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Using spent tea papers as low cost adsorbent to remove copper (II) from simulated wastewater; Kinetic and Equilibrium study

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Abstracts

copper ions removing from waste water was investigated. The sorption behavior of metal ions on spent tea papers, depending on contact time, pH, and initial metal concentration was studied in batch method. The adsorption process, which is PH dependent, shows maximum removal of copper ions at pH of 6; an initial copper ion concentration of 50-250 mg, dosage of 0.25 g, and the equilibrium was reached in 1 hr. The maximum efficiencies removed of Cu^{2+} (about 99.8%). The experimental data were analyzed using Langmuir, Freundlich, and Brauner, Emmett, and Teller (BET), isotherm models. The isotherm coefficients for all these models have been determined. Langmuir isotherm expressions were observed to give better fit to the experimental data compared to Freundlich and BET models. The kinetic data were assessed using Lagergren first order and pseudo second order kinetic models. Kinetic data correlated well with Lagergren first order kinetic model, showing that reversible reaction with an equilibrium being recognized between liquid and solid phase. The results indicate that spent tea papers can be used as an efficient adsorbent for removing copper ions from waste water.

Key words: sorption, spent tea papers, copper, wastewater, isotherm**.**

Introduction

Water pollution raises a great concern todays since water starts a basic requirement in life and therefore, is vital to all living things. The fast-paced development of industries such as metal mining operations, pesticides and fertilizers and paper industries have deliberately discharged numerous types of pollutants into the environment especially in developing countries. The absences of various pollutants such as industrial, mining and agricultural wastes, sewage and domestic wastes are continuously discharged into the water system and additional touching our ecosystem due to their harmful effects. With other issues, water contaminations by heavy metals are more distinct than other pollutants especially when heavy metals are subjected to the natural ecosystem. 'Heavy metals' refers to any features with atomic weights (63.5 - 200.6) and a specific gravity greater than 5.0 [1]. Cadmium, zinc, copper, nickel, lead, mercury and chromium, are some examples of heavy metals which originate from activities of metal plating, mining, battery manufacture, petroleum refining and paint manufacturing [2, 3]. Heavy metals are non-biodegradable pollutants and they are very difficult to eliminate naturally from the environment. Almost all heavy metal elements are highly toxic when their concentration exceeds their permissible limit in the ecosystem. High concentration of heavy metals may accumulate in the human body as soon as they interrupt in human food chain and possibly in effect, cause acute health problems if the metals exceed the permitted concentration [4]. Copper is one of the major contaminants released from metal-finishing, electroplating and electrical industries. In humans, copper toxicity causes dramatization, itching, and keratinization of the hands and soles of feet [5]. Severe gastro-intestinal irritation and possible changes in the liver and kidneys occur due to intake of large doses of copper [6].

In this concern, spent tea papers have been used by many researchers to remove heavy metals and organic pollutants from industrial wastewater. In the present study, a spent tea paper was used as a bio sorbent to remove copper from synthetic contaminated wastewater. Hence, the present study aims to investigate the potential application of spent tea papers as an inexpensive material for the treatment of wastewater contaminated with copper ions.

Materials and Methodes

Materials

Copper was selected as a representative of heavy metal contaminants. To simulate the wastewater's copper contamination, a solution of $Cu(NO_3)_2$ (manufactured by BDH, England) was prepared and added to the specimen to obtain representative concentration. Samples of tea waste were obtained from spent tea papers. Usually, one tea bag was steeped, under gentle stirring, in 125 mL of distilled water at 90°C for 3 min. After this time, spent tea papers were recovered and repeatedly washed with distilled water in order to remove soluble and colored compounds. Then the solid was washed with distilled water and oven dried at 60°C for 24 h. Finally, the dried sample were ground and sieved to particles <500 µm which were stored at room temperature until use.

Equilibrium studies:

Batch adsorption experiments were carried out to determine the best conditions of, initial pH, initial concentration, and contact time. This indicates that these tests are suited to identify the activity of the spent tea papers and the sorption isotherm. Series of 250ml flasks are prepared and each flask was filled with 100 ml of copper solution which has an initial concentration of 50 mg/l. About 0.25 g of adsorbent was added into each flask and the solution was kept stirred in high-speed orbital shaker at

270 rpm for 3 h. A fixed volume (20 ml) of the solution was pipetted out from each flask and this solution was filtered to separate the adsorbent and a fixed volume (10 ml) of the pure solution was taken for determination the concentration of copper ions still present in the solution. The measurements were carried out using atomic absorption Spectrophotometer (Norwalk, Connecticut (USA)). These measurements were repeated twice and the average value has been taken. The concentration of copper ions sorbed on the adsorbent was found by a mass balance. From the best experimental results, the amount of metal ion kept in the spent tea papers, C_s, was determined by using equation. [8]:

$$C_s = (C_o - C_e)\frac{v}{m} \qquad (1)$$

where C_s is the amount of metal separated from the aqueous solution (mg/g), C_o is the initial concentration of metal in the aqueous solution before mixing with adsorbent (mg/l), C_e is the concentration of metal remaining in the aqueous solution at the experiment (mg/l), *v* is the volume of solution in the flask (l), and m is the mass of spent tea papers in the flask (g). The sorption isotherms models were used to find the relationships between the C_s and C_e at the constant temperature. There are three major equations of sorption isotherm specifically the Langmuir , Freundlich and Brauner, Emmet and teller (BET)models. These models are usually used for the description of sorption data. The Langmuir model is:

$$C_s = \frac{qbCe}{1+bCe} \qquad (2)$$

Where *q* is the maximum sorption capacity (mg/g) and *b* is the saturation coefficient (l/mg).

The Freundlich isotherm is calculated by:

$$C_s = K_f Ce^{1/n} \qquad (3)$$

Where *n* is an empirical coefficient and K_F is the Freundlich sorption coefficient.

The BET isotherm has been used to describe sorption of metal ions on spent tea papers as seen in following equation:

$$\frac{X}{C_s\,(1-X)} = \frac{1}{ab} + \frac{(b-1)}{ab}X \qquad (4)$$

Where:

$X = C_e/q_e$

Where (b-1)/ab is the slope and 1/ab is the sorption capacity.

Adsorption kinetics:

Kinetics of sorption refer to uptake rate of the solute, which is turn governs the residence time of sorption reaction, is one of the important characteristics defining the efficiency of sorption. Many researchers have used various kinetic models to calculate the mechanism occupied in the sorption process. These include pseudo-first-order model, pseudo-second-order-order model, Webber and Morris sorption kinetic model, first-order reversible reaction model, external mass transfer model, first-order equation of Bhattacharya and Venkobachar, Elovich's model and Ritchies's equation. Pseudo first order and second order kinetic models are widely used.Lagergren showed that the rate of adsorption of solute on the adsorbent followed a pseudo first-order equation. The pseudo first order lagergren model is expressed as:

$\ln(q_e\text{-}q_t)=\ln q_e\text{-}k_1t$ (5)

$\ln(q_e\text{-}q_t)$ is plotted against t (min). The pseudo first order considers the rate of adsorption site to be proportional to the occupied sites. A pseudo second order equation based on the rate of adsorption is expressed as:

$$\frac{t}{qt} = \frac{1}{k_2\ qe^2}+\frac{t}{q_e} \quad (6)$$

Where K_2 is the second order reaction rate equilibrium constant (g/mg.min).

Results and discussion

Effect of Initial Copper Concentration

Initial copper concentration is important parameter for removing metal ions from simulated wastewater. Figure 1 shows the effect of initial Copper concentration on the percent removal of copper ions, respectively. From this fig.,It is showed that, the percentage removal decreased significantly from 98.76% to31.99% with raising in initial copper concentration from 50 mg/L to 250 mg/. This is because, at low metal ion/adsorbent ratios, metal ion adsorption involves higher energy sites giving higher adsorption efficiency. On the other hand, as the metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decreases in adsorptionefficiency[7].

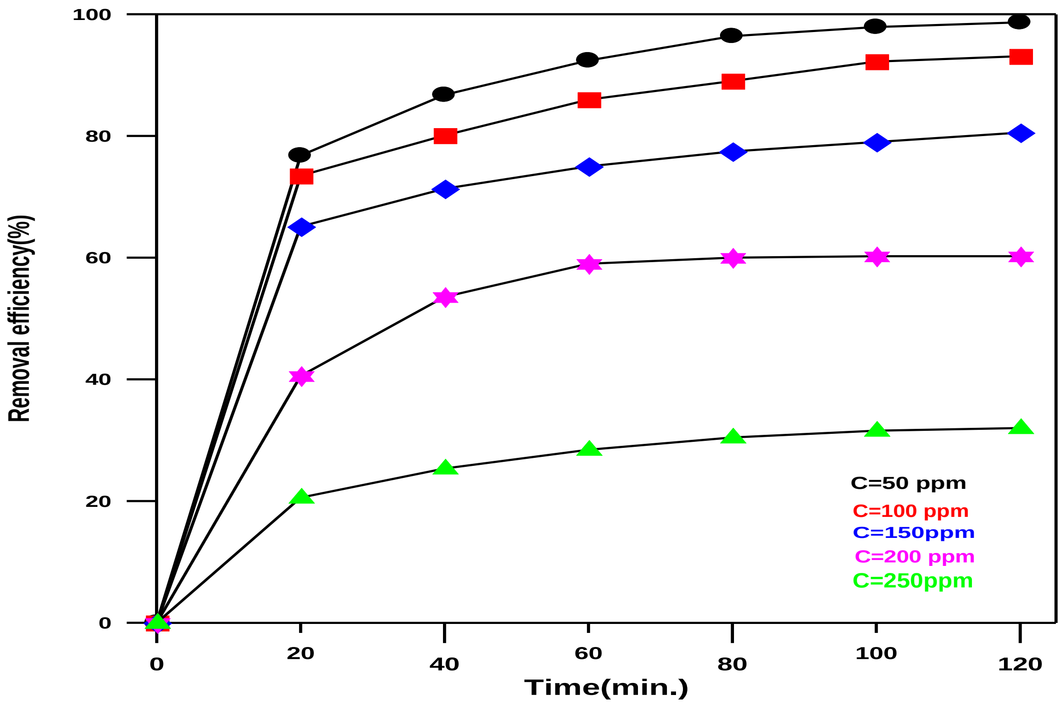

Fig.1. Effect of adsorbent concentration on removal efficiency of copper(contact time = 1 h; speed = 270 rpm; adsorbent dose =0.25 g/ 100ml; pH = 6; T = 25°C).

Contact Time and Initial pH

In batch experiments the time must be indicated at certain value which is attained the equilibrium state for separating. PH is an essential parameter for adsorption of metal ions from aqueous solution because

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it affects the solubility of the metal ions, the speciation of metal in wastewater, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. Therefore, in this research, we estimated the effect of pH on the adsorption of Cu (II) by spent tea papers. The gained results indicate that adsorption capacity of spent tea papers raises by increasing initial pH from 3 to 6. This increase in adsorption can be explained by considering the surface charge of tea waste. Adsorption at acidic pH values is low because of competition between metal ions and H+ ions for the binding sites of the adsorbent and where surfaces have strong positive charge like to that of the Cu ions. Furthermore, at low pH, the amine groups of spent tea papers are protonated to changing degrees, dropping the number of binding sites available for copper uptake [8, 9]. As a result, copper uptake is low in the presence of high concentrations of protons. Whereas at higher pH, the ligands (–COOH, –NH2) attract positively charged copper ion, and binding take place due to an efficient adsorption mechanism that includes an electrostatic interaction between the positively charged groups in spent tea paper and copper ions [10,11].

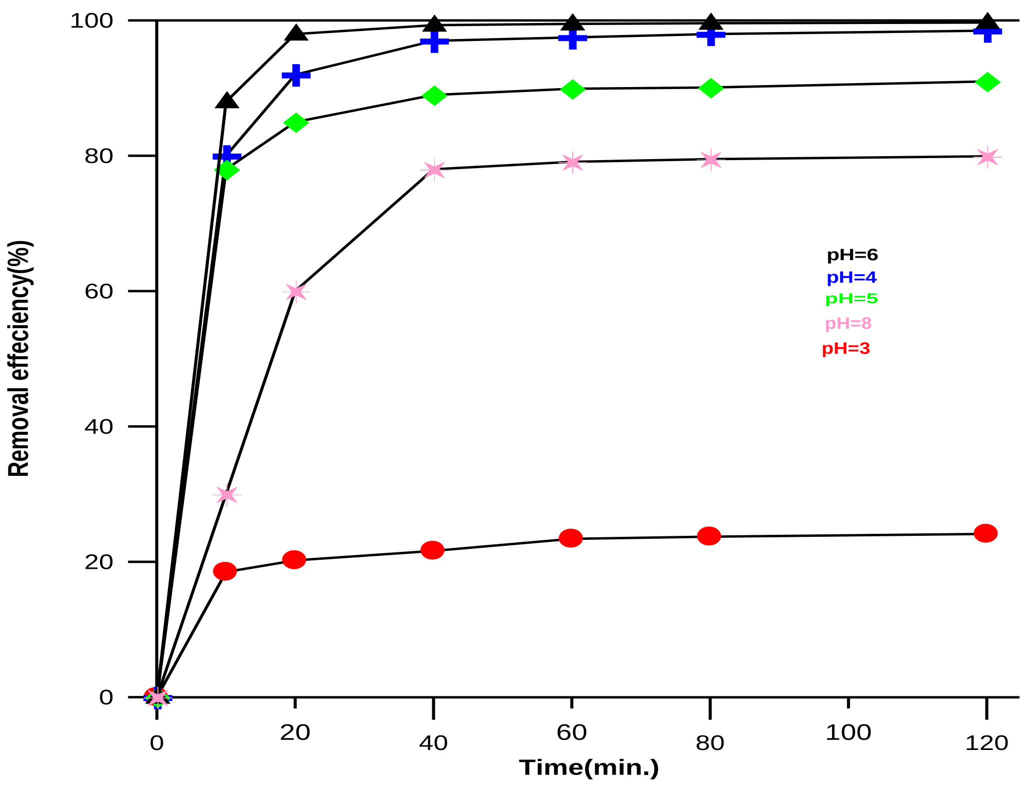

Fig. 2. Effect of pH on removal efficiency of copper (speed = 270 rpm; C_o = 50 mg/l; adsorbent dose=0.25 g/100 ml; T = 25°C).

Sorption Isotherms

Adsorption isotherms are very powerful tools for the evaluation of adsorption process. Adsorption isotherms determine the relationship between the equilibrium concentration and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. Langmuir, Freundlich, and BET isotherms models are widely used to investigate the adsorption process. The model parameters can be seen further, providing understanding on adsorption mechanism, surface properties, and an affinity of the adsorbent. The Langmuir, Freundlich, and BET adsorption constants are estimated from isotherms and their correlation coefficients are given in tables (1). The linearized Langmuir, Freundlich, and BET of copper ions for spent tea papers are given in figures (3), (4), and (5).

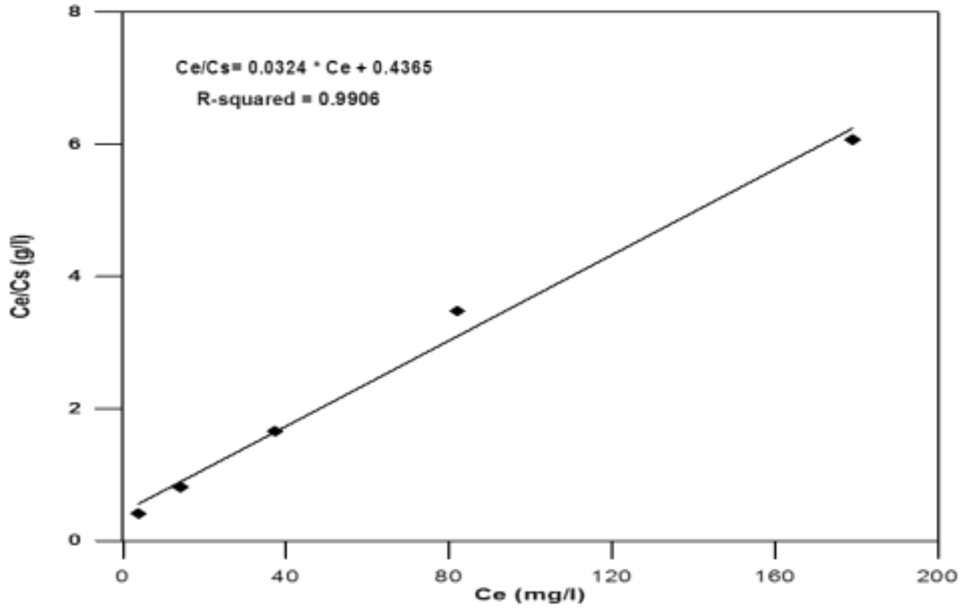

Figure (3): Langmuir model

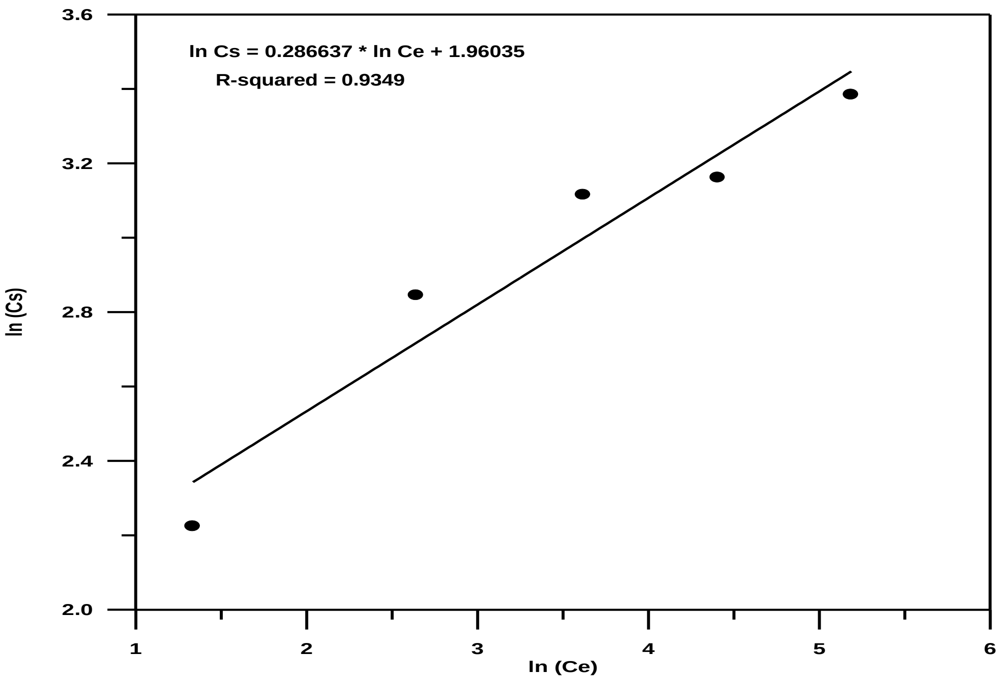

Figure (4): Freundlich model

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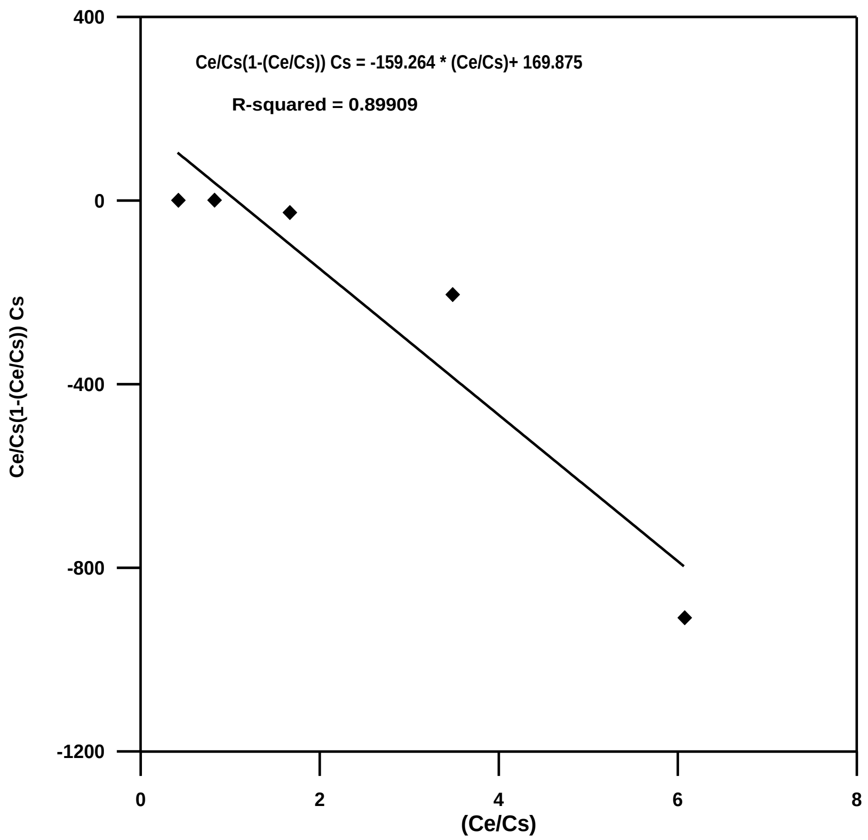

Figure (5): BET model

Table 1: Sorption isotherm constants with coefficients of determination for Cu^{+2} on spent tea papers.

Model	Parameters	Cu^{+2}
Langmuir	a	30.864
	b (l/mg)	0.0742
	R^2	0.9906
Freundlich	K_F (mg/mg)(l/mg)$^{1/n}$	7.1018
	1/n	0.286637
	R^2	0.9349
BET	a	0.0943
	b	0.0624
	R^2	0.89908

The essential feature of the equation can be expressed in terms of dimensionless separation factor, R_L, defined as:

$R_L = \frac{1}{1+b\,C_0}$ (٧) the value of R_L shows the shape of the isotherm to be unfavorable ($R_L > 1$), linear (R_L=1), favorable ($0 < R_L < 1$), or irreversible (R_L =0) [12, 13, 14]. The variation of R_L with the initial metal concentration of solution isshown in figure 6.

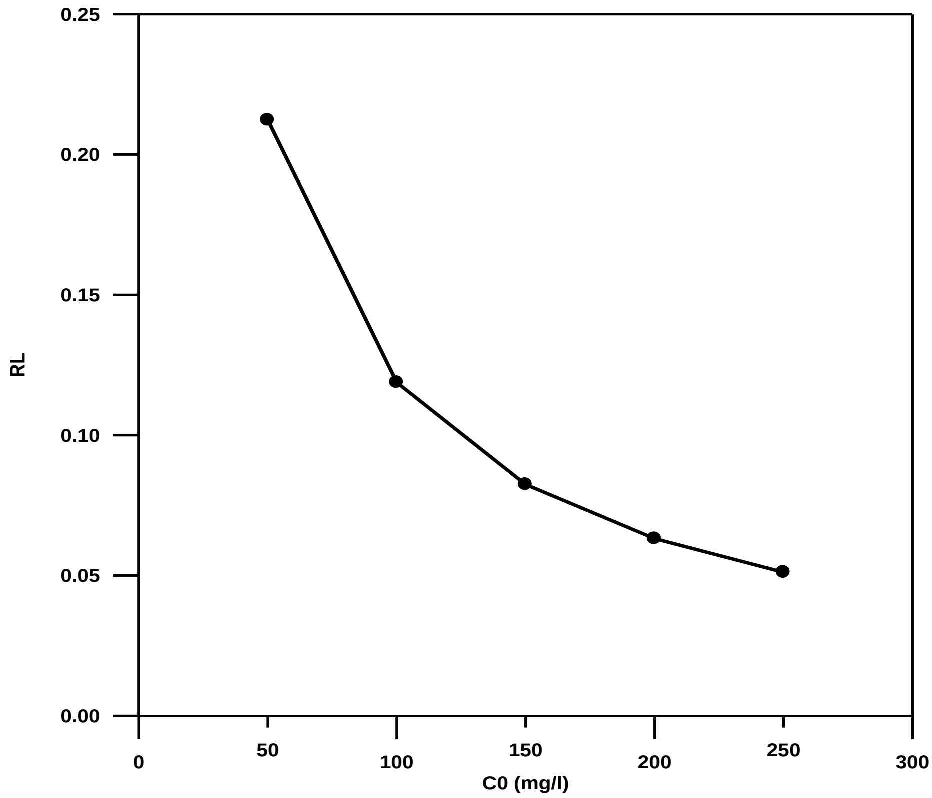

Figure. (6) Variation of adsorption intensity with initial metal concentration on spent tea papers.

It is clear from this figure that all values of S_f within the range from 0 to 1for different values of initial concentration of copper and, therefore, adsorption of copper ions on spent tea papers are favorable. Furthermore, the values of S_f are decreased with increasing of initial copper concentration. This indicates that sorption is more favorable for the higher initial concentration in compared with lower concentration for spent tea papers.

Sorption Kinetics

Kinetic models investigate the behavior of bio sorbent and the rate controlling mechanism of adsorption process.

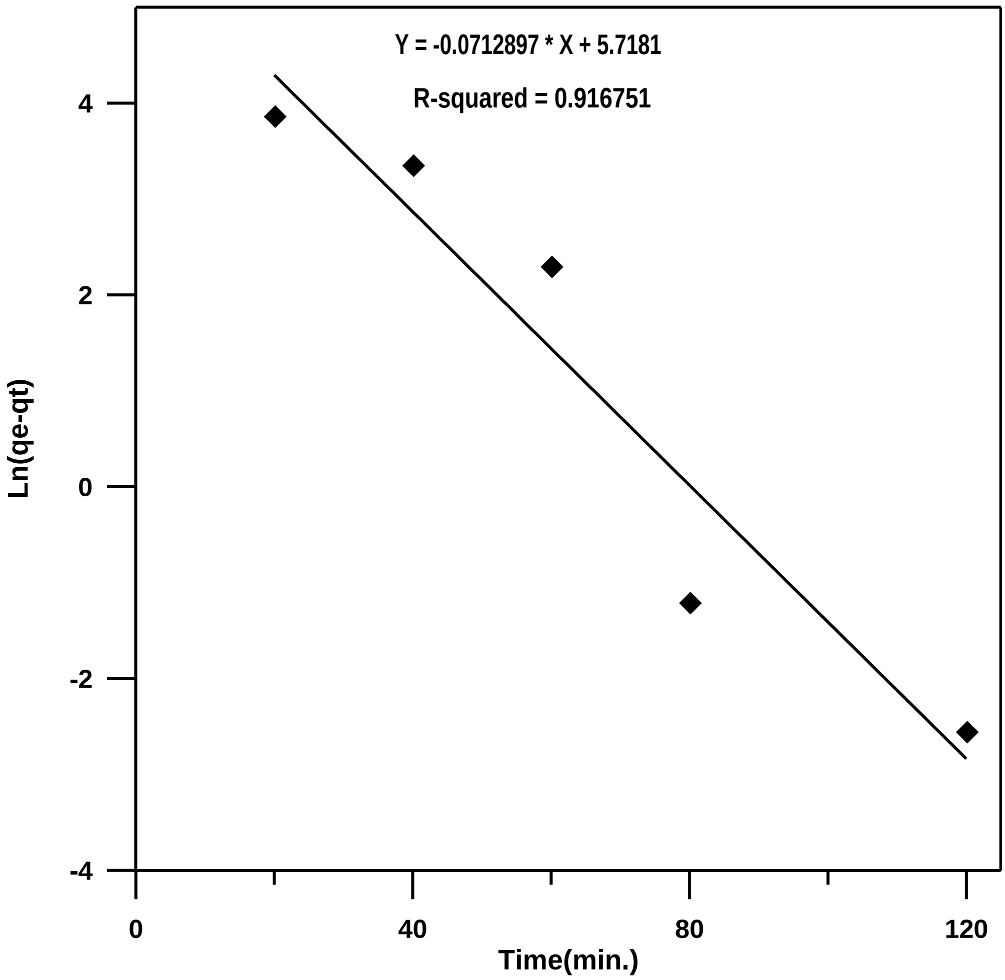

Figure (7): Test of Pseudo first order equation for adsorption of copper, on spent tea papers (PH, 6; speed, 270 rpm; T, 25 ^{0}C, concentration, 50 (mg/l).

Various kinetic parameters obtained for pseudo first-order model using kinetic uptake data for Cu(II) solution

Cu^{2+}Concentration	R^2	$K_1x10^{-3}(min^{-1})$	$q_{e,ex}(mgg^{-1})$	q_e (mg g^{-1})
50(mg/l)	0.916751	-71.2897	304.7901	304.2957

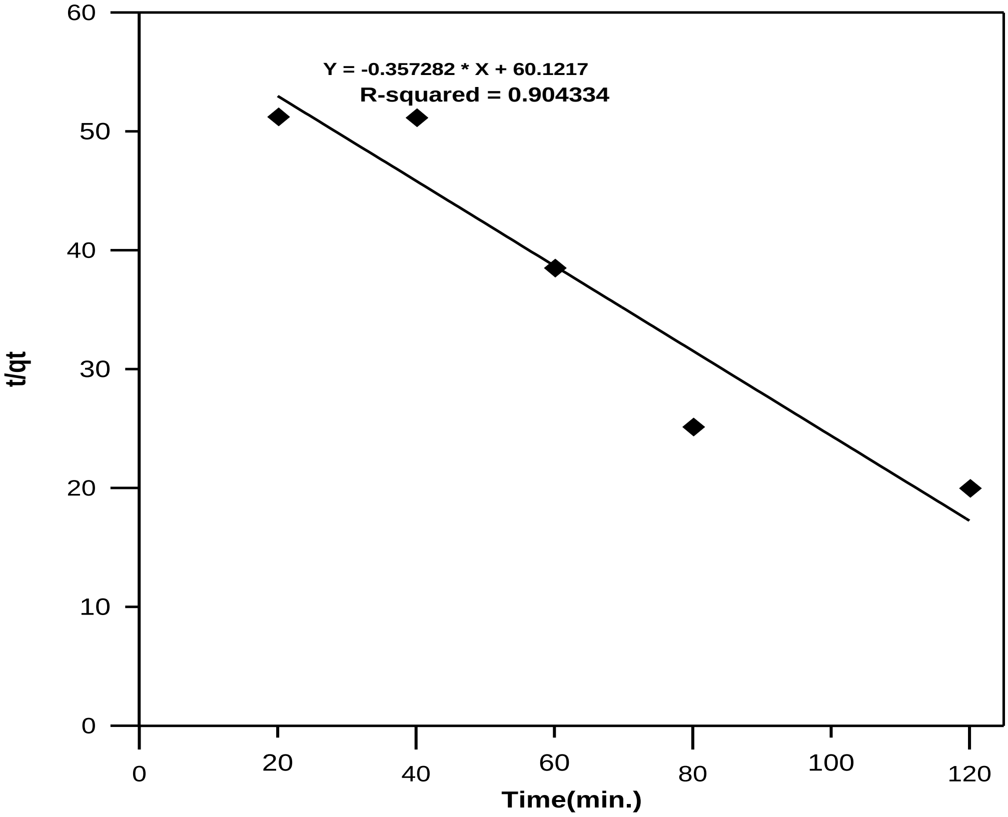

Figure (8): Test of Pseudo second order equation for adsorption of copper on spent tea papers (PH, 6; m, speed, 270 rpm; dosage, 0.25g, T, 25 ^{0}C, concentration, 50 mg/l).

Various kinetic parameters obtained for pseudo second-order model using kinetic uptake data for Cu(II) solution

Cu^{+2}Concentration	R^2	K_1 x 10^{-}(min^{-1})	$q_{e,ex}$(mg g^{-1})	q_e (mg g^{-1})
50(mg/l)	0.904334	1.594	3.2229	2.7989

Conclusion

Copper ions sorption on spent tea papers of its natural and endothermic natures. The copper ions binding capacity of bio sorbent was shown as a function of initial metal ion concentration and spent tea papers. The equilibrium data was fitted very well to both Lagergren and Langmuir sorption isotherms. The equilibrium sorption of copper ions was determined from the Langmuir equation and found to be 11.7 mg/g. The kinetics of copper ion sorption on adsorbent was based on the assumption of the pseudosecond- order mechanism with the chemisorption being important.

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