



## Biosorption of copper(II) ion from wastewater onto green waste tea: Isotherm and kinetic modeling studies

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### ABSTRACT

This paper studied the ability of using green tea waste (GTW) as an environment-friendly biosorbent for the removal of Cu(II) from aqueous solutions by batch operation. Various operating parameters such as equilibrium contact time, initial metal ion concentration, pH, and adsorbent dosage have been studied. The results indicated that the biosorption process was occurred within 120 min. equilibrium contact time for Cu(II) concentration range from 10 to 120 mg/l. It was found that, different concentration of copper solution reached equilibrium at different times. About 0.3 g of GTW was found to be enough to remove 91% of 10 mg/l initial copper ion concentration from 100 ml metal solution. The optimum biosorption capacity was at pH 6. The equilibrium adsorption data for Cu(II) were better fitted to the Freundlich adsorption isotherm model. The kinetic process of Cu(II) biosorption onto GTW was found to fit the pseudo-second-order model. Therefore, it is proven that the GTW can be used as efficient, economical means and environment-friendly to remove Cu(II) presence in the water/wastewater.

**Keywords:** Copper, Biosorption, Equilibrium, Kinetics, Wastewater, Tea Waste.

### INTRODUCTION

Industrial waste constitutes the major source of various kinds of metal pollution in natural water. There are at least 20 metals which cannot be degraded or destroyed. The important toxic metals are *Cd*, *Zn*, *Pb*, *Cr*, *Cu*, and *Ni* [1]. Heavy metals are highly toxic pollutants of increasing concern in developed countries for their significant impact on the environment and human health [2-5].

Copper is one of the major contaminants released from metal-finishing, electroplating and electrical industries [6]. In humans, copper toxicity causes itching and dermatisation and keratinisation of the hands and soles of feet [7]. Severe gastro-intestinal irritation and possible changes in the liver and kidneys occur due to intake of large doses of copper [8]. Inhalation of copper spray increases the risk of lung cancer among exposed workers [9]. According to the World Health Organization (WHO) and United State Environmental Protection Agency (USEPA), the maximum permissible limit of copper in drinking water is 1.3 mg/l [10]. Hence the removal of copper from wastewater before its discharge into aquatic systems is extremely important and deserves immediate attention.

Several treatment techniques have been investigated for the removal of metals from wastewater such as membrane filtration, reduction, adsorption/biosorption, ion-exchange, coagulation-flocculation, chemical precipitation, flotation and electrochemical method. Most of them are significantly costly and incapable of removing trace levels of heavy metal ions. Comparatively, biosorption/adsorption as an exception is the most effective and widely used technique due to higher output and lower cost of sorbents [11]. Therefore, widely available sorbents with high sorption capacity should be developed to treat wastewater from toxic heavy metals. So, biosorption/adsorption is one of the

most effective and cost-efficient approaches for removal of heavy metal. Biosorption is a fast and reversible reaction of the heavy metals with biomass. A wide variety of active and inactive organisms have been employed as biosorbent to sequester heavy metal ions from water/wastewater. It has been found that biosorbents are rich in organic ligands or the functional groups, which play a dominant role in the removal of various heavy metal contaminants [12, 13]. These biosorbents typically include algae, fungi, rice and wheat straw, hyacinth, pine bark, tea waste, starch, agricultural by-products and microbes [13]. For example some researchers studied the effect of sawdust [14], rice husk [15] and pomegranate peel [16] for removal of copper(II) and lead(II) from aqueous solution [17].

An economical adsorbent is defined as one which is abundant in nature, or is a by-product or a waste from industry and requires little processing [18]. After water, tea is the most widely consumed beverage in the world, as attested by the over 3,000,000 tons of tea leaves produced annually [19]. Although available in different varieties, such as green, black or Oolong tea, all tea beverages are obtained from the same basic tea (*Camellia sinensis L.*) leaves [19]. Once the beverage has been brewed, spent leaves become a waste that must be disposed of like other biomass residues, tea wastes represent an unused resource and pose increasing disposal problems [20]. Some studies have demonstrated the ability of tea wastes to remove synthetic dyes [21], turbidity [22] and even some types of heavy metal ions [22-25] from water and wastewater. However, there appears to be a large variability in the rate and degree of sorption, depending on the nature of the contaminant, the presence of other competitive species and the process conditions. Such variations require careful analysis of the properties of the sorbent at the specific conditions under which it will be used.

In a continuous attempt to search for potential cost-effective sorbents for removal of toxins from wastewater. The Green Tea Waste (*GTW*) leaves used as a novel sorbent for effective copper removal. Due to the insoluble part of the spent tea leaves consists of mainly cellulose (37%), hemicellulose and lignin (14%), and polyphenols (25%) [6]. According to chemical analyses [26], these chemical composition of the *GTW* acquired after heated water extraction of green tea, is polar in nature and have a specific binding sites accessible for adsorption of other atomic or ionic species. Case in point, polyphenols may tie with *Cu(II)* ions. What's more, electron-rich oxygen atom of  $-OH$  gatherings of cellulose can likewise act as active binding sites for uptake of *Cu(II)* ions. Thus, there are great prospects for sorption of different sorts of inorganic/natural mixes compounds onto *GTW*. So, this investigation experiment perform to evaluate the effectiveness of employing a Green Tea Waste for the adsorptive removal of *Cu(II)* from synthetic wastewater, using batch experiment, also isotherm and kinetics studies were done to determine the adsorption capacities and mechanism of biosorption respectively.

## MATERIALS AND METHODS

### 2.1 Biosorbent Material (Adsorbent)

Green Tea waste (*GTW*) was taken from the waste tea leaves after tea making process. Tea waste collected were washed and boiled with hot distilled water (85°C) up to color removal. After color removal it is dried in hot oven at 60°C for 24 hrs. The dried leaves were ground and sieved to particles 120  $\mu m$  which were stored in polyethylene bags until use.

### 2.2 Preparation of Stock Solution (Adsorbate)

Analytical grade reagents were used (Merck Co.). A stock solution of 1000 mg/l of *Cu(II)* was prepared by dissolving 3.9266 g of (*CuSO<sub>4</sub>.5H<sub>2</sub>O*) was added in 100 ml of double distillate water in 1000 ml volumetric flask. It was dissolved by shaking and the volume was made up to the mark.

### 2.3 Biosorption Experiments

Biosorption experiments were studied by batch technique. The experiments were performed in a rotary shaker at 200 rpm using 250 ml Erlenmeyer flask containing 0.3 g of waste tea powder and 100 ml of 10, 30, 50, 70, 100, and 120 mg/l of *Cu(II)* solution. The experimental set was repeated for various time intervals of 10, 20, 30, 40, 50, 60, 90, 120, and 150 min. At the end of each contact time, the content of each flask was filtered using Whatman filter paper No 41. The metal ion concentration in the supernatant was determined using a UV-Visible spectrophotometer (Unicam 8700). The amount of *Cu(II)* adsorbed by the biomass was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant. The effect of several parameters such as contact time, initial *Cu(II)* concentration, pH, and adsorbent dosage on the adsorption process were studied. The pH of the adsorptive solutions was adjusted by using 1 N of *HCl* and *NaOH* solutions and measured by digital pH meter (HI 8417, HANNA Instrument, accuracy  $\pm 0.01$ ). The temperature of the experiments was maintained at 30 °C $\pm 1$ . All experiments were carried out in triplicate and showed differences less than 1%.

The sorption efficiency of *Cu(II)* ions onto *GTW* were computed using Eqn. (1) [27]:

$$R (\%) = \left( \frac{C_o - C_e}{C_o} \right) * 100 \quad \dots\dots\dots (1)$$

where  $C_i$  and  $C_e$  are the initial and equilibrium concentration of  $Cu(II)$  ions ( $mg/l$ ) in solution. Also, the adsorption capacity was computed by using the mass balance equation for the sorbent [27];

$$Q = \left( \frac{C_o - C_e}{w} \right) * V \quad \dots\dots\dots (2)$$

where  $Q$  is the adsorption capacity ( $mg/g$ ),  $C_o$  and  $C_e$  are the initial and equilibrium concentrations of  $Cu(II)$  in solution ( $mg/l$ ) respectively,  $V$  is the volume of  $Cu(II)$  ion solution ( $l$ ) and  $W$  is the weight of the biosorbent ( $g$ ).

Adsorption isotherms were studied by using the Langmuir and Freundlich isotherms, and the pseudo-first order, and pseudo-second order kinetic models are used respectively.

## RESULTS AND DISCUSSION

### 3.1 Biosorption Parameters

#### 3.1.1. Effect of Contact Time

In order to establish the equilibration time for maximum uptake of the biosorption process, copper adsorption on *GTW* was investigated as a function of contact time. Figure 1 shows that by increasing the initial concentration of copper, the percentage removal is also increased. The contact time was maintained for an 150 *min.* to ensure that equilibrium was really achieved. It is noticed from Figure 1 that the time to reach equilibrium is almost 120 *min.*, and the percentage removal reach's 90, 88, 85, 82, 79, and 76% for initial  $Cu(II)$  concentrations 10, 30, 50, 70, 100, and 120 *ppm* respectively, that is reveals to the percentage removal is an initial concentration independent. Generally, in the initial stages for 40 *min.*, the removal efficiency of the  $Cu(II)$  ion by the *GTW* increased rapidly due to the abundant availability of active binding sites on the sorbent, and with gradual occupancy of these sites, the sorption became less efficient in the later stages after 50 *min.* Similar results were found by [25, 28-30]. So, the optimal contact time to attain equilibrium with *GTW* is 120 *min.*

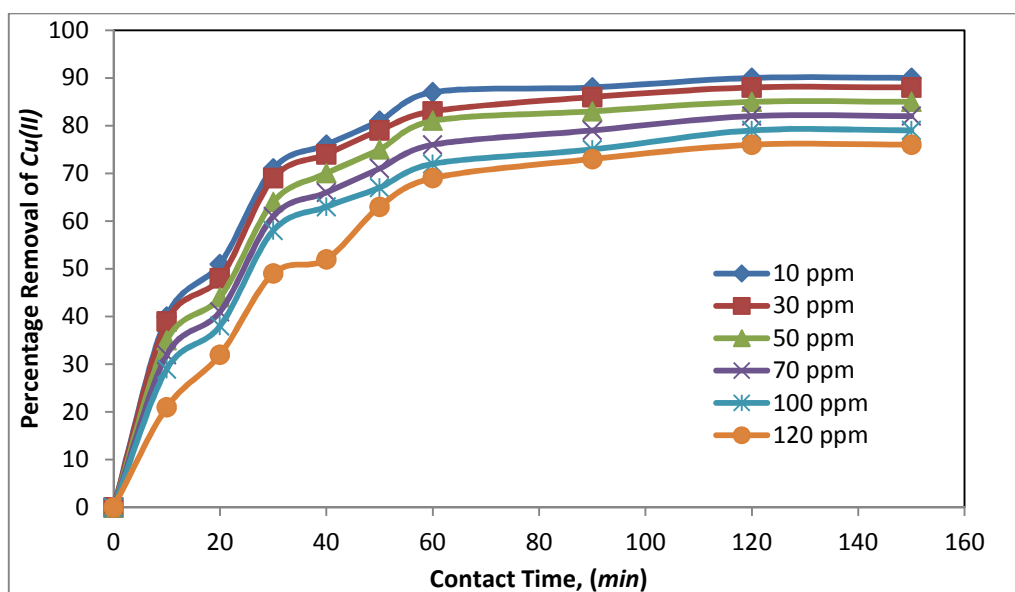


Figure 1. Effect of contact time on percentage removal of  $Cu(II)$  ions by *GTW* adsorbent (Adsorbent dosage=0.3 g/100 ml, solution pH 6, agitation rate=200 rpm and temperature =30 °C±1)

#### 3.1.2. Effect of Initial $Cu(II)$ Concentration

The effect of initial  $Cu(II)$  ion concentrations on the biosorption efficiency of *GTW* is shown in Figure 2. Biosorption experiments were carried out at different initial  $Cu(II)$  concentrations ranging from 10 to 120  $mg/l$  respectively for 120 *min.* as an equilibrium contact time with 0.3 g/100 ml of solution were used. The data shows that the  $Cu(II)$  uptake increases and the percentage removal of  $Cu(II)$  decreases from 90% to 76% with increase in

$Cu(II)$  ion concentration from 10 ppm to 120 ppm. This increase is a result of increase in the driving force (i.e. gradient of concentration). However, the decrease in percentage removal may be attributed to lack of sufficient surface area accommodate much more metal available in the solution.

At lower initial  $Cu(II)$  concentrations, almost all  $Cu(II)$  ions present in solution could interact with the binding sites and thus the percentage removal was higher than those at higher initial  $Cu(II)$  ionic concentrations. The results may be explained on the basis that the increase in the number of ions competing for the available binding sites in the biomass, and also because of the lack of active sites on the sorbent at higher concentrations. Therefore, more metal ions were left unadsorbed in solution at higher concentration levels. This behavior approved in many studies [25, 31, 32].

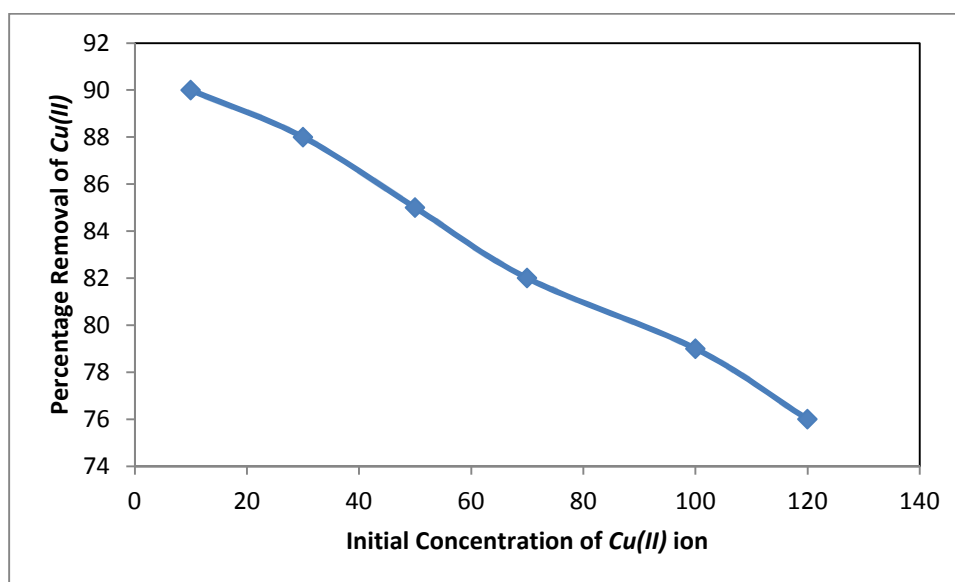


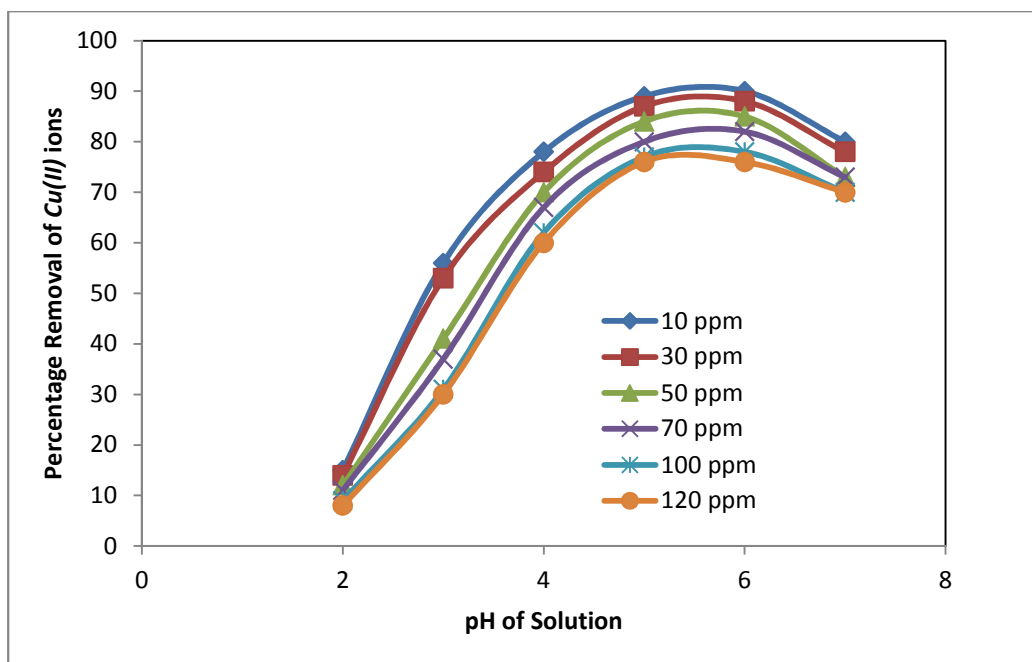
Figure 2. Effect of initial concentration of  $Cu(II)$  ion on percentage removal of  $Cu(II)$  ions onto GTW (Adsorbent dosage=0.3 g/100 ml, solution pH 6, agitation rate=200 rpm, contact time =120 min., and temperature =30 °C±1)

### 3.1.3. Effect of solution pH

pH variation is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions [25]. Figure 3 shows the effect of pH on percentage removal of  $Cu(II)$  ions onto GTW. These studies were conducted at an initial  $Cu(II)$  ions concentration of 10, 30, 50, 70, 100, and 120 ppm and constant adsorbent dosage 0.3 g/100 ml solution, and agitation rate 200 rpm for 120 min. as an equilibrium contact time for varying the solution pH ranged from 2 to 7.

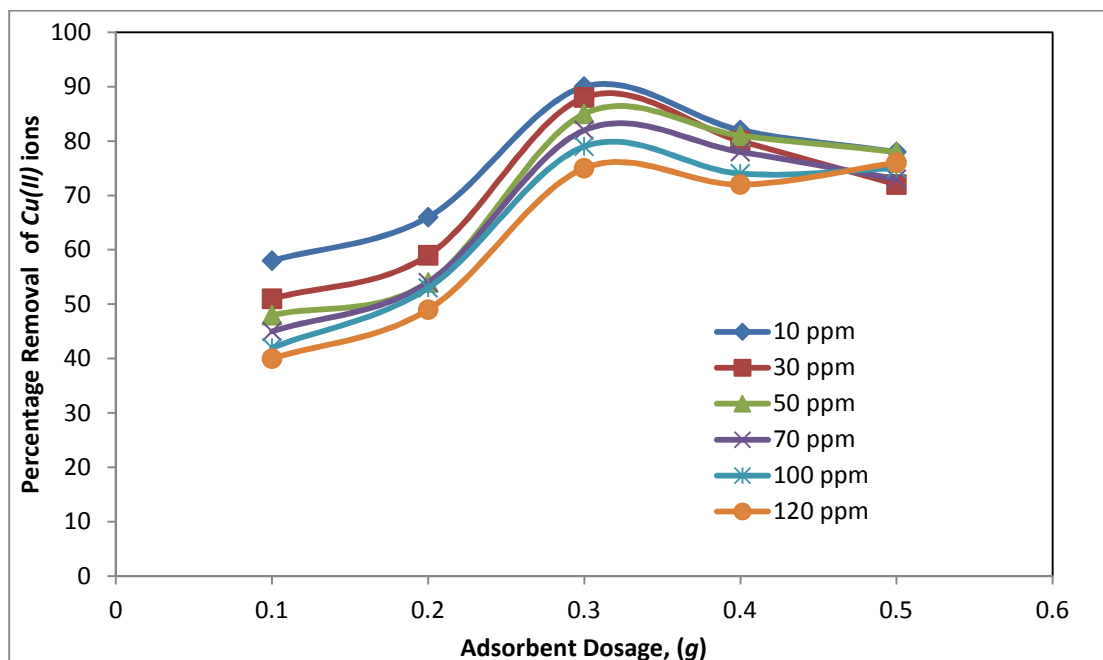
The percentage removal increases with pH to attain a maximum at pH ranged between 5-6. The maximum adsorption at 6 pH may be attributed to the partial hydrolysis of  $M^+$ , resulting in the formation of  $MOH^+$  and  $M(OH)_2$ .  $M(OH)_2$  would be adsorbed to a greater extent on the non-polar adsorbent surface compare to  $MOH^+$ . With increase of pH from 2 to 6, the metal exists as  $M(OH)_2$  in the medium and surface protonation of adsorbent is minimum, leading to the enhancement of metal adsorption [33]. In Figure 3 higher pH, that is, above optimum pH of 6, increase in  $OH^-$  ions cause a decrease in adsorption of metal ions at adsorbent-adsorbate interface.

Lower solubility's of hydrolyzed metal ions species may be another reason for the maximum adsorption at 6 pH. Since, in lower pH range, metal is present predominantly as metal ions in the adsorptive solution, there is a competition between  $H^+$  and  $M^+$  ions for adsorption at the ion exchangeable sites, leading to a low removal of metal. The extensive repulsion of metal ions due to protonation of the adsorbent surface at lower pH may be another reason for decrease in adsorption of metal in lower pH range [33].



**Figure 3. Effect pH of solution on percentage removal of Cu(II) ions onto GTW**  
(Adsorbent dosage=0.3 g/100 ml, agitation rate=200 rpm, contact time =120 min., and temperature =30 °C±1)

The increase in metal removal as the pH increases can be explained on the basis of a decrease in competition between proton and metal cations for the same functional groups and by the decrease in positive surface charge, which results in a lower electrostatic repulsion between the surface and the metal ions. Decrease in adsorption at higher pH (above 6 pH) is due to the formation of soluble hydroxyl complexes (this is due to precipitation of Cu(II) ions as a result of hydroxide anions forming Copper hydroxide precipitate. This result is similar to the report of studies [34-36].



**Figure 4. Effect adsorbent dosage on percentage removal of Cu(II) ions onto GTW**  
(pH of solution 6, agitation rate=200 rpm, contact time =120 min., and temperature =30 °C±1)

### 3.1.4. Effect of GTW dosage

Figure 4 shows that the adsorptive removal percent of  $Cu(II)$  over the range 0.2 to 0.5 g/100 ml, at pH 6, 120 min. as a contact time, and 200 rpm. The percentage removal of  $Cu(II)$  ions increases rapidly with increase in the dosage of the GTW due to the greater availability of the exchangeable sites or surface area [1, 27, 37].

Figure 4 show that there is a sharp increase in percentage removal for  $Cu(II)$  ions with GTW. The maximum removal of  $Cu(II)$  ions are 90, 88, 85, 82, 79, and 75% for initial concentrations 10, 30, 50, 70, 100, and 120 ppm respectively at 0.3 g of adsorbent dosage. Then the percentage removal of  $Cu(II)$  ions decrease with increase the adsorbent dosage more than 0.3 g. This is due to the fact that at higher adsorbent dose the solution ion concentration drops to a lower value and the system reaches equilibrium at lower values of adsorption capacity indicating the adsorption sites remain unsaturated [24].

## 3.2. Equilibrium Isotherms

The analysis and study the equilibrium data is very important in view to develop a model equation which can accurately represent the results and could be used for the design purposes [1].

### 3.2.1. Langmuir Isotherm

Langmuir proposed a theory to describe the adsorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm has found successful applications in many other real adsorption processes of monolayer adsorption. Langmuir's model of adsorption depends on the assumption that intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm model further assumes that adsorption takes place at specific homogeneous sites within the adsorbent [32]. It is assumed that once a  $Cu(II)$  molecule occupies a site, no further adsorption can take place at that site. Moreover, the Langmuir model is based on the assumption of a structurally homogeneous adsorbent where all adsorption sites are identical and energetically equivalent. Theoretically, the sorbent has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further adsorption can take place. The experimental data were fitted to the Langmuir model Eqn. (3), [27]:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad \dots\dots\dots (3)$$

where  $C_e$  (mg/l) is the equilibrium concentration of metal ion,  $Q_e$  (mg/g) is the adsorption capacity in equilibrium state,  $Q_m$  is the maximum adsorption capacity, and  $b$  is the Langmuir constant (equilibrium constant, l/mg) which reflects quantitatively the affinity between GTW and  $Cu(II)$  ions (Figure 5). The plotted data shows that the experimental data fitted reasonably with the linearized equation of Langmuir isotherm. The correlation coefficient ( $R^2$ ) value of 0.9858 further confirm the fitness of Langmuir model in describing the adsorption of  $Cu(II)$  by GTW. The parameters of Langmuir isotherm are shown in Table 1,  $Q_m$  and  $b$  were found to be 46.08 mg/g and 0.0633 l/mg respectively.

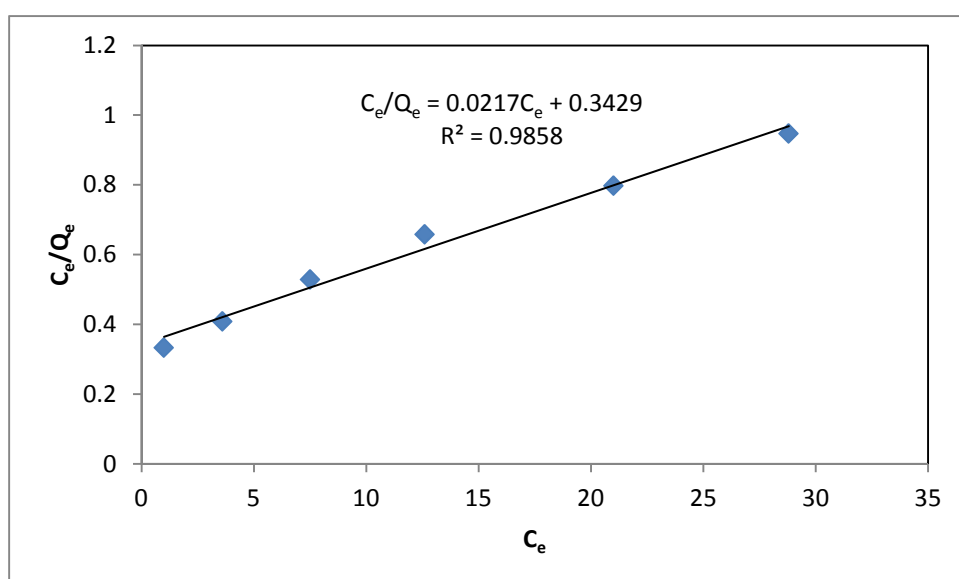


Figure 5. Langmuir isotherm plot for the biosorption of  $Cu(II)$  ions onto GTW at  $30\pm 1^\circ C$

The affinity between *Cu(II)* and *GTW* adsorbent can be predicted using the Langmuir parameter *b* from the dimensionless separation factor  $R_L$  [35]:

$$R_L = \frac{1}{1 + bC_o} \dots\dots\dots (4)$$

where  $C_o$  is the initial *Cu(II)* concentration, and *b* is Langmuir isotherm constant. The adsorption process as a function of  $R_L$  may be described as follows [35]:

$R_L > 1$  unfavorable,  $R_L = 1$  linear,  $0 < R_L < 1$  favorable, and  $R_L = 0$  irreversible.

The calculated  $R_L$  values for the adsorption of *Cu(II)* onto *GTW* are shown in Table 1. The  $R_L$  values were 0.612, 0.345, 0.24, 0.184, 0.136, and 0.116 for initial *Cu(II)* concentrations 10, 30, 50, 70, 100, and 120 ppm respectively, which indicates a highly favorable adsorption of *Cu(II)* onto *GTW*.

Table 1. Equilibrium model parameters of *Cu(II)* biosorption onto *GTW*

Isotherm	Parameters	Value
Langmuir	$Q_m$ (mg/g)	46.083
	$b$ (l/mg)	0.0633
	$R^2$	0.9858
Freundlich	$K_F$ (mg/g.(l.mg) <sup>1/n</sup> )	3.3016
	1/n	0.6861
	$R^2$	0.9911

3.2.2. Freundlich Isotherm

The Freundlich adsorption equation has the following general form [27]:

$$\ln Q_e = \ln K + \frac{1}{n} \ln C_e \dots\dots\dots (5)$$

where  $K_F$  and *n* are the isotherm parameters to be determined. The Freundlich adsorption isotherm represents the relationship between the corresponding adsorption capacity  $Q_e$  (mg/g) and the concentration of the metal in the solution at equilibrium  $C_e$  (mg/l).

The result shown in Figure 6 revealed that the adsorption of *Cu(II)* on *GTW* obeys the Freundlich adsorption isotherm with a correlation coefficient of determination  $R^2$  value of 0.99 which is close to unity. The high value of Freundlich constant  $K_F$  (3.3), showed easy uptake of *Cu(II)* ions from aqueous solution. The *n* value calculated (1.458) (as shown in Table 1) reflects the intensity of sorption and signifies that, the surface of the biosorbent is heterogeneous in nature i.e. fractional value  $1/n$  ( $0 < 1/n < 1$ ) [35].

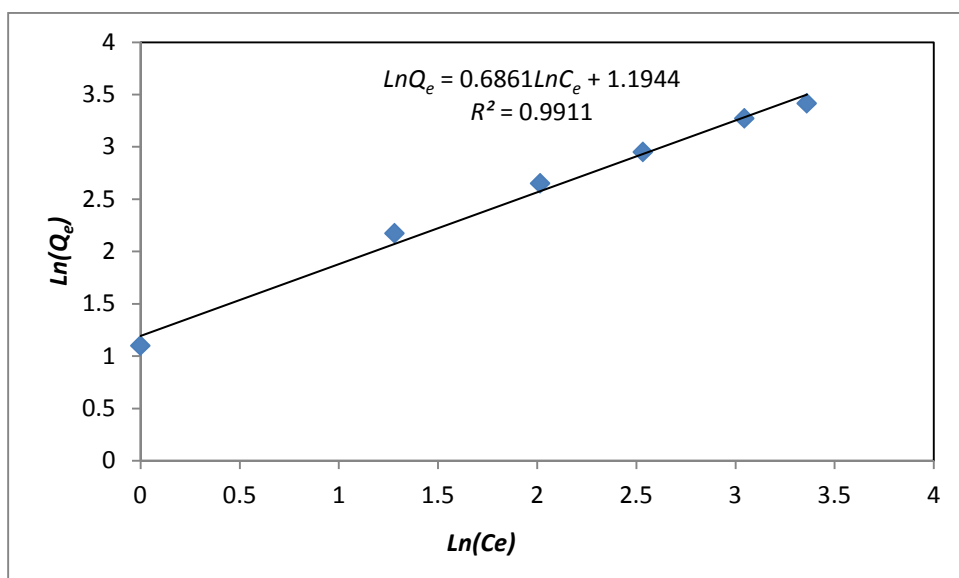


Figure 6. Freundlich isotherm plot for the biosorption of *Cu(II)* ions onto *GTW* at 30±1°C

From Table 1, it is shown that both models of Langmuir isotherm and Freundlich isotherm have a varies value of  $R^2$  from 0.9858 for Langmuir to 0.9911 for Freundlich. Thus, it is concluded that the Freundlich model is an

appropriate model to represent the biosorption equilibrium data. Similar results were found by Cay et al.[37] for *Cu(II)* and tea industry waste system.

A comparison of the maximum sorption capacity  $Q_m$ , obtained in the present study, with those obtained using other sorbents (Table 2). A close look at the values displayed reveals that the present sorbent (*GTW*) has a fair maximum *Cu(II)* uptake value as compared to the other sorbents used in the recent past.

Table 2. Comparison for adsorption capacity of *Cu(II)* ions by other natural biosorbents obtained by previous studies

Adsorbent	$Q_m$ (mg/g)	Ref.
Newspaper pulp	10.94	[38]
Tea fungal biomass	2.2	[39]
Orange peel	50.25	[40]
Potato peels	0.38	[41]
Chitosan-alginate beads	67.66	[42]
Green tea waste	46.083	Present work

It is well known that the Langmuir isotherm corresponds to a dominant ion exchange mechanism while the Freundlich isotherm shows adsorption-complexation reactions taking place in the biosorption process [37]. So, the ability of a *GTW* to bind copper or, more generally, heavy metal ions is the result of a variety of mechanisms, including chemisorption, complexation, adsorption-complexation on surface and pores, ion exchange, micro-precipitation, heavy metal hydroxide condensation and surface adsorption [43]. In order to understand how copper is removed by the *GTW*, it is essential to identify the functional groups responsible for metal binding. Although specific studies on this type of waste are lacking, charged and polar functional groups on the protein surface and phenolic compounds are believed to be primarily involved in metal removal [44, 45]. These groups have the ability to bind heavy metals by the replacement of hydrogen ions for metal ions or by donation of an electron pair to form metal complexes [43, 46].

### 3.3. Biosorption Kinetics

Kinetics of biosorption is one of the most important characteristics that is responsible for the efficiency of biosorption [47]. In order to investigate the mechanism of process and potential rate controlling steps, the experimental kinetic data for the uptake of copper at different initial concentrations, which is modeled by the pseudo-first order by Lagergren [48] and the pseudo-second order by Ho and McKay [49] as following;

#### 3.3.1. Pseudo-First Order Model

Lagergren rate equation (Pseudo-first order model) is one of the most widely used sorption rate equation to present the adsorption process. The pseudo-first-order equation is [48]:

$$\frac{dQ_t}{dt} = k_1(Q_e - Q) \quad \dots\dots\dots (6)$$

where  $Q$  is the amount of adsorbate adsorbed at time  $t$  (mg/g),  $Q_e$  is the adsorption capacity in equilibrium (mg/g),  $k_1$  is the rate constant of pseudo-first-order model (1/min), and  $t$  is the time. After definite integration by applying initial conditions at  $t = 0$ ,  $Q = 0$  and at  $t = t$ ,  $Q = Q_t$ , the equation becomes [48]:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \quad \dots\dots\dots (7)$$

The straight line plot of  $\log(Q_e - Q_t)$  against  $t$  gives the value of adsorption rate constant ( $k_1$ ) as shown in Figure 7.

The values of adsorption rate constant ( $k_1$ ) for removal of *Cu(II)* onto *GTW* are given in Table 3. These values indicated that the adsorption rate was very fast at the beginning of adsorption of copper onto *GTW*. But the correlation coefficient ( $R^2$ ) of the pseudo-first order model were not high as shown in Table 3, in which  $R^2$  ranged from 0.478-0.983 for 10-120 ppm of *C(II)* solutions. So,  $R^2$  values show that this model cannot be applied to predict the adsorption kinetic model. In most cases in the literature, the pseudo-first order equation of Lagergren does not fit well for systems [1, 27, 47, 50].



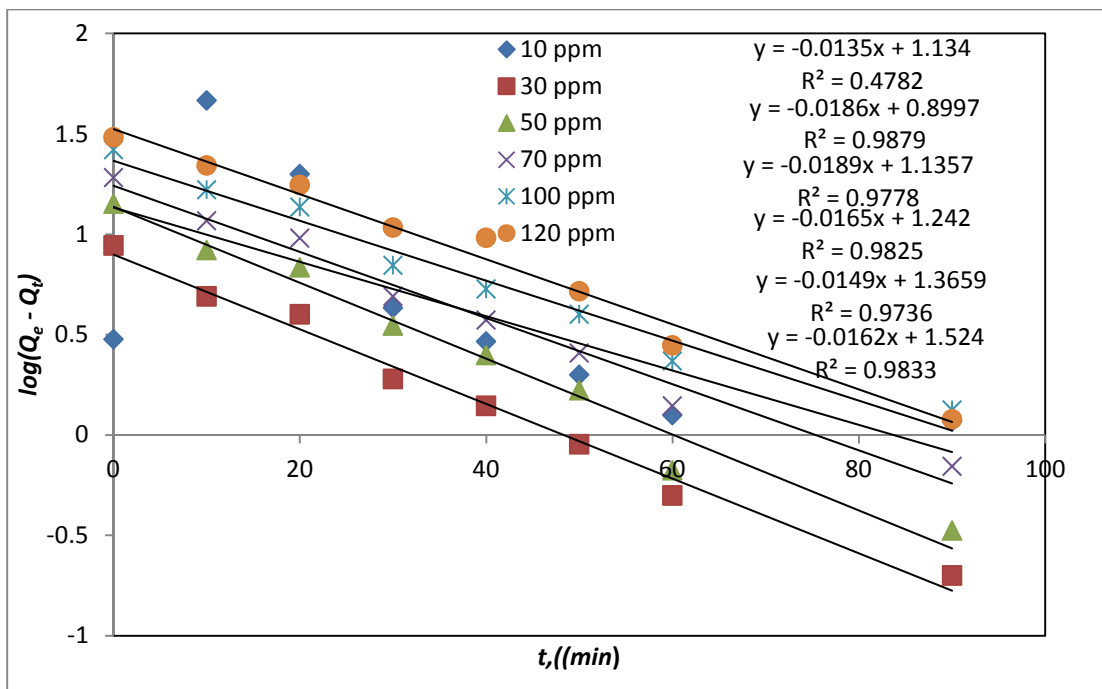


Figure 7. Fitting of pseudo-first-order model for Cu(II) biosorption onto GTW (30±1 °C, 0.3 g dosage/100 ml, 200 rpm, and 6 pH)

Table 3. Pseudo-first order model kinetic parameters for Cu(II) biosorption onto GTW

Initial Conc. (ppm)	10	30	50	70	100	120
<i>k<sub>1</sub></i> (1/min.)	0.0311	0.0428	0.0435	0.038	0.0343	0.0373
<i>Q<sub>e</sub></i> (mg/g)	13.621	7.941	13.674	17.467	23.235	33.441
<i>R</i> <sup>2</sup>	0.478	0.988	0.978	0.983	0.974	0.983

2.3.2. Pseudo-Second Order Model

The pseudo-second-order model can be represented in the following form [49];

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \tag{8}$$

where *k<sub>2</sub>* is rate constant of pseudo-second-order model (g/mg.min). After integrating equation for boundary conditions at *t=0, Q=0* and at *t=t, Q=Q<sub>t</sub>*, the following form of equation can be obtained [49]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{9}$$

The initial sorption rate in mg/g.min, as *t→0* can be defined as;

$$\left(\frac{dQ_t}{dt}\right)_{initial} = k_2 Q_e^2 \tag{10}$$

The initial sorption rate, the equilibrium adsorption capacity (*Q<sub>e</sub>*), and the pseudo-second order rate constant *k<sub>2</sub>* can be determined from plot of *t/Q<sub>t</sub>* versus *t* as shown in Figure 8.

Table 4 shows the parameters of pseudo-second order rate and the correlation coefficient. The higher *R<sup>2</sup>* values of the data confirm that the pseudo-second order model provided better correlation than pseudo-first order model, this behavior also approved by Amarasinghe & Williams [24]. The initial adsorption rate decreases with initial solution concentration increase and the rate constant decreases with the solution concentrations increases, as shown in Table 4.

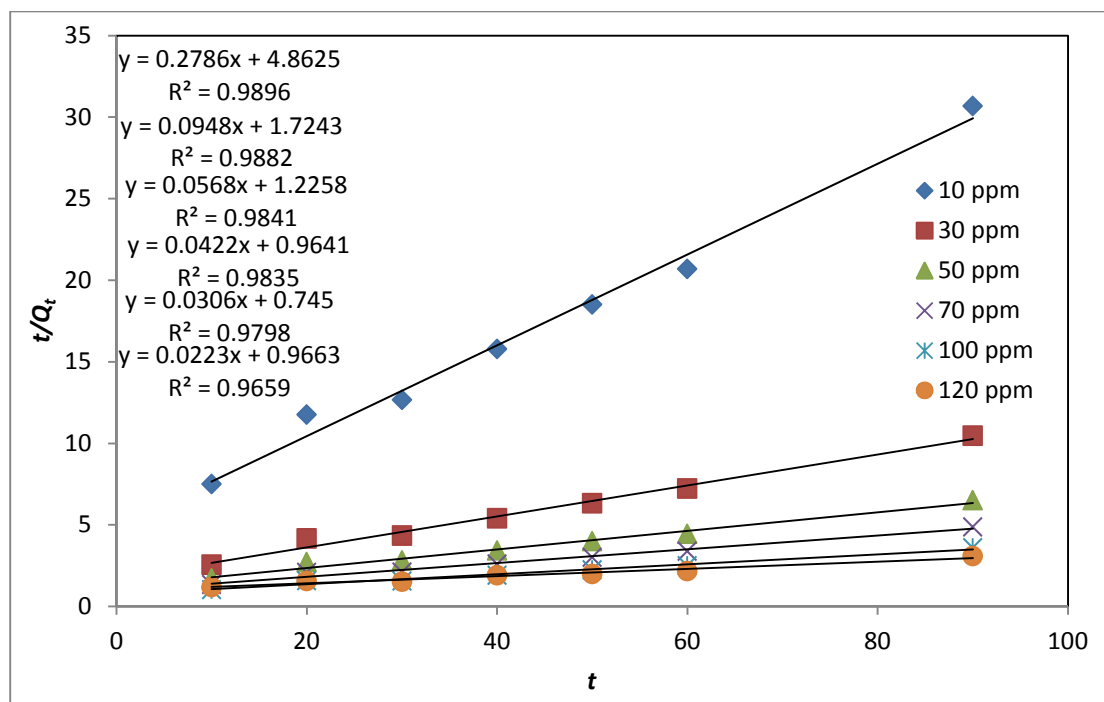


Figure 8. Fitting of pseudo-second-order model for  $Cu(II)$  biosorption onto GTW ( $30 \pm 1$  °C, 0.3 g dosage/100 ml, 200 rpm, and pH 6)

Table 4. Pseudo-second order model kinetic parameters for  $Cu(II)$  biosorption onto GTW

Initial Conc. (mg/l) Parameters	10	30	50	70	100	120
$Q_e$ (mg/g)	3.589	10.549	17.606	23.697	32.679	44.843
$k_2$ (g/mg.min)	0.377	0.01549	0.00396	0.00172	0.000698	0.00048
$(dQ/dt)_{\text{initial}}$ (g/mg.min.)	4.863	1.724	1.226	0.964	0.745	0.663
$R^2$	0.989	0.988	0.984	0.984	0.979	0.966

The pseudo-second order model is based on the assumption that the sorption of a metal by an adsorbent may involve a chemical sorption (Chemisorption) which can be the rate controlling step [35]. So, the At high concentration the difference between the metal ion concentration in the solution and that on the solid-liquid interface, which is not the driving force for the adsorption. In addition, the applicability of pseudo-second order rate also point to the fact that biosorption is the rate-limiting step, and that sorption of the metal ions involves two species, in this case, the metal ion and the biomass [51].

By comparing the coefficient determination  $R^2$  in Tables 3 and 4, it is observed that the pseudo-second order model fits the experimental data with higher  $R^2$  values (0.966 to 0.989) than the pseudo-first order  $R^2$  values (0.478 to 0.988). The higher  $R^2$  values confirm that adsorption is well represented by the pseudo-second-order model.

## CONCLUSION

The present study shows that waste green tea powder (GTW) was an effective biosorbent for the adsorption of  $Cu(II)$  ions from aqueous solutions. The effect of process parameters like contact time, metal ion concentration, pH, and adsorbent dosage were studied. The uptake of copper ions by the biomass was increased by increasing metal ion initial concentration but decreased in percent adsorption of the total initial metal concentration. The metal uptake was also increased by increasing pH up to 6. Higher pH than 6 led to decrease in metal uptake. The highest percent adsorption of 90% was attained by metal initial concentration of 10 ppm of  $Cu(II)$  solution. This suggest that, for industrial application of waste tea powder to be effective optimally for wastewater treatment, copper contaminated industrial effluent should be diluted to 10 ppm. The biosorption isotherms of  $Cu(II)$  onto GTW powder could be well fitted by the Langmuir and Freundlich equations. The biosorption could be best described by Pseudo-second order kinetic model. These results clearly support the possibility of using GTW for the removal of copper and, possibly, of other heavy metals from contaminated waters. The sorbent does not require any pretreatment or activation, and

hence used as an adsorbent for heavy metal ions can therefore be expected to be economically, technically feasible and an environment-friendly.

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