

# Removal of copper(II) from aqueous solution using spent tea leaves (STL) as a potential sorbent

Sunil Kumar Bajpai<sup>1\*</sup> and Arti Jain<sup>2</sup>

<sup>1</sup>Polymer Research Laboratory, Department of Chemistry, Govt. Model Science College (Auton.), Jabalpur (M.P.) 482001, India

<sup>2</sup>Department of Chemistry, Shri Ram Institute of Science and Technology, Jabalpur (M.P.) 482001, India

## Abstract

In this work spent tea leaves were used as a non-conventional, cost-effective sorbent for removal of Cu(II) from aqueous solutions in batch systems. The sorbent was characterised with respect to surface area, pore volume, density, etc. The equilibrium sorption data were applied to various sorption isotherm models, and the order of fitness was: Langmuir > Temkin > Freundlich. The maximum sorption capacity  $Q_0$  was found to be almost 90.9 and 68.4, as evaluated using Langmuir isotherms at 27°C and 37°C respectively. The observed decrease in sorption capacity with temperature indicated the exothermic nature of the uptake process. The kinetic uptake data were best interpreted by a pseudo second-order kinetic model with values of rate constants of adsorption of  $1.47 \times 10^{-2}$  and  $3.01 \times 10^{-2}$  g/mg-min, respectively, for the initial sorbate concentrations of 10 and 20 mg·l<sup>-1</sup> at 27°C. The sorption mean free energy was determined from the Dubinin Radushkevich (DR) isotherm model and was found to be 9.91 kJ·mol<sup>-1</sup>, indicating ion exchange/chemisorption nature of uptake process. The Cu(II) uptake was found to increase with the pH of the sorbate solution and maximum sorption was observed in the pH range of 1.0 to 4.8. Finally, thermodynamic parameters like  $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  were also evaluated.

**Keywords:** Spent tea leaves, copper(II), adsorption, Langmuir model

## Introduction

The presence of heavy metal ions from the transition metal series, viz, Ni, Fe, Cu, etc., in aquatic systems poses a major threat to the environment, due to their acute toxicity to many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not degrade into harmless end-products (Gupta et al., 2001). These metals enter into urban wastewater which, on being used in irrigation, results in accumulation of these metals in the surface soils. After saturation, surface soils release these contaminants into groundwater and soil solution for plant uptake. Wastewater irrigation further enhances the heavy metal content of soils (Singh et al., 2004).

Copper is one of the major contaminants released from metal-finishing, electroplating and electrical industries. In humans, copper toxicity causes itching and dermatisation and keratinisation of the hands and soles of feet (Huang et al., 2007). Severe gastro-intestinal irritation and possible changes in the liver and kidneys occur due to intake of large doses of copper (Ajmal et al., 1998). Inhalation of copper spray increases the risk of lung cancer among exposed workers (Aydin et al., 2008). According to the World Health Organisation (WHO) and United State Environmental Protection Agency (USEPA), the maximum permissible limit of copper in drinking water is 1.3 mg·l<sup>-1</sup> (Hach, 2003). Hence the removal of copper from wastewater before its discharge into aquatic systems is extremely important and deserves immediate attention.

Out of various methods employed for the removal of Cu(II) from aqueous solution, adsorption appears to be the most frequently adopted technique (Bajpai and Rohit., 2007). In addition, continuous attempts have been made to develop low cost non-conventional adsorbents for removal of toxic metal ions including Cu(II). These adsorbents include newspaper pulps (Chakravarty et al., 2008), pomegranate peel (El-Ashtoukhy et al., 2008) waste tea fungal biomass (Razmouky et al., 2008), potato peels (Aman et al., 2008), soybean hulls (Yadav et al., 2008), pine cone powder (Ofomaja et al., 2009), areca – a food waste (Zhang et al., 2008), orange peel (Ningchuan et al., 2008), pecan nutshell (Vaghetti et al., 2009), modified bagasse (Jiang et al., 2009), maple wood sawdust (Rahman and Islam, 2009), etc.

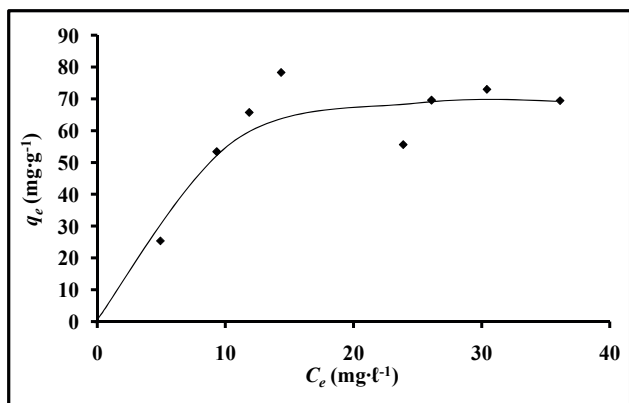
In a continuous attempt to search for potential cost-effective sorbents for removal of toxins from wastewater, we hereby propose spent tea leaves (STL) as a novel sorbent for effective copper removal. Tea is basically the dried and processed leaves of only one species of plant, *Camellia sinensis* (Mokgalaka et al., 2004). It is consumed by the largest number of people in the world and considered the second-most popular beverage in the world. It is estimated that somewhere between 18 and 20 billion cups of tea are drunk daily on our planet (Razmovski et al., 2008). Canned or bottled tea drinks as well as instant tea drinks are produced on industrial scale by hot water extraction of tea leaves, and producers face a great problem in disposing of the spent tea leaves after extraction. Therefore utilisation of STL is also desirable. The insoluble part of the spent tea leaves consists of mainly cellulose (37%), hemicellulose and lignin (14%), and polyphenols (25%). According to chemical analyses reported by Harler (1963), these components constitute almost 80% of the insoluble portion of spent tea leaves. The presence of hydroxyl and phenolic groups led us to think that these polar groups could work as active sorption sites for the uptake of transition metal ions like Cu (II).

\* To whom all correspondence should be addressed.

☎ +919993220651; fax: +91761320737;

e-mail: [polymerlab@rediffmail.com](mailto:polymerlab@rediffmail.com); [sunil.mnlbpi@gmail.com](mailto:sunil.mnlbpi@gmail.com)

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**Figure 1**  
Langmuir isotherm for methylene blue uptake on spent tea

## Experimental

### Materials

Chemicals copper sulphate, sodium hydroxide and potassium ferrocyanide were obtained from Hi Media Laboratories, Mumbai, India and used as received.

### Preparation of spent tea leaves (STL) sorbent

In order to prepare sorbent spent tea leaves (STL), dust tea (Flora Tea Company, Jabalpur, India) was purchased from a local shop and was boiled repeatedly with water until the filtrate was almost clear. The residue was oven-dried at 60°C for 48 h. The dried sample was ground and sieved to obtain a particle size of 250 to 211  $\mu\text{m}$  and stored in plastic bottles for further use. No other physical or chemical treatment was performed on the spent tea leaves (STL) thus obtained.

### Characterisation of STL sorbent

The specific surface area of the sorbent was determined using methylene blue (MB) sorption method, as described elsewhere (Unnithan et al., 2002). In brief, methylene blue aqueous solutions, in the concentration range of 10  $\text{mg}\cdot\text{l}^{-1}$  to 50  $\text{mg}\cdot\text{l}^{-1}$ , were allowed to agitate with 0.1 g of sorbent till the attainment of equilibrium. The concentration of MB solutions was determined at 664 nm. The adsorption isotherm data thus obtained (Fig. 1) was used to calculate specific surface area as per the equation below:

$$S_s = (M_f N / 10^5) A_m 10^{-20} \text{ m}^2\cdot\text{g}^{-1} \quad (1)$$

where  $M_f$  is the amount of MB (in  $\mu\text{mol}$ ) adsorbed per 100 g of the sorbent when the surface is completely covered with a monolayer of MB,  $N$  is the Avogadro number, and  $A_m$  is the cross-sectional area per molecule on the surface ( $130 \text{ \AA}^2$ ).

The value of  $M_f$  was obtained by extrapolating the isotherm to the  $q_e$  axis, and thus taken as point of monolayer coverage. In addition, other physical parameters such as moisture content, specific gravity, pore volume, true density and bulk density were also determined, as described elsewhere (Bajpai and Tankhiwale, 2008). The physical characteristics of STLs are given in Table 1.

Parameters	Value
Specific surface area ( $\text{m}^2\cdot\text{g}^{-1}$ )	175.5
Specific gravity ( $\text{g}\cdot\text{ml}^{-1}$ )	0.284
True density ( $\text{g}\cdot\text{ml}^{-1}$ )	1
Apparent density ( $\text{g}\cdot\text{ml}^{-1}$ )	0.25
Pore volume ( $\text{ml}\cdot\text{g}^{-1}$ )	3
Moisture content (%)	12.30

### Cu(II) uptake studies

The stock solution of Cu(II) was prepared by dissolving a pre-calculated quantity of  $\text{CuSO}_4$  in double-distilled water to obtain a final concentration of Cu(II) ions of 100  $\text{mg}\cdot\text{l}^{-1}$ . This stock solution was further diluted to obtain standard solutions with concentrations in the range of 10 to 60  $\text{mg}\cdot\text{l}^{-1}$ . To carry out adsorption experiments, 50 ml of Cu(II) solution of desired concentration was placed in a 125 ml Erlenmeyer flask containing 0.01 g of STL sorbent, and was agitated in a thermostat-controlled water bath (Rivotek, India) at a constant speed of 50 r/min for 2 h. At the end of the experiment the solution was filtered and supernatant was analysed spectrophotometrically (APHA, 1989) to determine the concentration of Cu(II). The per cent sorption and amount of sorbate sorbed in mg per gram of sorbent i.e.  $q_e$  ( $\text{mg}\cdot\text{g}^{-1}$ ) were evaluated using the following equations:

$$\% \text{ Sorption} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

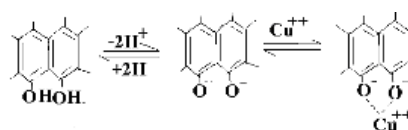
$$q_e = \frac{C_o - C_e}{W_o} \times V \text{ (mg}\cdot\text{l}^{-1}) \quad (3)$$

where  $C_o$  and  $C_e$  are the concentration ( $\text{mg}\cdot\text{l}^{-1}$ ) of Cu(II) solution at the beginning and at the end of the adsorption experiment, respectively,  $V$  is volume of sorbate solution ( $\ell$ ) and  $W_o$  is the amount (g) of sorbent

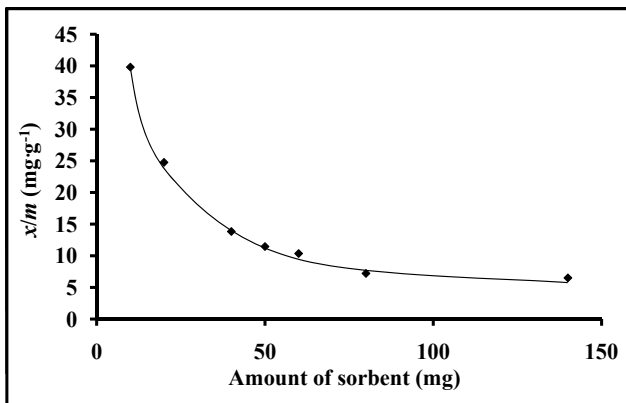
## Results and discussion

### Cu(II) uptake by spent tea leaves (STL)

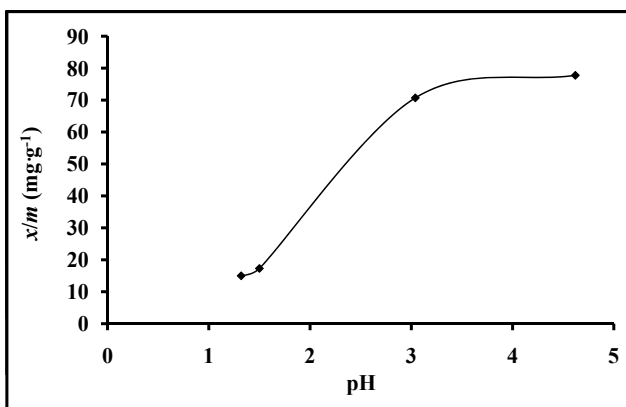
The chemical composition of the insoluble portion, obtained after hot water extraction of green tea leaves, is cellulose (37%), lignin and structure proteins (14.7%) hot water insoluble proteins (12%) and polyphenols (25%) as major constituents. Being polar in nature, these may have specific binding sites available for adsorption of other molecular or ionic species. For example, polyphenols may bind with Cu(II) ions as shown in Scheme 1. In addition, electron-rich oxygen atom of -OH groups of cellulose can also act as binding sites for uptake of Cu(II) ions. Hence, there are good prospects for adsorption of various types of inorganic/organic compounds onto waste tea residues.



**Scheme 1**  
Scheme showing adsorption of Cu (II) onto polyphenolic groups leaves



**Figure 2**  
Effect of sorbent dose on Cu(II) uptake at 27°C



**Figure 3**  
Effect of pH of the sorbate solution on Cu(II) uptake

### Effect of adsorbent dose on Cu(II) uptake

In order to investigate the effect of sorbent dose on the amount of Cu(II) sorbed per gram of sorbent (i.e.  $q_e$ ,  $\text{mg}\cdot\text{g}^{-1}$ ), experiments were conducted at initial Cu(II) concentration of  $40 \text{ mg}\cdot\text{l}^{-1}$ , by agitating sorbate solutions with varying amounts of sorbent. The results, as depicted in Fig. 2, clearly indicate that for a sorbent dose of 10 mg the Cu(II) uptake was around  $40.0 \text{ mg}\cdot\text{g}^{-1}$ , and continued to decrease with further increase in sorbent dose. This may simply be attributed to the fact that increase in sorbent dose occurs in a greater proportion relative to a corresponding enhancement in Cu(II) uptake. This finally results in a decrease in the amount of Cu(II) sorbed per gram of STL sorbent. Since various parameters involved in the interpretation of kinetic and equilibrium uptake data are evaluated using expressions involving the term  $q$ , it is important to assess the conditions for optimum uptake in terms of  $\text{mg}\cdot\text{g}^{-1}$ ; therefore, all further experiments were carried out by using 0.010 g of sorbent particles.

### Effect of sorbate solution pH on Cu(II) uptake

In the adsorption studies, final pH of the sorption system plays an important role in affecting the extent of sorption. The variation in pH of the sorbate solution not only affects the charge profile of the sorbent but also adds additional  $\text{H}^+/\text{OH}^-$  ions to the sorption system. These ions may sometimes compete with the sorbate in occupying active sites.

The effect of solution pH on Cu(II) uptake was studied by agitating 0.01 g of STL sorbent in 50 ml of  $40 \text{ mg}\cdot\text{l}^{-1}$

concentration of Cu(II) solutions with final pH range of 1 to 4.8 at 27°C. The results, as shown in Fig. 3, indicate that Cu(II) uptake increases with pH of the solution and later attains near-saturation approaching a pH value of 4.8. The observed findings may be explained as follows: When the pH of the copper (II) solution is quite low (i.e. 1.0) there is an excess of  $\text{H}^+$  ions in the solution, which compete with Cu(II) ions for adsorption onto binding sites available in the STL sorbent particles. As a result, Cu(II) uptake is quite low. However, as the pH of the solution is increased, the number of  $\text{H}^+$  ions in the sorbate solution continues to decrease, thus providing greater opportunity for Cu(II) ions to occupy available active sites. As the pH of the sorbate solution reaches 4.8, maximum copper (II) uptake is obtained. Similar observations have been reported by Razmowski et al. (2008) for adsorption of Cu(II) and Cr(VI) onto tea fungal biomass. Here it is noteworthy that the effect of pH could not be studied beyond a pH of 4.8 as the Cu(II) ions began to precipitate as hydroxides in the form of visible flocs. Therefore, beyond pH 4.8, the removal of Cu(II) from the solution is mainly due to precipitation, not adsorption (Alimohamadi et al., 2005).

### Equilibrium Cu(II) uptake studies

Studies of adsorption isotherms are essential for the description of how a sorbate distributes itself between the liquid phase and the solid phase, and are useful to optimise the experimental conditions for obtaining maximum sorbate uptake (Emmanuel et al., 2007). The Langmuir model (Langmuir, 1918) was applied to the equilibrium uptake data obtained for sorption of Cu(II) ions from their solutions, with initial concentrations in the range of 5 to  $45 \text{ mg}\cdot\text{l}^{-1}$ , onto STL sorbent particles at 27 °C and 37°C. The Langmuir isotherm model may be given as:

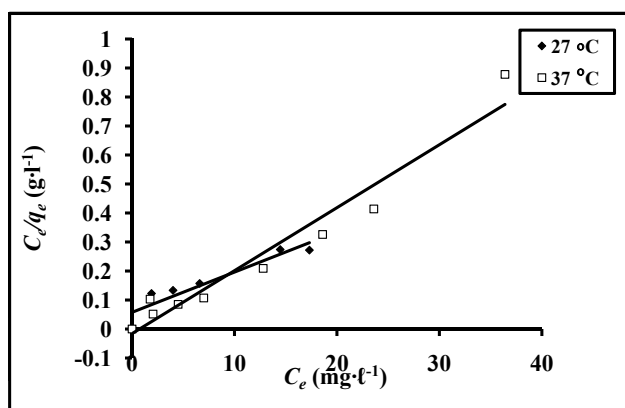
$$\frac{C_e}{Q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (4)$$

where  $C_e$  is the equilibrium concentration in  $\text{mg}\cdot\text{l}^{-1}$ ,  $Q_e$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the amount of Cu(II) sorbed at equilibrium,  $b$  ( $\text{l}\cdot\text{mg}^{-1}$ ) is the coefficient related to the affinity between sorbate and sorbent and  $Q_o$  ( $\text{mg}\cdot\text{g}^{-1}$ ), is the maximum sorbate uptake that could be obtained under the given conditions. The isotherms plotted are shown in Fig. 4. The relatively higher regression values of 0.9663 and 0.9477, obtained for Langmuir plots at 27°C and 37°C, respectively, indicated fair suitability of this model to the present sorbent-sorbate system. The values of Langmuir constant  $b$  and maximum sorption capacity  $Q_o$  were obtained using slopes and intercepts of the linear plots and are given in the Table 2, along with their corresponding theoretical values obtained by regression analysis. It is quite clear from the data given in Table 2 that experimental values of  $b$  and  $Q_o$  are in fair agreement with those obtained by regression analysis. Here, it is also worth mentioning that the reason for selecting 27°C and 37°C as the experimental temperature was that these are the room temperatures frequently found in different parts of

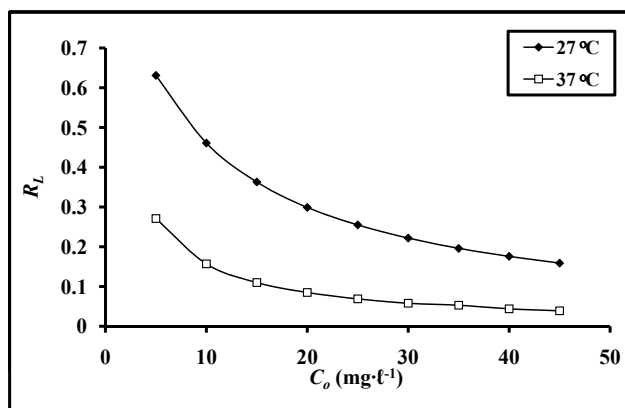
TABLE 2 Parameters for Langmuir isotherms obtained at 27°C and 37°C					
Temp. (°C)	$R^2$	Langmuir parameters obtained by:			
		Graphical method		Regression method	
		$Q_o$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$b$ ( $\text{l}\cdot\text{mg}^{-1}$ )	$Q_o$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$b$ ( $\text{l}\cdot\text{mg}^{-1}$ )
27	0.9663	90.90	0.116	90.82	0.120
37	0.9477	68.49	0.536	68.19	0.532

**TABLE 3**  
**A comparative depiction of values of  $Q_o$**   
**(i.e. maximum sorption capacity) obtained**  
**by using different adsorbents**

Name of adsorbent	$Q_o$ ( $\text{mg}\cdot\text{g}^{-1}$ )	Reference
Spent tea leaves	90.00	Present work
Newspaper pulp	10.94	Chakravarty et al., 2008
Nylon based membrane	10.97	He et al., 2008
Pomegranate peel	13.87	El-Ashtoukhy et al., 2008
Tea fungal biomass	2.20	Razmovski et al., 2008
Calcium alginate beads	0.08	Papageorgiou et al., 2008
Pecan nutshell	0.07	Vagheti et al., 2009
Orange peel	50.25	Ningchuan et al., 2008
Areca-A food waste	2.84	Zhang et al., 2008
Cation exchanger sawdust	26.10	Bajpai and Rohit, 2007
Potato peels	0.38	Amam et al., 2008



**Figure 4**  
 Langmuir plots for Cu(II) uptake at 27°C and 37°C



**Figure 5**  
 Variation of separation factor  $R_L$  with different initial concentrations

the country India, for most of the year, and so experiments can conveniently be carried out at these temperatures.

It is also evident that the value of maximum sorption capacity  $Q_o$  decreases with temperature thus suggesting that sorption is favoured at lower temperatures. This may simply be explained on the basis of the fact that at higher temperature kinetic energy of sorbate Cu(II) ions is so high that they do not bind firmly with the active sites available on the sorbent surface. Similar types of results have also been reported by other

workers (e.g. He et al., 2008; Papageorgiou et al., 2008) It is noteworthy to mention here that we also applied the Freundlich and the Temkin isotherm model on the equilibrium uptake data but the regressions were quite poor (i.e. < 0.8000) and hence data have not been reported. We also compared the maximum sorption capacity  $Q_o$ , obtained in the present study, with those obtained using other sorbents (see Table 3). A close look at the values displayed reveals that the present sorbent (STL) has a fair maximum Cu(II) uptake value as compared to the other sorbents used in the recent past.

According to Venkata et al. (2002), the essential characteristics of Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor  $R_L$  that is given as:

$$R_L = \frac{1}{1 + bC_o} \quad (5)$$

where  $C_o$  is the highest initial concentration of sorbate ( $\text{mg}\cdot\text{l}^{-1}$ ), and  $b$  ( $\text{l}\cdot\text{mg}^{-1}$ ) is the Langmuir constant. The value of  $R_L$  indicates the shape of the isotherm to be either unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ).  $R_L$  values between 0 and 1 indicate favourable adsorption. The  $R_L$  values were calculated using the equilibrium sorption data obtained at 27 °C and 37°C, and variation of  $R_L$  with initial concentration  $C_o$  are shown in Fig. 5. It can be seen that  $R_L$  values are in the range of 0.631 to 0.159 and 0.271 to 0.039 for 27 °C and 37°C, respectively, thus indicating that although adsorption is favourable at both temperatures, it is more favourable at 27°C. In addition, at high initial Cu(II) concentrations it is almost irreversible. Similar results have also been reported elsewhere (Razmovski et al., 2008).

Finally, in order to find out the nature of the uptake process, i.e. whether physical or chemical, the equilibrium data, obtained for 27°C, were analysed using the Dubinin Radushkevich (D-R) isotherm model which is given as:

$$C_{ad} = C_m \cdot \exp(-B\varepsilon^2) \quad (6)$$

where  $C_{ad}$  is amount of Cu(II) sorbed in  $\text{mol}\cdot\text{g}^{-1}$ ,  $C_m$  is the maximum amount of Cu(II) that could be sorbed under optimised experimental conditions,  $B$  is a constant with a dimension of energy, and  $\varepsilon$ , Polyanyni potential, is given as:

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (7)$$

where  $R$  is the gas constant in  $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ,  $T$  is absolute temperature and  $C_e$  is equilibrium concentration in  $\text{mol}\cdot\text{l}^{-1}$ . The linearised form may be given as:

$$\ln C_{ad} = \ln C_m \cdot \exp(-B\varepsilon^2) \quad (8)$$

The equilibrium Cu(II) uptake data, obtained at 27°C, was used to draw a plot between  $\ln C_{ad}$  and  $\varepsilon^2$  as shown in Fig. 6. A higher regression of 0.9672 indicates suitability of D-R isotherm on equilibrium uptake data. The computed value of  $B$ , obtained from slope of the linear plot, was  $5.1 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-2}$ . From the calculated value of  $B$ , the mean sorption energy was computed as  $E = 1/\sqrt{-2B}$ , which is the free energy of transfer of 1 mole of solute from infinity to the surface of the sorbent. The numerical value of  $B$  was found to be  $9.910 \text{ kJ}\cdot\text{mol}^{-1}$ , which lies within the prescribed range of 8 to  $16 \text{ kJ}\cdot\text{mol}^{-1}$  for ion-exchange or chemisorption. Bajpai and Rohit (2009) report a similar finding in a study on uptake of Cr(VI) onto a sawdust ion-exchanger.

## Kinetic studies of Cu(II) uptake

The effect of contact time and initial concentrations of Cu(II) solutions on dynamic uptake of Cu(II) was investigated with Cu(II) solutions of initial concentrations of 10 and 20 mg·l<sup>-1</sup> at 27°C. The results, as depicted in Fig. 7, indicate that for a given initial concentration of sorbate solution, the amount of Cu(II) sorbed per unit mass of sorbent (i.e.  $q_t$  in mg·g<sup>-1</sup>) increases with time and then attains saturation value. Moreover, for a given time, the amount of Cu(II) uptake increases with increase in initial concentration of solution. The amounts of Cu(II) sorbed at equilibrium were found to be 36.40 and 62.55 mg·g<sup>-1</sup> for the Cu(II) solutions with initial concentrations of 10 and 20 mg·l<sup>-1</sup>, respectively. Indeed, the initial concentration provides an important driving force to overcome all mass transfer resistances of Cu(II) between solution and solid phase. So, a higher initial concentration shall always enhance the sorption process. It is also indicated from Fig. 7 that maximum Cu(II) uptake takes place in the first 10 minutes and then the sorption process becomes slower and finally attains equilibrium.

The main issue when searching for an appropriate sorption mechanism is to select a mathematical model that not only fits the data with satisfactory accuracy but also complies with a reasonable sorption mechanism. In the present studies 2 kinetic models, namely, the pseudo second-order kinetic model and simple Elovich model, were applied to the kinetic Cu(II) uptake data to make quantitative interpretations.

The pseudo second-order model can be presented in the following form (Ho and McKay, 1999):

$$\frac{dq_t}{dt} = k_s (q_e - q_t)^2 \quad (9)$$

where  $k_s$  is the rate constant of pseudo-second-order model (g·mg<sup>-1</sup>·min). On definite integration of Eq. (9) for boundary conditions  $q_t = 0$  when  $t = 0$ , the following form of equation can be obtained.

$$\frac{t}{q_t} = \frac{1}{(k_s q_e)^2 + \left(\frac{1}{q_e}\right)t} \quad (10)$$

The initial sorption rate constant,  $h$  (mg·g<sup>-1</sup>·min), at  $t = 0$  can be defined as (Ho and McKay, 1999):

$$h = k_s q_e^2 \quad (11)$$

The kinetic Cu(II) uptake data displayed in Fig. 7, were applied to Eq. (10) and plots were obtained between  $t/q_t$  and  $t$  which were almost linear with fairly high regressions (see Fig. 7). The Elovich equation is used successfully to describe second-order kinetics, assuming that the actual solid surface is energetically heterogeneous (Rudzinski and Panezyk, 2002). The Elovich equation is given as

$$q_t = \alpha + \beta \ln t \quad (12)$$

where  $\alpha$  and  $\beta$  are Elovich constants. Figure 8 shows the  $q_t$  versus  $\ln t$  plots obtained using kinetic Cu(II) uptake data for Cu(II) solutions with initial concentrations of 10 and 20 mg·l<sup>-1</sup> at 27°C. The plots obtained were quite linear with relatively lower regressions relative to the pseudo second-order model. Finally various kinetic parameters employed in the above models were obtained by using slopes and intercepts of linear plots depicted in Figs. 8 and 9; these are given in Table 4. A close look at the data displayed reveals

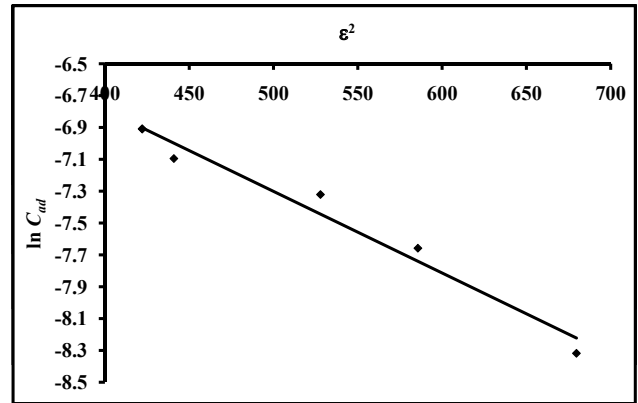


Figure 6

Dubinin-Radushkevich (DR) isotherm for Cu(II)-uptake at 27°C

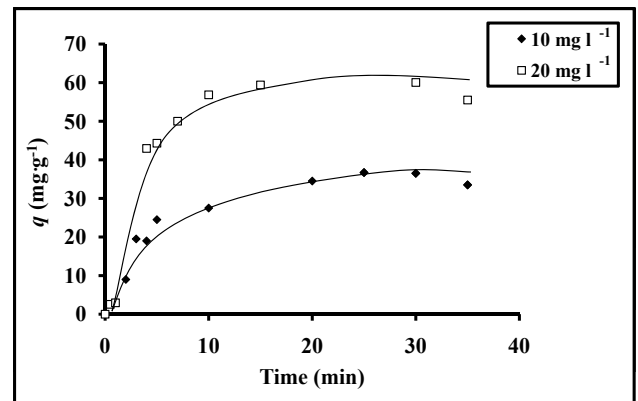


Figure 7

Dynamic uptake of Cu(II) as a function of time for sorbate solutions with initial concentrations of 10 and 20 mg·l<sup>-1</sup> at 27°C

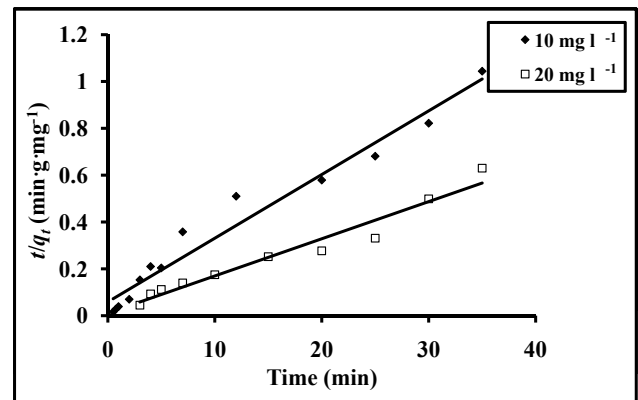


Figure 8

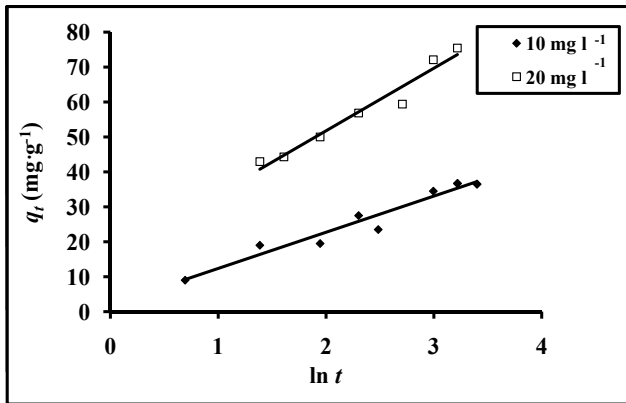
Pseudo second-order kinetic plots for Cu(II) uptake from copper solutions with initial concentrations of 10 and 20 mg·l<sup>-1</sup> at 27°C

that experimental  $q_e$  values (i.e. Cu(II) sorbed in mg·g<sup>-1</sup>) are in close agreement with the theoretical values, thus establishing the fair fitness of the pseudo second-order kinetic model to uptake data. The Elovich constants  $\alpha$  and  $\beta$  have also been depicted. In addition, regression values obtained also indicate that the pseudo second-order model indicates better suitability.

The uptake mechanism of a sorbate onto the adsorbent involves film diffusion, pore diffusion and intra-particle

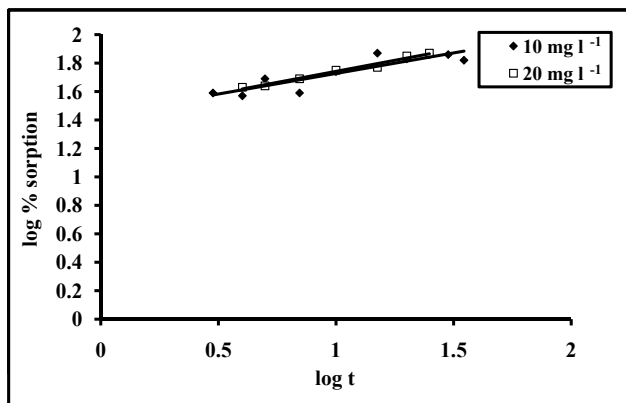
**TABLE 4**  
**Various kinetic parameters obtained for pseudo second-order model and the Elovich model using kinetic uptake data for Cu(II) solutions at 27°C**

Conc. of Cu(II) (mg·ℓ <sup>-1</sup> )	Pseudo second-order model				Simple Elovich model			
	$k_s \times 10^2$ (g·mg <sup>-1</sup> ·min <sup>-1</sup> )	$h$ (min <sup>-1</sup> ·mg·g)	$R^2$	$q_{e'}^{exp}$ (mg·g <sup>-1</sup> )	$q_{e'}^{theor}$ (mg·g <sup>-1</sup> )	$\alpha$	$\beta$	$R^2$
10	1.47	19.43	0.9662	36.36	36.40	4.20	9.44	0.9072
20	3.01	118.70	0.9624	62.80	62.55	5.37	22.15	0.9671



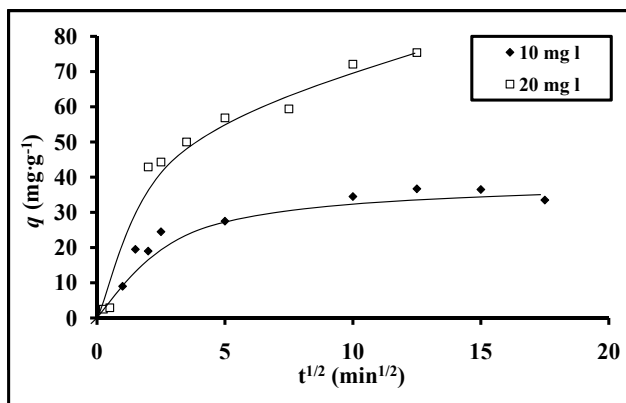
**Figure 9**

Simple Elovich model plots for Cu(II) uptake from copper solutions with initial concentrations of 10 and 20 mg·ℓ<sup>-1</sup> at 27°C



**Figure 10**

Log (% sorption) vs. log t plots for confirmation of intraparticle diffusion



**Figure 11**

Cu(II)-uptake vs.  $t^{1/2}$  plots for sorbate solutions with initial concentrations of 10 and 20 mg·ℓ<sup>-1</sup> at 27°C

transport (Nadeem et al., 2006), of which the slowest is rate limiting and controls the overall sorption process. Generally, the pore diffusion and the intra-particle diffusion are often rate-limiting in a batch reactor (Goswami and Ghosh, 2005). In order to confirm the occurrence of the intra-particle diffusion phenomenon, we followed the observations of Raghuvanshi et al. (2004) who suggested a linear plot between log (time) and log (per cent adsorption) in the case of intra-particle diffusion. The plots of log (time) versus log (per cent adsorption), as shown in Fig. 10, clearly confirm that intra-particle diffusion does occur in the present study. An empirically functional relationship, common to most adsorption processes, is that the sorbate uptake varies almost proportionally with  $t^{1/2}$ , the Weber Morris plot, rather than with the contact time,  $t$  (Weber and Morris, 1963):

$$q_t = k_{id} t^{1/2} + C \quad (13)$$

where  $k_{id}$  is the intraparticle diffusion rate constant. According to Eq. (13), a plot of  $q_t$  versus  $t^{1/2}$  should be a straight line with a slope  $k_{id}$  and intercept  $C$  when the adsorption mechanism follows the intra-particle diffusion process. The value of the intercept gives an idea about the thickness of the boundary layer, i.e. the larger the intercept the greater will be the boundary layer effect (Unnithan et al., 2002). In Fig. 11, plots of mass of Cu(II) ions sorbed per unit mass of STL sorbent,  $q_t$  versus  $t^{1/2}$ , are presented. It is evident that the plots are not only linear but also pass through the origin, thus indicating that the Cu(II) uptake by STL sorbent is almost intra-particle diffusion controlled. The values of  $k_{id}$  obtained using slopes of the linear plots for 10 and 20 mg·ℓ<sup>-1</sup> Cu(II) solutions were found to be  $841.2 \times 10^{-2}$  and  $1637.0 \times 10^{-2}$  mg·g<sup>-1</sup>·min<sup>-1/2</sup>, respectively. Higher values of  $k_{id}$  for higher concentrations of Cu(II) solutions may simply be due to the fact that higher sorbate concentration adds to a greater driving force for diffusion of sorbate molecules into the pores.

### Evaluation of thermodynamic parameters

The thermodynamic parameters that must be considered to characterise the uptake process are the enthalpy of adsorption ( $\Delta H^\circ$ ), the standard Gibbs free energy ( $\Delta G^\circ$ ), and the entropy ( $\Delta S^\circ$ ) changes due to transfer of 1 mole of solute from solution to solid-liquid interface. The standard free energy change ( $\Delta G^\circ$ ) was evaluated by the relation:

$$\Delta G^\circ = -RT \ln K_c \quad (14)$$

where  $R$  is the ideal gas constant (8.314 J mol<sup>-1</sup>·K<sup>-1</sup>) and  $T$  is the absolute temperature (K). The apparent equilibrium constant ( $K_c$ ) of the adsorption process is defined as:

$$k_c = \frac{C_{ad,eq}}{C_{eq}} \quad (15)$$

where  $C_{ad,eq}$  and  $C_{eq}$  are the concentrations of Cu(II) at the adsorbent (mg·ℓ<sup>-1</sup>) and equilibrium concentration (mg·ℓ<sup>-1</sup>)

Temp. (°C)	ln $K_c$	$\Delta G^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta S^\circ$ (JK <sup>-1</sup> ·mol <sup>-1</sup> )
27	0.451	-1.128	-117.91	-0.389
37	0.618	-1.595		-0.375

respectively. The standard enthalpy  $\Delta H^\circ$  is related to the Langmuir constant  $b$  by the well-known Vant Hoff equation

$$\ln \frac{b_1}{b_2} = \frac{-\Delta H^\circ}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad (16)$$

where  $b_1$  and  $b_2$  are Langmuir constants at temperature  $T_1$  and  $T_2$ , respectively. The above relation was used to calculate  $\Delta H^\circ$ . Finally the standard enthalpy change  $\Delta S^\circ$  was calculated using the well-known relationship:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (17)$$

The various thermodynamic parameters, calculated using the above-mentioned relationships, are given in the Table 5. The negative standard free energy change  $\Delta G^\circ$  is indicative of the spontaneous nature of the Cu(II) sorption process. In addition, negative value of  $\Delta H^\circ$  indicate the exothermic nature of the sorption process. The negative value of  $\Delta S^\circ$  indicates greater order during the sorption process. This may probably be explained on the basis of the fact that during the sorption process the co-ordinated water molecules which are displayed by copper ions gain less translational entropy than is lost by Cu(II) species, resulting in decreased randomness. Similar negative entropy change has also been reported elsewhere (Unnithan et al., 2002).

## Conclusion

From the above study it may be concluded that spent tea leaves (STL) bear great potential to be used as a cost-effective adsorbent material for effective removal of Cu(II) ions from aqueous solutions. The sorbent does not require any chemical modification and hence may be considered as an environment-friendly sorbent.

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