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Sorption of Cu (II) ion from aqueous solution by scrap tyre

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ABSTRACT

The use of Scrap Tyre (ST) for the sorption of Cu (II) ion from aqueous solution has been studied in a batch experiment. Investigation includes the effect of initial Cu (II) ion concentration and agitation speed. Three kinetic models (Pseudo first order, pseudo second order and Elovich kinetic models), were employed to predict the overall rate constant of sorption, the equilibrium sorption capacity and the initial sorption rate. The equilibrium sorption of Cu (II) ion by ST was analysed using Langmuir, Freundlich and Temkin isotherm models. The monolayer sorption capacity (mg/g) of ST for Cu (II) ion was 34.84. Thermodynamic parameters were calculated and the sorption process was found to be spontaneous and exothermic. The use of ST as a sorbent in Cu (II) ion attenuation in wastewater shall help to reduce the cost of treating Cu (II) ion bearing wastewater and to curtail the negative environmental impact of ST as a solid waste.

Keywords: Adsorptions; Copper ion; Scrap tyre; Mass transfer; Intraparticle; Liquid film

1. Introduction

Different water and wastewater treatment technologies have been used for the removal of Cu (II) ion from aqua streams. Conventional methods that have been used include ion exchange, reverse osmosis, electrochemical treatment, evaporative recovery and adsorption (Kalavathy, *et al*., 2005). These conventional technologies can reduce metal ions but they do not appear to be highly effective due to the limitations in the pH range as well as the high material and operational cost.

Adsorption, as a means of treating water and wastewater, is highly favored in the water industry. This is because of the simplicity and economy of the process. During adsorption, pollutants are sorbed onto the sorbent surface from the aqua medium. The amount of pollutant sorbed by the sorbent depends largely on the adsorption capacity of the solid sorbent. Arrays of investigations have been made to identify promising low-cost sorbents for pollutant attenuation in water and wastewater. A few have been found to have comparable adsorption capacity, with known commercial sorbent like activated carbon. Those that have been identified include peat (Viraraghavan and Dronamraju, 1993), Wollastonite (Yadava *et al*., 1991), biogas residue (Namasivayam and Yamuna, 1995) and fly ash (Srivastava *et al*., 2006) etc.

The mechanisms of adsorption of solutes on solid sorbent particles have been extensively studied and reported by several researchers (Ho and Mc Kay 1998a, 1998b, 1999; Tien 1994; Lazaridis and Asouhidou 2003; Chen and Wang 2004). An overview of the different sorption mechanisms , propounded by different authors, showed that the overall mechanisms can be depicted as a succession

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of four different steps: mass transfer of solute from the bulk solution to the boundary film surrounding the solid sorbent; external diffusion of solute from the boundary film to the surface of the solid sorbent; intraparticle or pore diffusion of solute from the surface of the sorbent to the intraparticles/pores active site and uptake of solution on the active sites either by physiosorption or chemisorptions. In the study of the mass transfer properties of solid sorbents, the first and the last step are not considered as a rate limiting step because the hydrodynamic condition outside the particles can be easily influenced by the agitation of the reacting mixture. This helps to avoid a concentration gradient in the solution. The uptake of solute on the active sites is regarded as a quasi-instantaneous mechanism. External diffusion of solute and intraparticle or pore diffusion are the major rate controlling steps. In the use of adsorption, as a method of water and wastewater treatment, knowledge of the mass transfer properties of the sorption of a named pollutant by a solid sorbent is required to understand the variables which influence the sorption of solute from aqueous medium by a sorbent. The data generated can used to determine the equilibrium time of a sorption process and the rate of adsorption obtained can be employed to develop predictive models for column experiment.

The potentialities of scrap tyre in pollutant attenuation in waste streams have been investigated and reported by different researchers. Thian (1974), Knocke and Hemphill (1981), and Al-Asheh and Banat (2000) have reported the use of scrap tyre rubber for heavy metal removal from aqua system. Park and Jhung (1993) also reported that ground tyre rubber could remove the vapour of organic compounds, emitted from an activated sludge aeration basin. Ground tyre has been used in civil engineering application, as an additive in road pavement (Savas *et al.*, 1996). Other applications include in playground surface; rubber roofs; drainage systems and floor mats (Siurn, 1998a, b, c and 1997). A major market for scrap tyres is their utilization as solid fuels (Blumenthal, 1996). Manchon-Vizuete is of the opinion that these applications of the tyre rubber do not appear to be sufficiently profitable as tyres are frequently dumped in the open, becoming a serious source of environmental pollution. Al-Asheh and Banat (2000) studied the effect of physical and chemical activation on the ability of scrap rubber to adsorb copper ion from solution. Oladoja *et al.*, (2006) also evaluated the potential of ST as an adsorbent for Cu ion and the process variables (pH, sorbent dosage, contact time, and initial sorbate concentration) that define the process.

The present study aimed at elucidating the mechanism of the use of ST as a low cost sorbent for Cu (II) ion removal from aqua waste stream. The effect of initial Cu (II) ion concentration and agitation speed shall be investigated. The kinetics of Cu (II) ion sorption on the ST shall be analysed using pseudo first order, pseudo second order and Elovich kinetic models. The equilibrium sorption of Cu (II) ion by ST shall be tested with Langmuir, Freundlich and Temkin isotherm models, to determine the best-fit isotherm equation and the thermodynamic parameters evaluated.

2. Materials and methods

2.1. Sorbent preparation

Scrap tyre (ST), used as a sorbent in these studies, was collected from a tyre dealer. The different parts were dismembered and the rubber part was collected and washed thoroughly under running tap and then with distilled water. The washed rubber part was pulverized, using an abrader (commonly used by local cobblers to grind shoe sole), at ambient temperature, typical of a tropical region (29–33°C) and sieved through 180 µm sieve (SF 500, A.J.COPE and Son Ltd) and used as such.

2.2. Determination of surface functional group on ST

The surface functional groups of the ST were determined. The determination was based on the Boehm titration method (Boehm, 1966). Solutions of $NaHCO_3$ (0.1 M), Na_2CO_3 (0.05 M), NaOH (0.1 M), and HCl (0.1 M) were prepared with deionised water. A volume of 50 mL of these solutions was added to vials containing 1 g of ST and shaken (100 rpm) until equilibrium (24 h), and then filtered. Five solution blanks (without the ST) were prepared. The excess of base or acid was then determined by back titration using NaOH (0.1 M) and HCl (0.1 M) solutions.

2.3. Sorbate preparation

Copper stock solution was prepared using $CuSO_4.7H_2O$ (BDH, Analytical grade) salt in distilled water obtained by demineralizing water through a Barnstead demineraliser and then distilled in an all-glass apparatus. The different concentrations of copper solution, needed for the experiments, were prepared from the copper stock solution.

2.4. Adsorption experiment

Except where a reaction condition is being investigated, a typical experiment was conducted by contacting a known weight (0.5 g) of the adsorbent with a known concentration of the sorbate in a litre borosilicate conical flask and placed in a thermostatic shaker/water bath, agitated at a rate of 200 rpm for a known period of time. At the end of each study period, the sorbent was removed by filtration and the equilibrium concentration was determined by Atomic Absorption Spectrometer (AAS) (Buck model 200 A). Copper uptake by the ST was calculated using the mass balance equation stated below:

$$q_t = \frac{V\left(c_o - c_f\right)}{m} \tag{1}$$

where q_t is the amount of sorbate sorbed per gramme (g) of adsorbent (mg/g), c_o is the initial concentration of Cu (II) ion (mg/l); c_f is the final residual Cu (II) ion concentration (mg/L) and, m is the mass of ST (mg).

The kinetics of adsorption was determined by analyzing adsorption uptake of the Cu (II) ion by ST from aqueous solution at different time intervals (10–120 min). The effect of initial Cu (II) ion concentration on the kinetics of adsorption by ST was studied at: 98.07, 131.35, 258.00 and 371.35 (mg/L) while the effect of agitation speed was studied at 100, 200 and 300 (rpm) using 258.00 mg/L of Cu (II) ion solution. The results obtained were evaluated using the Lagergren pseudo-first order; the chemisorptions pseudo-second order (Ho, 1995); Elovich kinetic model; the intraparticle diffusion model (Weber and Morris, 1963) and liquid film diffusion model (Boyd *et al.*, 1949).

The linearized form of the pseudo-first order equation of Lagergren is generally expressed as follow:

$$\log\left[q_e - q_t\right] = \log\left[q_e\right] - \left[\frac{k_1}{2}.303\right]t \tag{2}$$

where q_e and q_t are the sorption capacity at equilibrium and at time t, respectively (mg/g). k_1 is the rate constant of pseudo first-order adsorption.

The plot of log ($q_e - q_t$) versus, t, should give a linear relationship from which k_1 and q_e can be calculated from the slope and intercept of the plot, respectively.

The pseudo second order kinetic model is represented by the linear equation:

$$\frac{t}{q_t} = \frac{1}{kq_e{}^2} + \frac{1}{q_e}t \tag{3}$$

where q_e, q_t, and t have the same meaning as explained above. k_2 is the overall rate constants of pseudo second order sorption [g/mg/min]. If pseudo-second order kinetics is applicable, the plot of t/q_t against t of Eq. (3) should give a linear relationship, from which q_e, and k_2 can be determined from the slope and intercept of the plot.

If the initial sorption rate is

$$h = kq_e^2 \tag{4}$$

then Eq. (3) becomes

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \tag{5}$$

A simplified linearized form of Elovich kinetic equation is presented thus:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{6}$$

If the sorption of Cu (II) ion on scrap tyre fits the Elovich model, a plot of q_t versus ln(t) should yield a linear relationship with a slope of (1/β) and an intercept of $\frac{1}{\beta}\ln(\alpha\beta)$.

Several steps are involved in the sorption of sorbate by a sorbent. These involve transport of the solute molecules from the aqueous phase to the surface of the solid particulates and diffusion of the solute molecules into the interior of the pores, which is usually a slow process. The intra-particle diffusion rate constant (k_{id}) is given by the equation:

$$q_t = k_{id}t^{0.5} \tag{7}$$

When intra-particle diffusion plays a significant role in controlling the kinetics of the sorption process, the plots of q_t versus $t^{0.5}$ yield straight lines passing through the origin and the slope gives the rate constant, k_{id}.

However, when the transport of the solute molecules from the liquid phase up to the solid phase boundary plays the most significant role in adsorption, the liquid film diffusion model may be applied:

$$\ln(1 - F) = -k_{fd}t \tag{8}$$

where F is the fractional attainment of equilibrium ($F = q_t/q_e$), k_{fd} is the adsorption rate constant. A linear plot of ln (1 – F) versus t with zero intercept would suggest that the kinetics of the sorption process is controlled by diffusion through the liquid film surrounding the solid sorbent.

2.5. Equilibrium isotherm studies

Adsorption isotherms are basic requirements to understand the mechanism of adsorption. The equilibrium isotherm data, obtained from the equilibrium isotherm studies of the sorption of Cu (II) ion by ST, were tested with three classical adsorption isotherm models (i.e. Langmuir, Freundlich and Temkin isotherm models).

The monolayer coverage of the sorbate on a sorbent surface at constant temperature is represented by the Langmuir isotherm. The Langmuir isotherm hints towards surface homogeneity. The linearized form of the equation can be represented thus:

$$\frac{c_e}{qe} = \frac{1}{K_L q_m} + \left[\frac{1}{q_m}\right]c_e \tag{9}$$

where c_e is the concentration of the sorbate at equilibrium (mg/L); q_e is the amount of Cu (II) ion adsorbed, at equilibrium per unit mass of ST (mg/g); q_m is the monolayer capacity (mg/g) and; K_L is the adsorption equilibrium constant, given by the ratio k_a/k_d, k_a and k_d being the rate constant of the adsorption and desorption processes respectively.

The monolayer coverage can be obtained from a plot of c_e/q_e versus c_e which should give a straight line. The slope and the intercept of this line give the value of q_m and K_L.

The Freundlich equation for adsorption isotherm indicates the surface heterogeneity of the sorbent. The linearized form of the isotherm is expressed thus:

$$\ln q_e = \ln k_f + \frac{1}{n}\ln c_e \tag{10}$$

where k_f (the measure of the sorption capacity) and n (the sorption intensity) are Freundlich coefficients, obtainable from the plots of ln q_e versus ln c_e , q_e is the amount of Cu (II) ion adsorbed per specified amount of ST (mg/g), c_e is the equilibrium concentration(mg/L).

Temkin isotherm considers the effect of the heat of adsorption that decreases linearly, with coverage of the adsorbate and adsorbent interactions (Choy and Mc Kay 1999). The linear form of the isotherm is presented below:

$$q_e = B_1 \ln k_t + B_1 \ln c_e \tag{11}$$

where $B_1 = \frac{RT}{b}$,

K_t (L/g) (the equilibrium binding constant corresponding to the maximum binding energy) and B_1 (which is related to the heat of adsorption) are the Temkin constants which are obtained from the slope and intercept of the linear plot of q_e versus ln c_e.

2.6. Thermodynamic studies

Equilibrium adsorption isotherms were determined at 309, 333 and 353 K and the thermodynamic parameters were estimated using the classical thermodynamic equations. The Gibbs free energy change, ΔG^o is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Reactions occur spontaneously at a given temperature if ΔG^o is a negative quantity.

The free energy of a sorption reaction, considering the sorption equilibrium constant, K_L, is given by the following equation:

$$\Delta G^{\circ} = -RT \ln K_L \tag{12}$$

where ΔG^o is the standard free energy change (J), R the Universal gas constant, 8.314 J/molK, and T is the absolute temperature (K).

Considering the relationship between free energy and equilibrium constant change in equilibrium constant with temperature can be obtained in the differential form as follows (Ho and Ofomaja 2006):

$$\frac{d \ln K_L}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{13}$$

After integration, the integrated form of Eq. (13) becomes

$$\ln K_L = \frac{\Delta H^\circ}{RT^2} + Y \tag{14}$$

where Y is a constant.

Eq. (14) can be rearranged to obtain

$$-RT \ln K_L = \Delta H^\circ - TRY \tag{15}$$

Let

$$\Delta S^{\circ} = RY \tag{16}$$

Substituting Eqs. (15) and (16), the Gibbs free energy change, ΔG^o, can be represented as follows:

$$\Delta G^{\circ} = \Delta H^\circ - T\Delta S^\circ \tag{17}$$

3. Results and discussion

3.1. Determination of surface functional groups on ST

The surface functional group analysis, determined by the Boehm titration method, showed that the prevalent surface functional groups on the ST were acidic in nature viz: strong acidic (carboxylic group) 0.32 meq/g; weakly acidic (carboxylic, lactonic and enolic) 0.93 meq/g; phenolic 0.58 meq/g. The magnitude of the basic functional groups, determined using 0.1 M of HCl, was relatively low (0.43 meq/g). The prevalence of the acidic functional groups on the surface of the ST is an indication that the Cu^{2+} ion can interact chemically with the polar functional groups of these acidic functional groups as chemical bonding and ion exchange viz:

$$2ST^- + Cu^{2+} \leftrightarrow STCu$$

or

$$2HST + Cu^{2+} \leftrightarrow STCu + 2H^+$$

where ST^- and HST are the polar sites on the ST surface and Cu^{2+} is the Copper ion in the aqua system.

3.2. Adsorption experiment

The results obtained from the different studies show the affinities of the scrap tyre (ST) for Cu (II) ion, under varying operational conditions. A number of ingredients are added to the base polymer, in tyre compounding, to enhance its service life. The main ingredients added come under the following classifications: Curative (or the vulcanizing agent), Fillers, accelerator, activator and protective agent. The conventional curative is sulphur or sulphur containing compounds. The propensity of sulphur bearing surfaces for metal ions uptake has been reported (Gomes-Serano *et al*., 1998; Macias Garcia *et al*., 1995). This could be ascribed to the ability of sulphur to coordinate metal ions. This is possible because sulphur is an anionic monodentate ligand. Irrespective of the forms in which it is present on a surface (e.g. thiocyanate, isothiocyanate, sulfate, and sulfite etc.) it is a susceptible site for binding metal ion. Some of the other ingredients, added to the base polymer, also contain functional groups (e.g. phenolics, carboxyl, and amino etc.) that are capable of sequestrating metal ions. Carbon black, the filler used in tyre compounding has a large surface area and possesses surface activity that favours the attraction of metal ions. The chemical nature of the carbon black particle surface, as elucidated by Blow and Hepburn (1982), shows that carbon black consists of 90–99% elemental carbon. The principal functional groups, present on the carbon surface are phenolic, ketonic and carboxylic together with lactones. It may also contain small amount of sulphur depending upon the nature of hydrocarbon used for the preparation. A large percentage of the accelerator and the protective agents used in tyre compounding contain amine, phenolic and sulphur functional groups. Amine and phenolic groups are also monodentate ligands that can co-ordinate metal ions.

3.3. Studies on adsorption kinetic

The kinetic properties of adsorbate uptake are required for selecting optimum operating conditions for the full scale batch process (Gupta *et al*., 1997). The kinetic parameter, which is helpful for the prediction of adsorption rate, gives important information for designing and modeling adsorption processes. In order to understand and elucidate the underlying mechanism of any sorption process, different kinetic models have been proposed and used to analyze data obtained from different sorption experiments. Consequent upon this, data obtained from studying the effect of initial Cu (II) ion concentration and agitation speed were analyzed using different kinetic models to explicate the mechanism guiding the sorption of Cu (II) ion by ST.

3.4. Effect of initial Cu (II) ion concentration

Different experiments were conducted to study the effect of initial Cu (II) ion, concentration on the kinetics of adsorption by ST. A range of Cu (II) ion concentration from 98.07 to 371.35 mg/L was used. Agitation was carried out at 200 rpm for 120 min. The effect of initial concentration on the sorption of Cu (II) ion is presented in Fig. 1. The plot obtained, when the amount of Cu (II) ion adsorbed per gram of scrap tyre was plotted against time showed that the rate of sorption was fast at the inception of the sorption studies and became immeasurably slow, when the state of equilibrium was approached. The sorbate removal increased with the increase in the initial concentration. This is because the resistance to the uptake of the sorbate decreased with the increase in sorbate concentration. The initial rapid uptake could be ascribed to the concentration gradient, created at the start of the adsorption process, between solute concentration in solution and that at the ST surface. As the metal ion loading increases, on the ST, this gradient reduces and gives way to slower uptake.

In order to understand the underlying mechanism of this sorption process, under the influence of varying initial Cu (II) ion concentration, the data obtained from the sorption process were tested with different kinetic models, as previously highlighted. When the data got from the adsorption experiment were interpreted with these kinetic models, the Lagergren pseudo-first order kinetic model was the least to conform to the description of the sorption of Cu (II) ion by ST (Table 2). The pseudo

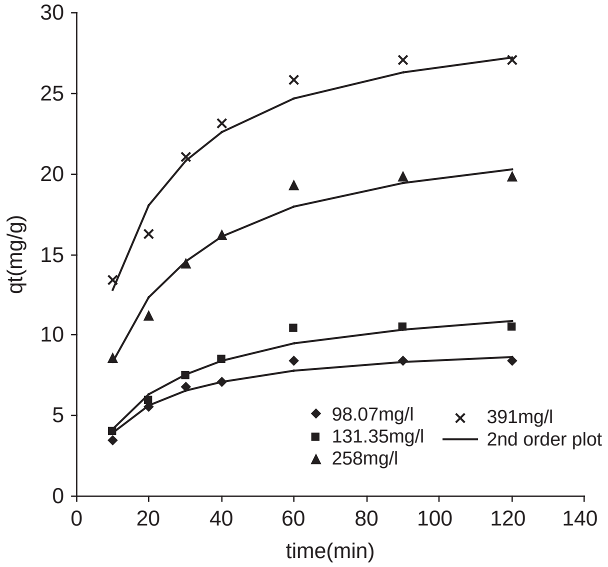

Fig. 1. Comparison of pseudo-second-order kinetic model in predicting q(mg/g) for Cu ion sorption at different initial Cu (II) ion concentration.

Table 1
kinetic parameters for the sorption of Cu (II) ion by ST at varying initial concentrations (mg/L).

Initial Conc. (mg/L)	Pseudo First order			pseudo2nd order				Elovich		
	K_1	q_e	R^2	$K_2 \times 10^{-3}$	q_e	h	R_2	β	A	R_2
98.07	0.0401	20.05	0.8764	7.26	9.643	0.675	0.9944	0.489	1.577	0.9232
131.35	0.0345	23.16	0.8814	3.94	12.642	0.630	0.9914	0.350	2.184	0.948
258.00	0.0261	27.51	0.9375	2.4	23.310	1.304	0.9939	0.199	1.429	0.9512
391.35	0.0215	25.70	0.9854	2.36	30.675	2.22	0.9966	0.166	1.021	0.9491

first order kinetic parameters and the linear coefficients (r^2) are presented in Table 1. The adsorption first order rate constant were in the range 0.0215–0.0401 (min^{-1}) for initial Cu (II) ion concentration of 391.35–98.07 mg/L. Kalavathy *et al*., 2005 obtained a range of 0.0181–0.0336 (min^{-1}) when the effect of initial concentration on the sorption of Cu (II) ion by H_3PO_4- activated rubber wood saw dust was studied. These values are close to those obtained in the present study but a direct comparison of these values is not possible due to the different nature of the sorbate-sorbent system. The regression coefficient values were found to be in the range of 0.9854–0.8764 (Table 1) which shows that the model can be applied but is not appropriate to describe the entire process

Ho *et al*., (2000) considered pseudo second order equation to be appropriate for studying metal ion sorption. This is because metal ions are small, compared with dye molecules, with short contact time to equilibrium. Sequel to this, the data obtained from the sorption experiment was tested with the pseudo second order kinetic model. The pseudo second order kinetic model considers the rate limiting step as the formation of chemisorptive bond involving sharing or exchange of electrons between the sorbate and the sorbent. In contrast to the other kinetic models, it predicts the behaviour over the whole range of studies supporting a pseudo second order equation (Ho and McKay, 1998).

The applicability of the pseudo second order kinetic model to experimental data is presented in Fig. 2. The pseudo-second-order rate constant (k_2), the initial sorption rate (h) and the equilibrium sorption capacity (q_e) were obtained from the slope and intercept of Eq. (3). The, h and q_e, values of the ST increased with increase in the initial concentration of the Cu(II) ion while a reduction was noted in the value of k_2, with increase in the initial Cu (II) ion concentration. The deviations between the calculated q_e values and the experimental q_e values were relatively low and a regression coefficient of >0.99 shows that the model can be applied for the entire adsorption process and confirms the chemisorptions of Cu (II) ion by ST.

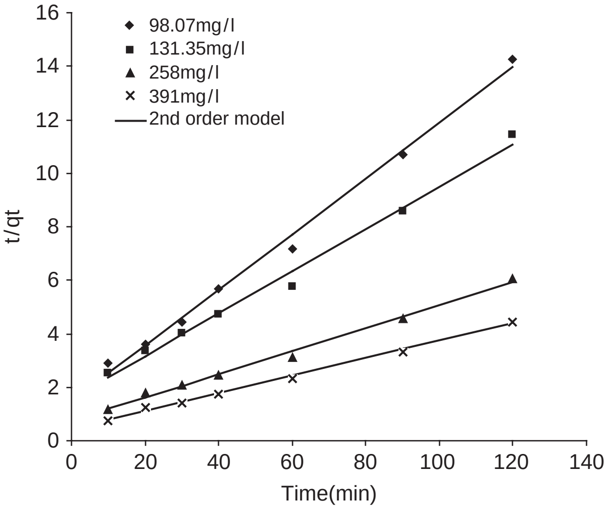

Fig. 2. Applicability of pseudo-second-order kinetic model to experimental data at different initial Cu (II) ion concentration.

The logarithmic plots of pseudo-second-order constants q_e and h versus initial Cu (II) ion concentrations were made and the plots were found to give straight lines whose linear regression (r^2) were 0.9886 and 0.9756 respectively. Mathematical expressions were therefore drawn relating the pseudo second order constants and initial Cu (II) ion concentrations; thus,

$$q_e = 0.0723 c_{\circ}^{3.1892}$$

and

$$h = 0.0019 c_{\circ}^{-0.3978}$$

The corresponding linear plots of the values of q_e and h against c_o were regressed to obtain expression for these values in terms of the initial Cu (II) ion concentration. The empirical parameters have value:

A_q : 0.0723, B_q: 3.1892, r^2 : 0.9886
A_h : 0.0055, B_h : 0.0036, r^2 : 0.9729.

Therefore, it is further considered that q_e and h can be expressed as a function of C_o for Cu (II) ion as follow:

$$q_e = \frac{c_{\circ}}{A_q c_o + B_q} \tag{18}$$

$$h = \frac{c_{\circ}}{A_h c_{\circ} + B_h} \tag{19}$$

Substituting the values of, $q_{e,}$ and, h, into Eqs. (18) and (19) and then into Eq. (5) the rate law for a pseudo-second-order and the relationship of q_e, C_o and t can be represented thus:

$$q_t = \frac{t}{\dfrac{1}{0.0055c^{\circ} + 0.0036} + \dfrac{1}{0.0723c^{\circ} + 3.1892}} \tag{20}$$

Equation (20) represents the generalized predictive models for Cu (II) ion adsorbed at any time and the initial Cu (II) ion concentration within the given range. The Equation can be used to derive the amount of dye sorbed at any given concentration and reaction time.

Application of Elovich kinetic model to the interpretation of the kinetics of adsorption of Cu (II) ion by ST yielded good linearities (r^2 = 0.9232 – 0.9512). The Elovich equation has been found useful in describing predominantly chemical adsorption on highly heterogeneous adsorbents, but no definite mechanism for adsorbate-adsorbent interactions could be worked out (Ho and Mc Kay, 2002 and 1998). Thus although the mechanism is uncertain, it is predicted that Cu (II) ion are held strongly to the ST by chemisorptive bonds. The Elovich parameters (α and β) obtained from the linear plot of q_t versus ln t are presented in Table 1.

In order to obtain the rate determining step in the sorption process, intraparticle diffusion model was used to analyze the results obtained from this study. According to the intraparticle diffusion model, a plot of the amount of sorbate sorbed per unit weight of sorbent, (q_t), versus square root of contact time, $\sqrt{t}$, gives a linear plot which indicate that intraparticle/pore diffusion is the rate limiting step in the sorption process. This is because fractional uptake will vary with the function $(\Delta t/r^2)^{1/2}$. The results obtained, when the intraparticle diffusion model was used to interpret the results of the effect of initial concentration of Cu (II) ion on the sorption process is presented in Fig 3. The plots obtained contrasted the prediction of the intraparticle diffusion model. This indicates that intraparticle/pore diffusion is not the singular rate limiting step in the adsorption process. If a multilinear plot is obtained, instead of a linear plot, as predicted by Weber and Morris (1963), then two or more steps influenced the adsorption process. The mathematical dependence of fractional uptake of adsorbate on $t^{0.5}$ is obtained if the adsorption process is considered to be influenced by diffusion in the cylindrical (or spherical) and convective diffusion in the adsorbate solution (Strivastava *et al.*, 2006). It is assumed that the external resistance to mass transfer surrounding the particles is significant only in the early stages of adsorption. This is represented by first sharper portion. The second linear portion is the gradual adsorption stage with intraparticle diffusion dominating.

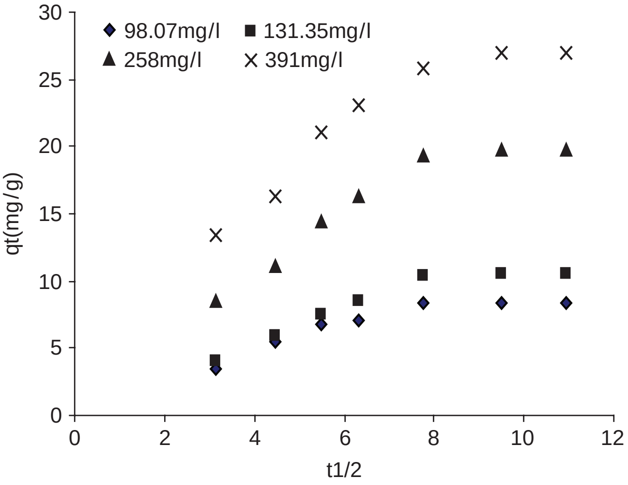

Fig. 3. Intraparticle diffusion model.

The results presented in Fig. 3 shows that the data points can be related by two straight lines. The first straight line portion depicts macropore diffusion and the second represents micropore diffusion. The slopes and intercept of these plots give the rate parameters and the measure of boundary layer thickness (Table 2). The values of the rate parameters for both the macropore and micropore diffusion (k_{id1} and k_{id2} respectively), obtained from this plots showed that both the k_{id1} and k_{id2} values increased with increase in the initial sorbate concentration. A comparison of the k_{id} values for both the macropore and micropore diffusion shows that the rate limiting step is the micropore diffusion stage. This is because the k_{id2} values are lower than the k_{id1} values which is a pointer to the fact that the rate of micropore diffusion is the slower step and the rate determining step. The boundary layer effect, as obtained from the intercept of the plot was also of greater effect at this stage than at the macropore diffusion stage.

Owing to the inability of the intraparticle diffusion model to adequately describe this adsorption process, liquid film diffusion model was also employed in the interpretation of the results obtained. In order to test for the possibility of Cu (II) ion diffusion, from the bulk liquid phase to the surface of the ST, playing a significant

Table 2
Intraparticle diffusion parameters.

Initial Conc. (mg/L)	K_{id1}	Intercept	r^2	K_{id2}	Intercept	r^2
98.07	1.1707	0.0157	0.9528	0.0128	8.2761	0.7924
131.35	1.4289	0.5135	0.9979	0.0353	10.142	0.7924
258.00	2.4861	0.5135	0.991	0.1764	17.979	0.7924
391.35	3.1952	2.9595	0.9768	0.3882	22.989	0.7924

Table 3
Liquid film diffusion parameters.

Initial conc. (mg/L)	Overall			First 40 min		
	K_{fd2}	Int	R^2	K_{fd1}	Int	R^2
98.07	0.0914	0.8512	0.88	0.0446	0.1505	0.9664
131.35	0.0804	0.8163	0.8795	0.0388	0.0765	0.9991
258.00	0.06	0.3248	0.9394	0.0389	0.1265	0.9885
391.35	0.0494	0.0498	0.9861	0.0431	0.1835	0.9795

role in the determination of the rate of adsorption, $-\ln(1-F)$ was plotted against t, in accordance with the liquid film diffusion model. A linear plot of $-\ln(1-F)$ versus t, with zero intercept would suggest that the kinetics of the adsorption process is controlled by diffusion through the liquid film surrounding the ST.

This was tested for the entire period of study and for the first 40 min of the sorption process. The results presented in Table 3 showed that the k_{fd1} values (liquid film rate parameters for the first 40 min) were lower than the k_{fd2} (rate parameters for the entire period of study) which implies that the liquid film diffusion played a significant role in the rate determining process at the inception of the sorption process. The intercept of the plots were also closer to the origin, at the inception of the sorption process than that of the overall sorption process. This further confirms the significance of liquid film diffusion in rate determination at the inception of the sorption of Cu (II) ion by ST.

3.5. Effect of agitation speed

Experiments were conducted using agitation speed of 100, 200 and 300 rmp. All other variables were kept constant. The time-concentration profile of the sorption of Cu (II) ion at different agitation speed is presented in Fig. 4. The effect of increasing agitation speed is to reduce the boundary layer resistance to mass transfer (Mc Kay *et al.*, 1981). This helps to avoid concentration gradient in the solution. The results in Fig. 4 showed that the increase in the agitation speed from 100 to 300 rpm has, but, little influence on the amount of Cu (II) ion sorbed per gram of the ST. The results obtained, when the data obtained from this study was analyzed with different kinetic models are presented in Table 4. The pseudo second order model also described this sorption process better than the two other kinetic models (Table 4), when the effect of agitation speed was optimized. The results of the fitting of the pseudo second order kinetic model to the experimental data, obtained from this study, are presented in Fig. 5. The values of h, k and q_e are presented in Table 4. The corresponding linear plots of the values of $q_{e,}$ and h against agitation speed (r_o) were also

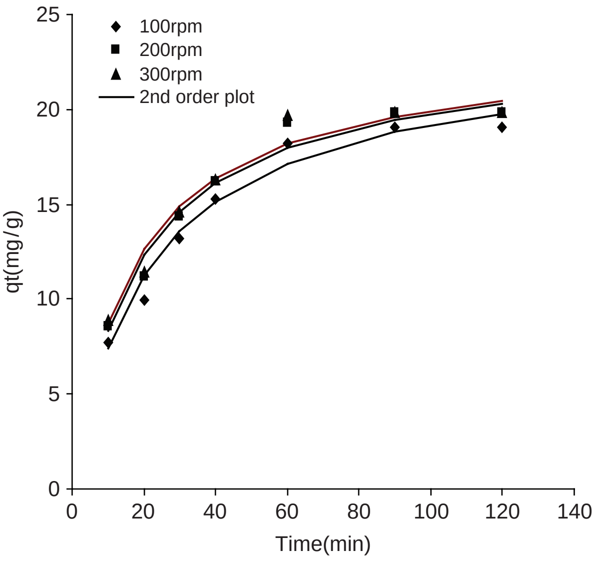

Fig. 4. Comparison of pseudo-second-order kinetic model in predicting q (mg/g) for Cu ion sorption at different agitation speed.

Table 4
Kinetic parameters for the sorption of Cu (II) ion by ST at varying agitation speed (rpm).

Agitation speed (rpm)	Pseudo-First order			Pseudo-second order				Elovich		
	K_1	q_e	R^2	K_2	q_e	h	R^2	β	α	R^2
100	0.0227	24.01	0.9571	2.05	23.041	1.088	0.9916	0.195	1.654	0.9543
200	0.0261	27.51	0.9375	2.41	23.310	1.309	0.9939	0.199	0.542	0.9512
300	0.0339	39.42	0.8844	2.59	23.148	1.388	0.993	0.202	0.303	0.9433

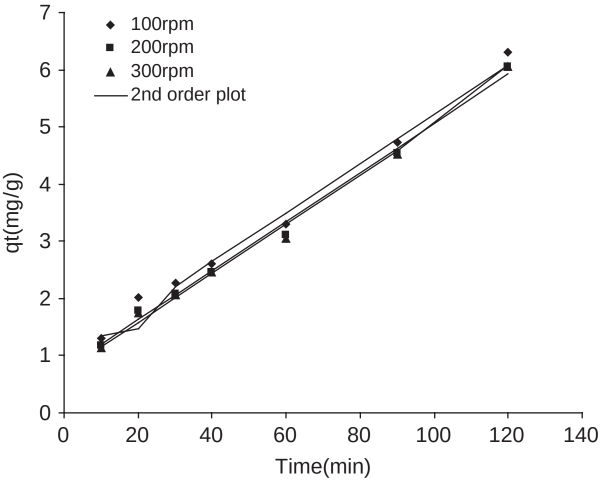

Fig. 5. Applicability of pseudo-second-order kinetic model to experimental data at different agitation speed.

regressed to obtain expressions for these values in terms of agitation speed with high correlation coefficient (r^2 = 0.9863 and 0.9305 respectively). Following the procedure highlighted under the effect of initial concentration, the generalized predictive model which can be used to predict the amount of Cu ion sorbed at any given agitation speed and reaction time was obtained thus:

$$q_t = \frac{t}{\dfrac{1}{0.0015r_{\circ} + 0.9617} + \dfrac{1}{0.0013r_{\circ} + 0.22.897}} \tag{21}$$

Amongst the kinetic models used to analyze the data obtained from the present studies, the applicability of the pseudo second order kinetic model was found to be the best, as shown in the value of the correlation coefficient (r^2) obtained (Tables 1 and 4). This indicates consistency in predicting the amount of Cu (II) ion adsorbed for the entire sorption time and for different initial Cu (II) ion concentration and agitations speed. The q values (mg/g) were predicted by applying the calculated kinetic constants in the kinetic expression for Cu (II) ion. The predicted q (mg/g) values for the pseudo second order kinetic model for the sorption of Cu (II) ion onto ST at different initial Cu (II) ion concentration and agitation speed were plotted against time and presented in Figs. 1 and 4. It was observed that for the entire sorption process and at all initial Cu (II) ion concentration and agitation speed, the pseudo second order kinetic model best predicted the sorption kinetics.

Table 5.
Sorption isotherm models constants and coefficients of determination for the sorption of Cu (II) ion by ST.

Langmuir	Freundlich	Temkin
KL (dm^3/mg) = 0.016	K_f (mg/g)(dm^3/mg)$^{1/n}$ = 2.391	K_t (l/mg) = 2.373
q_m (mg/g) = 34.84	n = 0.4972	B_1 = 6.0688
r^2 = 0.9118	r^2 = 0.9814	r^2 = 0.8776

3.6. Equilibrium isotherm studies

The dynamic adsorptive separation of solute from solution onto an adsorbent depends upon a good description of the equilibrium separation between two phases. The corresponding Langmuir, Freundlich and Temkin isotherm parameters with the regression coefficients values are presented in Table 5.

The equilibrium adsorption plots, relating solid and liquid phase concentrations, for the different isotherms are presented below and the comparative fit of different isotherms with the equilibrium data plotted as q_e versus C_e are presented in Fig. 6.

Langmuir Isotherm:

$$q_e = \frac{0.5574c_e}{1 + 0.016c_e} \tag{22}$$

Freundlich Isotherm:

$$q_e = 2.391{c_e}^{0.4972} \tag{23}$$

Temkin Isotherm:

$$q_e = 6.0688 \ln 2.373c_e \tag{24}$$

The Freundlich isotherm fitted the data better than either the Temkin or Langmuir isotherm models. The Freundlich isotherm is an empirical equation that

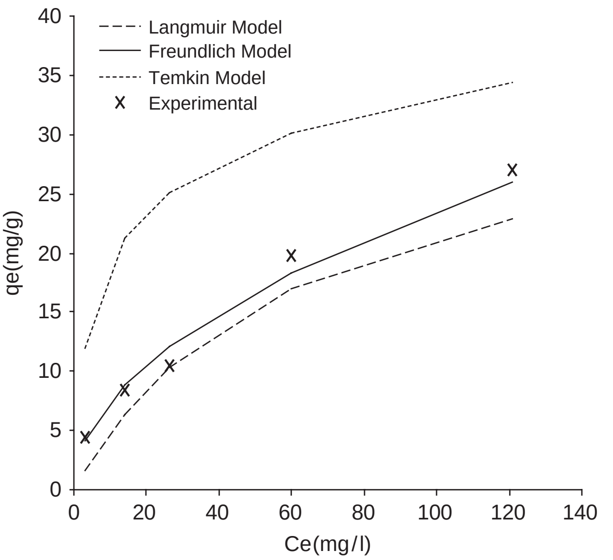

Fig. 6. Applicability of different isotherm plots to experimental data.

Table 6
Comparison of sorption of Cu (II) ion on ST with other adsorbents.

Sorbent	sorption capacity (mg/g)	References
Bagasse fly ash	2.26	Gupta and Alli (2000)
Cork biomass	3.00	Chuba et al., (2004)
Herbaceous peat	4.84	Gundogan et al., (2004)
Oil shale ash	0.098	Shawabkeh et al., (2004)
Rice hulls active carbon	3.92	Teker et al., (1999)
Rubber wood active carbon	5.729	Kalavathy et al., (2005)
Sawdust	0.005	Ajmal et al., (1998)
Scrap tyre	34.84	Present study
Thuja orientalis	19.23	Nugoglu and Oguz (2003)
Turkish coals	1.62	Karabulut et al., (2000)
Wheat shell	10.84	Basci et al., (2004)

encompasses the heterogeneity of sites and the exponential distribution of sites and their energies. Since the *n* (2.011) value is in the range 2–10, it indicates a favorable adsorption. The results presented in Table 6 gives a comparison of the adsorption capacity of Cu (II) ion on different adsorbents taken from the literature.

3.7. Thermodynamic studies

In order to determine if the process of sorption of Cu (II) ion by ST is spontaneous or not, thermodynamic consideration of the sorption process is required. The sorption equilibrium constant, $K_{L,}$ was obtained form the

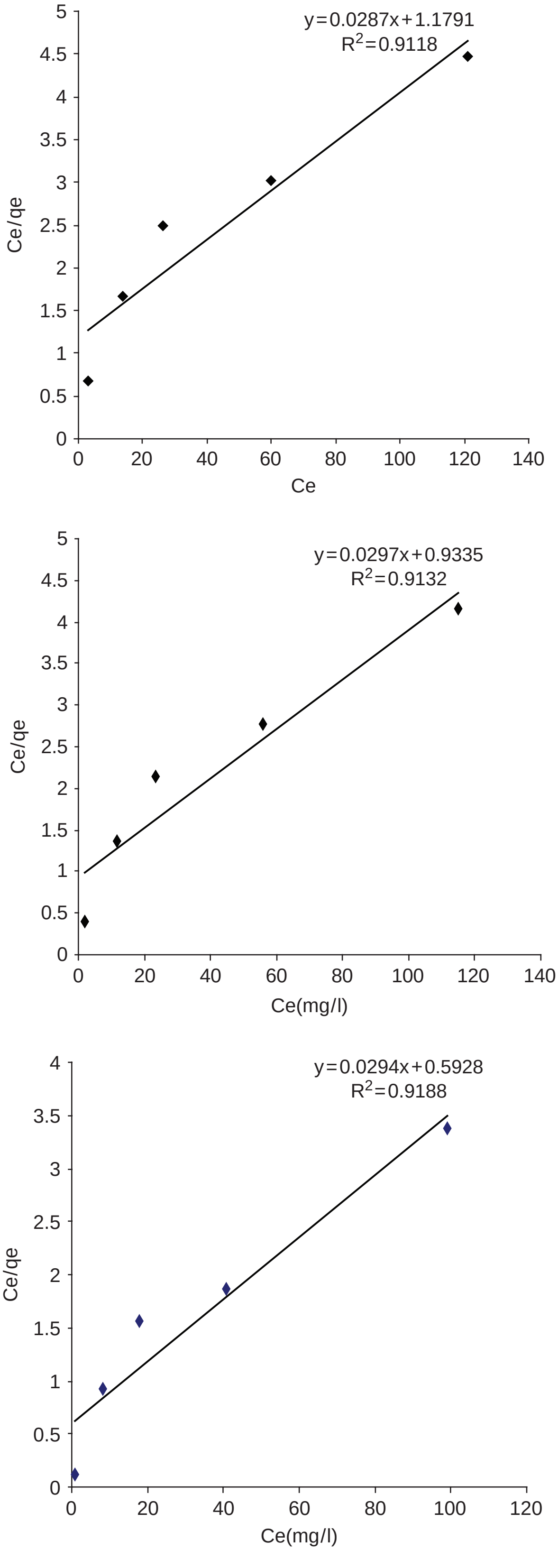

Fig. 7. Langmuir isotherm plot at different temperatures (*a* = 309 K; *b* = 333 K; *c* = 353 K)

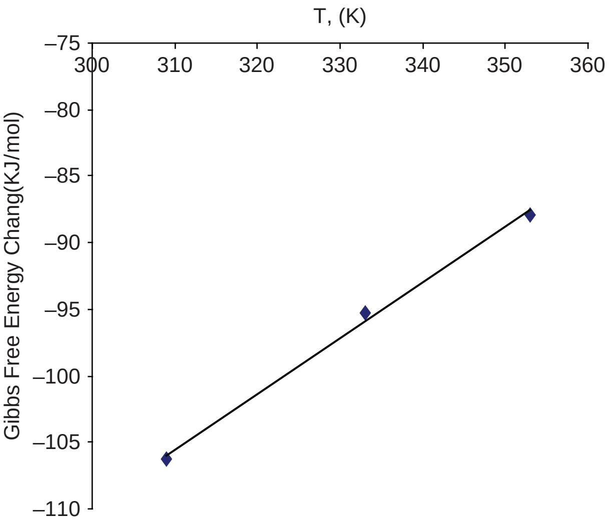

Fig. 8. Relationship between Gibbs free energy change (ΔG^o) and temperature (K) of sorption of Cu (II) ion by ST.

Table 7
Calculated Langmuir constants and thermodynamic parameter for Cu (II) ion sorption by ST.

Temp. (K)	*KL* (dm^3/mg)	q_m (mg/g)	r^2	ΔGo	ΔHo	ΔSo
309	0.016	34.84	0.9118	–106.23	–234.93	0.4174
333	0.032	33.67	0.9132	–95.29		
353	0.050	34.01	0.9188	–87.92		

Langmuir plot of the sorption data at different temperatures (Fig. 7a–c) to obtain the thermodynamic parameter ΔG^o. A plot of Gibbs free energy change ΔG^o versus temperature T (K) was found to be linear (r^2= 0.9964) Fig. 8. The thermodynamic parameters, the free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) were calculated to evaluate the thermodynamic feasibility of the sorption process and to confirm the nature of the process. All the thermodynamic parameters, as calculated, are presented in Table 7. With the increase in temperature, from 309 K to 353 K, the ΔG^o values decreased from –106.23 to –87.92. This indicates that the favorable Cu (II) ion sorption takes place on the ST with decreasing temperature. The negative value of ΔH^o, indicate the exothermic nature of the sorption process. The positive value of ΔS^o reflects the affinity of the ST for Cu (II) ion and suggest some structural changes in Cu (II) ion and ST interactions (Gupta, 1998). In addition positive value of ΔS^o shows increasing randomness at the solid/liquid interface during the sorption of Cu (II) ion onto ST (Ho and Ofomaja 2006).

4. Conclusion

The ability of ST to remove Cu (II) ion from solution was investigated based on the assumption of the Largergren pseudo-first order; the chemisorptions pseudo-second order and the Elovich kinetic model. The effects of initial Cu (II) ion concentration and agitation speed were studied. The overall rate constant of sorption, the equilibrium sorption capacity and the initial sorption rate were predicted with the two process variables. The equilibrium sorption capacity of the ST, as predicted from the kinetic model is a function of the initial Cu (II) ion concentration and agitation speed. The equilibrium sorption of Cu (II) ion by ST was analysed using the Langmuir, Freundlich and Temkin isotherm models. The monolayer sorption capacity of the ST for Cu ion was 34.84 mg/g. The Freundlich isotherm model was the best fitting models for the sorption of Cu (II) ion by ST. The thermodynamic interpretation of the sorption process at different temperatures showed that the sorption of Cu (II) ion by ST is a spontaneous and exothermic process.

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