from aqueous solutions in the recent past include dried pine fruits [2], magnetite [3], natural and treated bentonites [4], diaspore [5], and modified and unmodified coconut fiber [6].

Low-cost clay adsorbents have become particularly attractive [7] due to their availability, ease of preparation and stability in a wide range of conditions compared to other adsorbents [8]. Bleaching earth, a layer silicate mineral, consists mainly of montmorillonites and has the capacity to remove colored substances and undesirable residues from crude vegetable oil. The earth is used to bleach edible oil in the refining process. The spent bleaching earth (SBE) which contains 25-35% w/w residual oil is disposed off in landfills without further treatment. Due to its bulkiness, disposal of SBE poses serious handling problems. Other than the potential leaching of the fatty materials into soil and water sources, it can get oxidized resulting in spontaneous auto-ignition, and it emits foul smell [9]. Thus, due to the increasingly high cost of disposal and the ensuing environmental concerns, it is desirable to reuse the material for other purposes instead. Alternative utilizations include cementation of furnaces, addition to animal feeds, utilization in brick and tile industry and in biogas digesters [10].

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On the other hand, copper is considered the most versatile industrial metallic element after iron and its vast usage has created an extensive pollution interface between man and environment. In particular, emerging reports on copper contamination of water sources [11] and marine products [12, 13] among upcoming African states are raising serious public health concerns in the region. As a result, removal of labile copper from aqueous streams has attracted a lot of research interest in the recent past [14-16]. The present work assess the potential of heat regenerated spent bleaching earth; a low-cost clay waste material from an edible oil refinery in Industrial Area, Nairobi, Kenya for the removal of copper ions from aqueous solutions. The annual production of the SBE in this company alone is about 2500 tonnes and no use of this waste material has been found. The kinetics and equilibrium properties of the sorption process as well as the influence of selected parameters were evaluated in addition to the equilibrium sorption capacity, the mechanism of sorption, the equilibrium rate constants, the order of the reaction and the standard free energy for the reaction was established.

EXPERIMENTAL

Preparation of materials

Spent bleaching earth (SBE) was collected at the point of disposal from edible oil refinery in Industrial Area – Nairobi, Kenya. It was air-dried and the residual oil extracted using methyl-ethyl ketone [17]. The material was left to dry at room temperature then reactivated for 12 hours by heat treatment at 370 °C in a muffle furnace. The resulting materials were designated regenerated spent bleaching earth (RSBE).

Batch sorption experiments

One-gram samples of RSBE were mixed with 10 mL aliquots of adsorbate solution containing 5.4×10^{-3} M Cu(II) ions. To determine optimum time of contact, the mixture was agitated on a reciprocating shaker for 1/4, 1/2, 1, 2, 4, 6, 12, 24, 36, and 42 hours according to the method of [18]. The equilibrium studies were carried out by six-hour agitation of 1 g samples of RSBE in 10 mL aliquots of adsorbate solution containing Cu(II) ions in the range 0 to 5.4×10^{-3} M. The effect of adsorbent dosage was studied by varying RSBE loading from 50-400 g/L while the effect of pH and initial adsorbate concentration were studied by pH adjustments from 1 to 8 by addition of small amounts of 1 M NaOH or 1 M HNO₃. The pH of the solutions was measured before and after equilibration. The effect of adsorbate concentration and equilibrium analysis was studied using serial dilution of 0.1 M Cu(NO₃)₂ to obtain adsorbate concentration between 5.3×10^{-4} and 8.5×10^{-3} M Cu(II) ions. All experiments were carried out in triplicate at room temperature (22 ± 3 °C). The supernatant solution was separated by centrifugation and its copper concentrations 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_(aq) as a supporting electrolyte [19, 20] and the adsorbate uptake (mol/g) calculated [21].

RESULTS AND DISCUSSION

Effect of time of contact

On exposing the adsorbate solution to the adsorbent for varying lengths of time, the percentage adsorption of copper onto SBE rapidly increased with increasing time of contact in the initial stages as presented in Figure 1.

Over 70% of copper removal was realized within the first four hours. This was followed by a gradual increase such that at forty-two hours over 90% copper removal was recorded. This

indicated that copper could effectively be removed from aqueous solutions by adsorption method using RSBE within just four hours of agitation. That way diffusion of the metal ions into inner core sites of the materials could be avoided for easy adsorbent clean-up and stem ultimate incorporation of copper in the ecosystems.

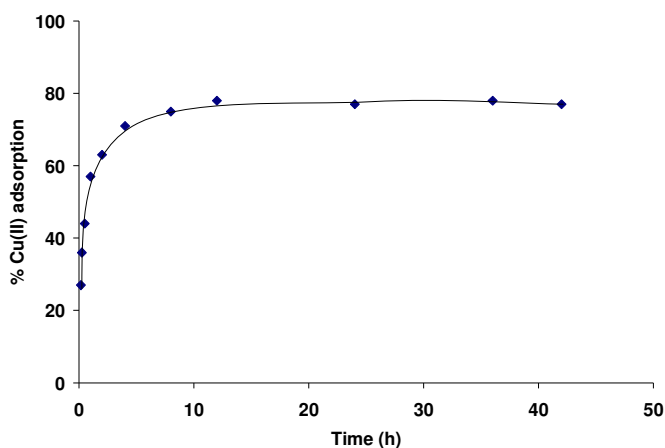


Figure 1. Effects of time of contact on Cu(II) removal by heat regenerated spent bleaching earth (adsorbate concentration, 5.3×10^{-3} M; adsorbent dosage 100 g/L).

Effect of ionic strength of the background solution

The effect of change in ionic strength was investigated and the results presented in Figure 2.

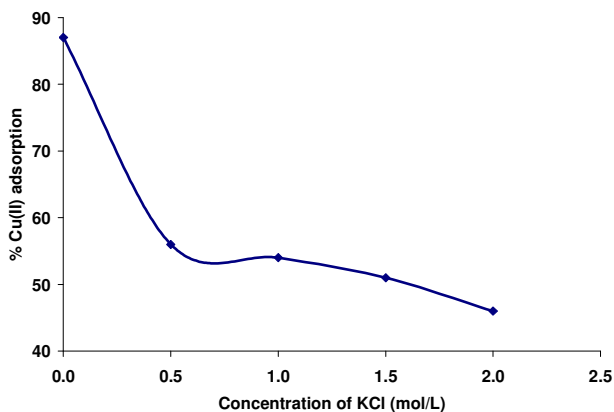


Figure 2. Effects of ionic strength on SBE sorption of Cu(II) ions at 22 ± 3 °C, pH 2.9, 100g/L adsorbent loading using 4.3×10^{-3} M initial Cu(II) concentration

The ionic strength of the adsorbate solution influenced Cu(II) adsorption on RSBE strongly. The percentage Cu(II) adsorption decreased drastically from 85% to 55% when the ionic strength of the adsorbate solution was increased from 0 to 0.5 M KCl. The decline was then more gradual reaching 46% at 2 M KCl. The K^+ ions must have saturated the adsorptive surfaces of the material reducing its Cu(II) ion uptake. This means that, as KCl concentration

increased, the thickness of the electrical double layer on the adsorbent surface increased creating a viscous drag close to the adsorbent surface which inhibited the mobility of Cu(II) ions to the soil surface thus retarding their adsorption. This shows that, the presence of alkali ions would retard Cu(II) uptake by RSBE.

Effect of adsorbent dosage

The effect of adsorbent dosage was studied by varying RSBE loading from 50-400 g/L at 5.3×10^{-4} M Cu(II) adsorbate solution. Figure 3 shows that the overall percentage Cu(II) removal from solution increased almost exponentially with increase in RSBE dosage between 50 and 400 g/L batch loading.

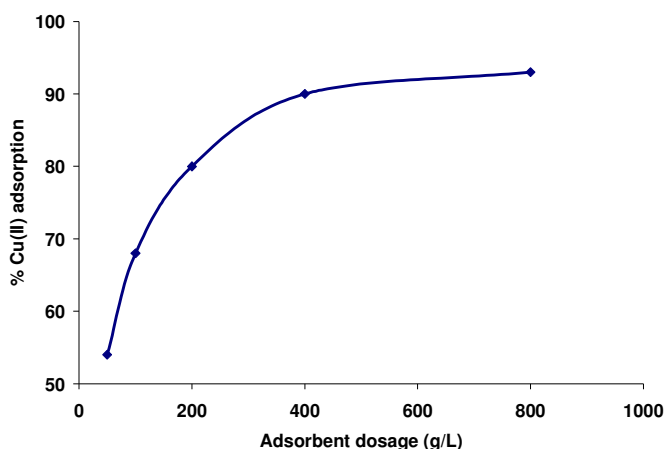


Figure 3. Variation in SBE Cu(II) sorption with change in adsorbent loading at 22 ± 3 °C, using 4.3×10^{-3} M initial Cu(II) concentration.

The rapid rise in Cu(II) adsorption with increasing adsorbent dosage was due to increased availability of adsorptive surface [22, 23]. Clearly, high loading capacities (≥ 200 g/L) were desirable to achieve highest removal efficiency. However, for adsorbent dosages greater than 400 g/L the slurry became too thick to agitate effectively.

Effect of adsorbate solution pH

The influence of adsorbate pH on the adsorption of Cu(II) ions on RSBE is illustrated in Figure 4. Percentage Cu(II) adsorption increased with increasing pH to a limiting value at pH 6. At low pH, H^+ ions compete with Cu(II) ions for adsorbent sites inhibiting Cu(II) adsorption. However, as pH increases, surface H^+ ions are replaced by OH^- ions increasing negative surface charge favorable to cationic adsorption and result in increased Cu(II) uptake by the adsorbent [22].

The diminishing Cu adsorption gradient towards neutral pH suggest increased aqueous Cu(II) complexation [24] and surface precipitation [25] leading to surface accumulation of insoluble Cu(II) products and deterioration in adsorbent surface in these pH values.

Adsorption kinetics

In order to determine the copper adsorption kinetics, the adsorption data was fitted to first order (Eq. 1) and pseudo-second order (Eq. 2) Lagergren models and the Morris-Weber intra-particle diffusion (Eq. 3) model [4, 6]. The Cu(II) adsorption process was found to follow

Lagergren pseudo-second order kinetics complimented by intra-particle diffusion kinetics at prolonged periods of equilibration. The corresponding kinetic parameters are presented in Table 1.

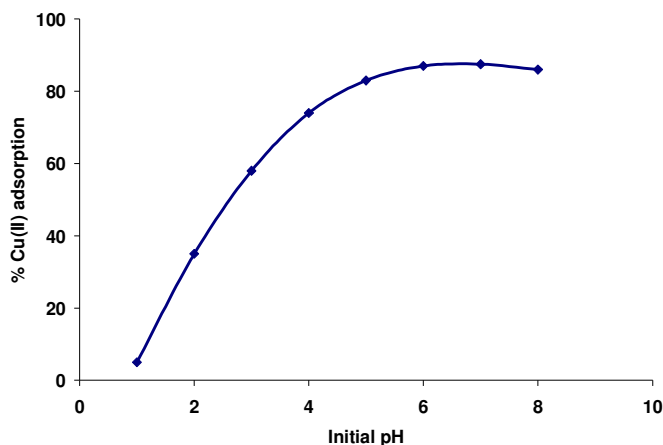


Figure 4. Effects of adsorbate pH on RSBE Cu(II) adsorption at 22 ± 3 °C and 0.1 mg/mL adsorbent loading using 4.3×10^{-3} M initial Cu(II) concentration.

Table 1. Equilibrium and kinetics constants for the adsorption of Cu(II) on heat regenerated spent bleaching earth.

Pseudo-second order kinetics			
$K_{2ad} \times 10^{11}$	$q_e \times 10^8$	$h_o \times 10^6$	R^2
5.54	2.79	4.30	0.9994
Pseudo-first order kinetics			
$K_{1,ad}$	R^2		
0.000144	0.5784		
Intra-particle diffusion model			
$k_w \times 10^{-7}$	R^2		
6.92	0.7435		

The linear form of the first-order rate expression based on solid capacity was used in its linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_{1,ad}}{2.303} t \quad (1)$$

where q_e and q_t are the amounts of metal ions adsorbed onto the material (mol/g) at equilibrium and at time t (min), respectively and $k_{1,ad}$ is the first-order rate constant (min^{-1}). First order rate constant, $k_{1,ad}$ could be calculated from the slope of the linear plot of $\log(q_e - q_t)$ against t . The Lagergren first order plot is shown in Figure 5. The correlation coefficient, R^2 , for pseudo first order model (0.5784) was too low showing that the Lagergren pseudo-first order model did not fit well to the adsorption data. The results suggested that copper adsorption on RSBE does not follow first-order kinetics. This agrees with what has been reported in the literature [26].

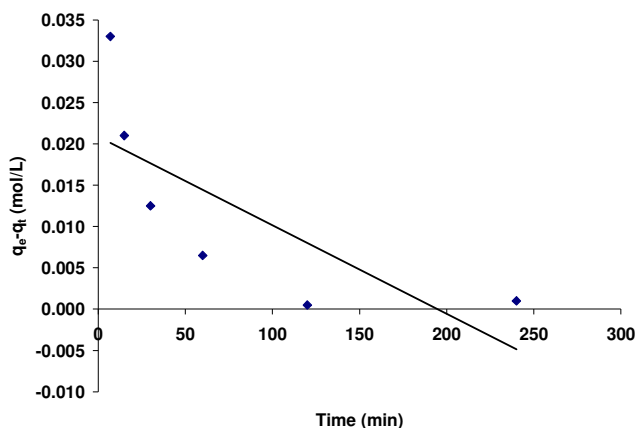


Figure 5. Pseudo-First order adsorption kinetics of Cu(II) on heat regenerated spent bleaching earth in the initial six hours of the sorption process.

For the second order kinetics, pseudo-second order equation based on the sorption capacity of the solid has the following linear form:

$$\frac{t}{q_t} = \frac{1}{k_{2,ad}q_e^2} + \frac{1}{q_e}t \quad (2)$$

$k_{2,ad}$ is the second order rate constant (g/mol min^{-1}), q_e the amount of metal ions adsorbed at equilibrium (mol/g) and q_t the amount of solute adsorbed on the surface of the adsorbent (mol/g) at any time t (min). Adherence to this model gives a linear plot of t/q_t against t from which the second order rate constant $k_{2,ad}$ and the equilibrium adsorption q_e are calculated. The resulting linear plots of copper sorption data and the resultant kinetics constants obtained in this work are shown in Figure 6 and Table 1, respectively.

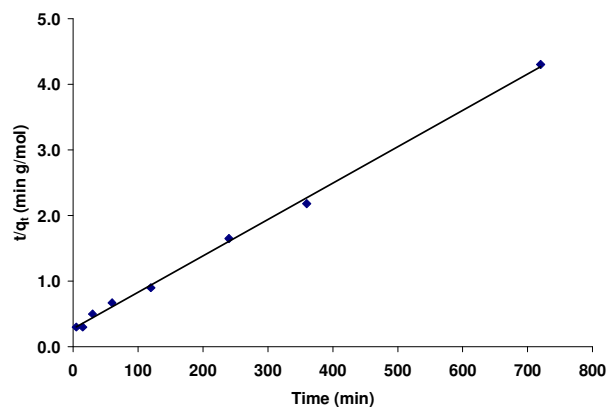


Figure 6. Pseudo-second order adsorption kinetics for of Cu(II) on heat regenerated spent bleaching earth for forty-two hours of the sorption process.

The Lagergren second order model gave an excellent fit to the copper adsorption data with $R^2 = 0.9994$. The adsorption of Cu(II) ions onto RSBE therefore follows pseudo-second order

kinetics. This means that chemical interaction between adsorbent sites and aqueous metal ions could be the sole rate determining step. The values of the second order rate constant ($k_{2,ad}$), equilibrium adsorption capacity (q_e) and the initial sorption rate (h_0) were such as found in the literature [4, 18, 27].

To determine the diffusivity of the Cu(II) ions into the mesopores of the adsorbent, the following equation based on the Weber-Morris intra-particle diffusion model which is often used in the form of Eq. 3 was utilized as follows:

$$q_t = \frac{k_w}{m} t^{1/2} \quad (3)$$

where m is the mass of adsorbent (g), q_t the amount of metal ions adsorbed at time t (mol/g) and k_w is the initial rate of intra-particle diffusion ($\text{mol L}^{-1} \text{min}^{-0.5}$). A linear plot between q_t and $t^{1/2}$ indicates that the adsorption kinetics follow this model. The resulting plot obtained in this study is shown in Figure 7.

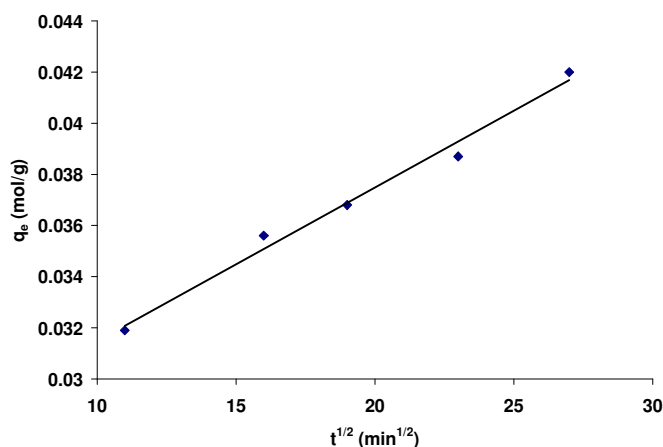


Figure 7. Intra-particle diffusion adsorption kinetics for of Cu(II) on heat regenerated spent bleaching earth after the initial two hours of the sorption process up to forty-two hours equilibration time.

The correlation coefficient was considerably lower for intra-particle diffusion kinetics ($R^2 = 0.7435$). Nonetheless the equation had a more favorable correlation ($R^2 = 0.9664$) in the latter stages of equilibration (>2 hours contact times). This means that intra particle diffusion play a significant role in copper adsorption at prolonged equilibration periods. It means that surface sites in the material get rapidly exhausted within the initial 4 hours allowing adsorption to less exposed sites in the mesoporous structure of the material in the latter stages of the process. However, the portion of the graph of q_e against $t^{1/2}$ in these latter stages did not extrapolate through the origin indicating that even at prolonged periods of agitation, intra-particle diffusion of Cu(II) species into meso-structure of the adsorbent is not the sole rate determining step in RSBE copper adsorption. It means therefore, that there is limited immobilization of metal ions in the mesoporous structure of the material.

Equilibrium analysis

Different equilibrium models are often used to predict adsorption properties of adsorbents. Analysis of the equilibrium data for the sorption of Cu(II) ions onto heat regenerated spent

bleaching earth was undertaken using the Dubinin-Radushkevich (D-R) isotherm and the Temkin isotherm. The resulting isothermal constants are presented in Table 2.

Table 2. D-R isotherm and Temkin isotherm equilibrium constants for the adsorption of Cu(II) ions on heat regenerated spent bleaching earth.

D-R isotherm			
X_m (mol/g)	β (mol ² /kJ ²)	E (kJ/mol)	R ²
0.302	-0.0285	4.19	0.9855
Temkin isotherm			
A (L/mol)	B (kJ/mol)	R ²	
0.0048	0.0016	0.9450	

Many soil systems are heterogeneous in the adsorption surfaces. Temkin isotherm is often used to describe adsorption behavior of such heterogeneous surfaces [2, 28]. The isotherm is given by:

$$q_e = A + B \ln C_e \quad (4)$$

where A is the Temkin adsorption potential, and B the Temkin constant relating to the heat of sorption while q_e (mol/g) and C_e (mol/L) are equilibrium adsorbate concentrations in the solid and aqueous phases, respectively. It was found that copper isothermal adsorption could be expressed by Temkin isotherm.

The equation gave a satisfactory correlation to the experimental data with regression coefficients of 0.945. The Temkin isothermal constants; A and B were found to be 0.0048 and 0.0016, respectively. The low values of the Temkin constants in the present study indicate a weak interaction between the adsorbate and adsorbent consistent with ion-exchange mechanism or physical interface between Cu(II) and RSBE surfaces [29].

To estimate the characteristic porosity of the adsorbent and the apparent energy of adsorption, the copper adsorption data was also fitted to the D-R isotherm in the following linear form [29]:

$$\ln q_e = \ln X_m - \beta \varepsilon^2 \quad (5)$$

where q_e (mol/g) is the concentration of the adsorbate sorbed in the adsorbent, X_m (mol/g) is the maximum sorption capacity, β (mol²/kJ²) is a constant related to the mean adsorption energy and ε is the Polanyi potential [30] expressed as:

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (6)$$

R is the gas constant (kJ/(mol K)) and T is temperature (K). The results of this analysis are shown in Figure 9. The D-R isotherm gave a good fit to the equilibrium data with a regression coefficient, R^2 , value of 0.9855.

The adsorption parameter, β , was found to be -0.0285 mol².kJ² with high adsorption capacity, $X_m = 0.302$ mol/g. The quantity β relates to the mean molar sorption energy, E , of the adsorbate particles by the equation:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (7)$$

The mean sorption energy, E , was 4.19 kJ/mol. Values of E between 1 and 8 kJ/mol are typical of physisorption whereas values in excess of this limit indicate that ion-exchange and chemisorption could be the dominant adsorption mechanisms [30]. The D-R isotherm therefore related to the heterogeneity of energies of the adsorptive sites in RSBE which was consistent with electrostatic interactions between adsorptive sites and metal ions. These

findings are in agreement with those of previous studies [10] and with earlier postulates that spent bleaching earth is dominated by aluminum hydroxy-silicates [7] which have been associated with electrostatic physical metal ion adsorptions [31].

A comparison of D-R isotherm adsorption energy (E) and maximum Cu(II) adsorption capacity, X_m , of RSBE with those of other low cost adsorbents reported in the literature is given in Table 3.

Table 3. Comparison RSBE D-R isotherm constants with literature values for selected low-cost adsorbents.

Adsorbent	X_m (mol/g)	E (kJ/mol)	R^2
Unreactivated SBE [this work]	0.0436	0.903	0.9701
370 °C RSBE [this work]	0.302	4.19	0.9855
Green algae mean values [32]	0.00483	1.12	0.7693
Carbon green algae mean values [32]	0.00709	2.75	0.8078
Calcareous soil mean values [33]	0.0354	15.8	0.9541

Although mean copper adsorption energy of calcareous clays was more than that of RSBE, overall D-R adsorption properties of RSBE were superior to most of those of other low-cost adsorbents reported in literature. Differences in Cu adsorption capacities are due in part to dissimilarity in properties of the adsorbents, mode of preparation and adsorbate solution parameters. As expected, RSBE had superior adsorption properties to un-reactivated spent bleaching earth showing that heat-treatment greatly increased copper adsorptive capacity of the material (Table 3).

Adsorption thermodynamics

At infinite dilution, the adsorption partition coefficient, K_D becomes the standard equilibrium constant, K_c' from which the standard Gibbs free energy ΔG^0 may be calculated according to the expression [28]:

$$\Delta G^0 = -RT \ln K_c' \quad (8)$$

The standard thermodynamic equilibrium constant (K_c') for adsorption of copper onto RSBE was estimated by extrapolating values of K_D at zero concentration of initial metal concentration [6]. The value of ΔG ($-11.96 \text{ kJmol}^{-1}$) was negative as expected for a spontaneous process. Its magnitude was consistent with electrostatic type of interactions between the adsorbate and the adsorbent surfaces [28] confirming that ion-exchange interactions between the adsorbent and adsorbate particles did not play a role in the adsorption of Cu(II) ions on RSBE.

CONCLUSIONS

It is clear from this work that solvent oil extraction followed by heat-treatment at 370 °C of spent bleaching earth which is an environmental pollutant could offer a plausible low-cost adsorbent for the removal of copper(II) ions from aqueous solutions. The Cu(II) adsorption on RSBE was found to be a rapid spontaneous phenomenon based on electrostatic interactions between the metal ions and the adsorbent surfaces requiring only 2 hours to equilibrate and modeled along Lagergren pseudo-second order kinetics complimented by intra-particle diffusion kinetics at prolonged periods of time. The metal uptake by the adsorbent was found to be strongly influenced by the concentration, adsorbent dosage, ionic strength and adsorbate pH and the equilibrium properties could be described by Dubinin-Radushkevich (D-R) and the Temkin isotherms.

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