

# REMOVAL OF COPPER (II) FROM AQUEOUS SOLUTION BY TEA WASTE

Yash Johri<sup>1</sup>, Shobha Ram<sup>2</sup>

<sup>1</sup>M.Tech Civil Engineering (Environmental Engineering), Gautam Buddha University, Greater Noida, India

<sup>2</sup>Assistant Professor, Department of Civil Engineering, Gautam Buddha University, Greater Noida, India

**Abstract :** Numerous Industries discharge their waste water comprise of heavy metal into the water bodies. Water contamination by heavy metals is a major environmental problem because to their acute toxicity. Many investigations have been performed to expel heavy metals using diverse techniques. However, Adsorption method is considered as one of the finest method as it is cost effective, efficient according to many studies. Several adsorbents have been utilized to remove different type of heavy metal ions from wastewater. For this research, Tea waste is used as an adsorbent for the removal of Cu from constituted waste water. Batch experiment was directed to govern optimum condition. Effect of parameter like pH, adsorbent dose, contact time and initial metal ion concentration were also determined. The optimum condition obtained is pH 5, Contact time 120 minute and initial concentration of 10ppm. The maximum removal of Cu by tea waste 91 % at an adsorbent dose of 0.5 gram /100 ml. The equilibrium data obtained from this study was fitted to various isotherm models and the Freundlich model with correlation coefficient  $R^2 = 0.99$  was seen to be the best fitted model. The adsorption kinetics uptake for Cu (II) was examined by the pseudo-first-order, pseudo-second-order and it was revealed that the process follow a pseudo second with correlation coefficient  $R^2 = 0.99$  for Cu by utilizing tea waste.

**Keywords :** Copper, Tea Waste, Adsorption, Isotherm, Kinetics

## 1. INTRODUCTION:

Ecological Contamination has altered into a key point of convergence of worry for the entire globe, as not only the developing countries but developed nations as well, is influenced by and experiences the ill effects of it. Amongst all the environmental pollutions, pollution of water resources is a matter of great concern. Several Industries such as electroplating, chemical and petrochemical, metal and mining, leather, textile, ceramic, cement, fertilizer, tanneries, batteries, paper industry release their waste water consist of toxic chemicals and heavy metal in water bodies which pollute the environment. Heavy metals are among the most imperative sorts of contaminant in the environment. They can be characterized in an assortment of routes, based on their physical, chemical and biological properties. The term heavy metal alludes to any metallic chemical element that has a moderately high density and is toxic or noxious even at low concentration [1]. The specific gravity is generally in excess of 5.0 g/cm<sup>3</sup>. Various Heavy metals that are toxic to human beings and ecological environment are mercury, copper, lead, cobalt etc. Among all heavy metals, Copper is the major available form of heavy metal in the aquatic environment. It can cause destructive biochemical effects, noxiousness and dangerous ailment in human beings. Extreme intake of Cu through air, water and food can cause harmful disease such as headaches, diarrhea, and queasiness. There are various ways and strategies for treating industrial waste water comprise of heavy metals such as Adsorption, Chemical Precipitation, Coagulation & Flocculation, Electro-chemical treatment, Flotation, Ion exchange, Membrane Filtration. Adsorption is considered as one of the most prominent technology as it is cost effective, easily operative. There are various adsorbents available which re capable to remove heavy metal from waste water such as Rice husk, sawdust, coconut husk, oil palm shell, bark [2], bagasse, paddy husk, corn cob. Tea waste is a cheap and compelling adsorbent for the removal of metal ions from waste water. It is easily available; cost effective can be gathered from any nearby store

## 2. RESEARCH METHODOLOGY:

### 2.1 Adsorbate Preparation

A required amount of hydrated Copper sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) was added in 1000 ml of distilled water. Copper Concentration of this solution was 1000 mg/l. Furthermore, standard solution of desired Cu concentration was set up from this stock solution. All glassware was washed with distilled water. HCl and NaOH were used to alter the pH of solution. Distilled water was used throughout the experimental studies.

### 2.2 Adsorbent Preparation

Tea Waste was gathered from the hostel mess washed with tap water and then afterward overflowed with hot distilled water up to color removal. After Color expulsion it is Sundried for 2 days and afterwards kept in hot oven at 100°C for 12 hours. The dried material is then changed over into powder form by mixer grinder and then screened to size 300  $\mu\text{m}$ . Again, this powder dried at 85°C for 6 hours and after that put away in the air tight container. Now it was prepared to use as an adsorbent



Fig 2.1: Grinded Tea Waste

### 2.3 Batch Adsorption experiments

To study about the influence of various parameters the Batch operation was observed to be appropriate. Experimental studies were performed in four distinctive batches at room temperature for the exclusion of heavy metal from synthetic solution. Each batch consists of four samples (100 ml each) solution of various known copper conc. i.e. 10ppm, 20ppm, 40ppm, 50 ppm. The well-known weight of Adsorbent (Tea Waste) dose are in between 0.25g - 1.5g. Predetermine time interval is (20-180 Minute). The pH of solution was balanced physically by adding 0.1 M HCL and 0.1 M NaOH. From this, each sample of adsorbent dose were added in desired known copper conc. at different pH for predetermined time interval and mixture were set to shaken in orbital shaker machine. Suspension of adsorbent was isolated from arrangement by filtration using Whatman No.1 filter paper. The residual heavy metal conc. in solution was stately by Atomic Adsorption Spectrophotometer. The several parameters studied are –

#### 2.3.1 Effect of Adsorbent Dose

It is a vital factor to influence the efficiency of copper removal. To determine the efficiency, effect of doses was examined with well-known copper conc. (10, 20, 40, 50 ppm) by adding varying amount of dose (0.25-1.5g) of adsorbent and shaken in a rotatory shaker for 3 hour interval at 150 rpm. The equilibrium was achieved and the Suspension of adsorbent was isolated from arrangement by filtration using Whatman No.1 filter paper. Then, the conc. of metal ion was determined by using AAS.

#### 2.3.2 Effect of Contact time

Experiment for contact time were conducted with well-known copper conc. with a constant dose of 0.5 g tea waste at agitation speed of 180 rpm, at room temperature for different time interval up to 180 minutes. The solution was left for attaining equilibrium and then filtered by using Whatman No.1 filter paper. Then, the conc. of metal ion was determined by using AAS.

#### 2.3.3 Effect of pH

The impacts of pH were examined with well-known copper conc. with a constant dose of 0.5 g tea waste at agitation speed of 180 rpm with different pH range. The pH of solution was balanced physically by adding 0.1 M HCl and 0.1 M NaOH and estimated by using digital pH meter. After attaining Equilibrium, the solution was separated and the final conc. of metal ion at varying pH was measured by using AAS.

#### 2.3.4 Effect of Initial Metal Ion concentration

To govern the effectiveness, well-known copper conc. (10, 20, 40, 50 ppm) was treated with varying amount of dose (0.25-1.5gm) keeping the pH and time constant. The solution was left for attaining equilibrium and then separated by using Whatman No.1 filter paper. Then, the conc. of metal ion was determined by using AAS.

The aftereffects of these investigations were used to get the optimum conditions for maximum heavy metal removal from aqueous solution. The % removal (R) of heavy metal was calculated using equation – [3]

$$\text{Metal ion removal } R (\%) = [(c_o - c_e) / c_o] \times 100$$

Here  $c_o$ : Initial metal ion conc. of solution, mg/l.

$c_e$  : Final equilibrium conc. of solution, mg/l.

The extent of metal ions adsorbed per unit mass of adsorbent ( $q_e$ ) were calculated for each run by following expression –

$$q_e = \frac{(c_o - c_e) V}{m}$$

Here,  $c_o$ : Initial metal ion conc. of solution, mg/l.

$c_e$  : Final equilibrium conc. of solution, mg/l.

V is volume of solution in litre.

m is mass of adsorbent in gram.

## 2.4 Adsorption Isotherms

Adsorption Isotherms describe the equilibrium relationships between adsorbent and adsorbate. In order to model the adsorption behavior and calculate the adsorption capability of adsorbent for expulsion of heavy metal from various adsorbate solutions, adsorption isotherms were studied for the known metal ion conc. The equilibrium sorption of Copper (II) was carried by containing 0.5 g of tea waste with 100 ml solution of concentration ranging 10 -100 mg/litre in conical flask.

## 2.5 ADSORPTION KINETICS.

It investigates the mechanism of adsorption of adsorbate species on the surface of adsorbent and rate controlling steps. The kinetics data was analyzed by using pseudo-first order and pseudo second order kinetics.

## 3. RESULTS AND DISCUSSION:

### 3.1 Effect of Adsorbent Dose

Figure 3.1 illustrate the relationship between percentage removal of Cu and adsorbent dosage of tea waste. The percentage removal varies at different dosage. The maximum elimination of Cu is about 91 % and 86 % for the initial conc. of 10 mg/l and 20 mg/l Copper at 0.5g dose of tea waste. The Removal efficiency of the copper generally enhanced on expanding adsorbent dose due of the way that the higher dosage of adsorbents in the solution gives the more prominent accessibility of exchangeable sites for the ions. Thereafter, the expulsion of copper began to decay with additionally increment in measure of adsorbent dosage because of certainty that the equilibrium conditions came to and consequently the amount of ions bound to the adsorbent and the amount of free ions in the solution stay consistent even with more addition of the dose of adsorbent [4,5].

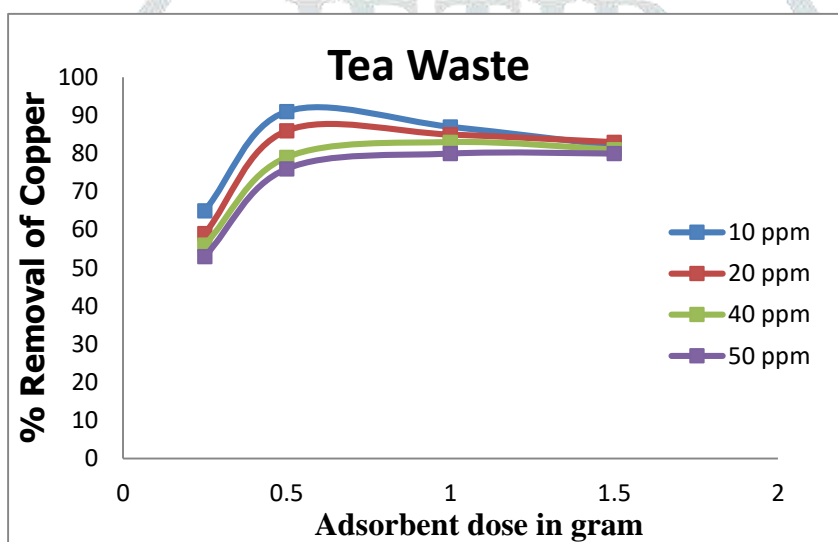


Fig 3.1: Effect of dose on % removal of copper ion by tea waste

### 3.2 Effect of Contact time

Figure 3.2 illustrate the relation between percentage removal of Cu and contact time. The metal ions removal was expanded with an expansion in contact time. The maximum percent expulsion of copper is 90 % for tea waste at 120 minutes. The percent expulsion comparatively increases from 30 minutes to 120 minutes and afterwards starts decreasing at 180 minutes. Equilibrium was reached after 120 minutes. There were substantial numbers of empty active binding sides in both the adsorbents, subsequently substantial amount of Cu ions were bound quickly onto adsorbents. The coupling site was shortly become limited and the residual vacant surface sites are hard to be possessed by copper ions due of the arrangement of repulsive forces amongst the copper on the solid surface and liquid phase. Also, the meso-pores end up immersed at the underlying phase of adsorption where the metal ions are adsorbed. Accordingly, the driving force of mass exchange amongst fluid and solid stage in a aqueous adsorption framework diminishes with time slip by [30, 28]. Further, the metal ions need to go through the more profound surface of the pores for binding and experience significantly much larger resistance which backing off the adsorption during the later stage of adsorption.

### 3.3 Effect of pH

pH dependent experiment were conducted and the results are illustrated in Figure 3.3. The extreme adsorption was attained at pH 5 and from that point it diminishes with additionally increment in pH. The percentage removal expanded with increment in pH from 2 to 5 and after that step by step begins diminishing. The Maximum removal efficiency at optimum pH is about 90% for tea waste from solution with initial conc. of 10 ppm. Increment in metal removal with increased pH can be cleared up based on the decrease in competition among proton and metal cations for same functional groups and by decrease in positive surface charge, which brings about a lower electrostatic repulsion amongst surface and metal ions. Diminishing in adsorption at higher pH (>pH 5) is due to the formation of soluble hydroxy complexes. The extensive repulsion of metal ions because of protonation of the adsorbent surface at lower pH might be the explanation behind lessening in adsorption of metal in lower pH range [6].

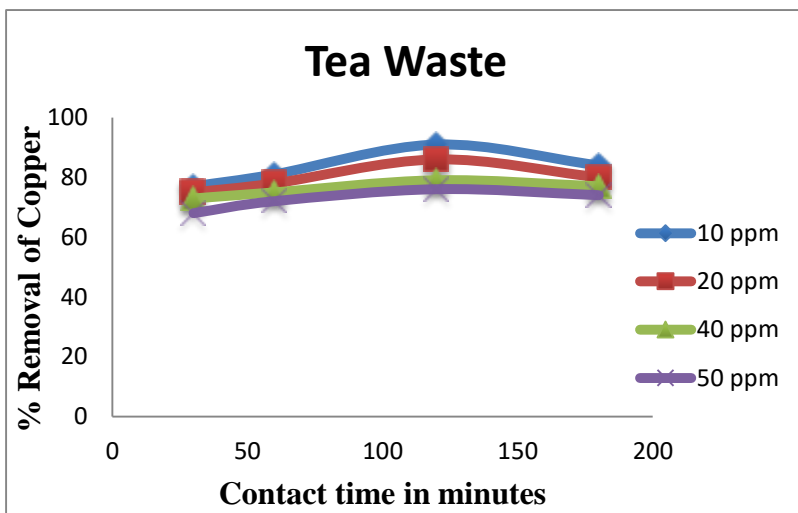


Fig 3.2: Effect of contact time on % removal of copper ion by tea waste

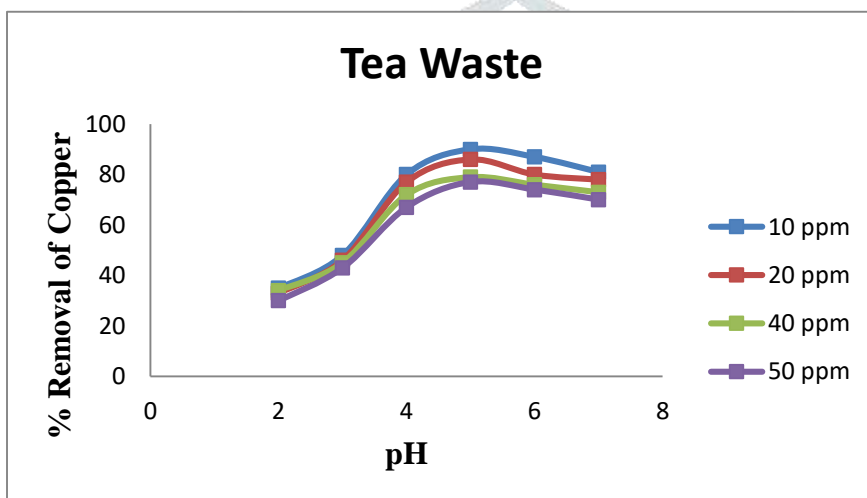


Fig 3.3: Effect of pH on % removal of copper ion by tea waste

**3.4 Effect of Initial Metal Ion Concentration**

The effect of initial conc. on the % removal of heavy metals by tea waste is illustrated in figure 3.4. It can be observed from the figure, that, there is reduction in the removal percentage with increment in initial conc. The maximum expulsion of Cu is 91 at 10 ppm for tea waste at varying doses. These outcomes might be clarified on the premise that there is increment in the quantity of ions competing for the available binding sites and furthermore due to the lack of active sites on the adsorbent at higher conc. At lower initial metal ion conc. adequate adsorption locales are available for adsorption of the substantial metals particles. In this manner, the fractional adsorption is independent of initial metal ion conc. However, at higher conc. the quantities of heavy metal ions are moderately higher contrasted to accessibility of adsorption sites.

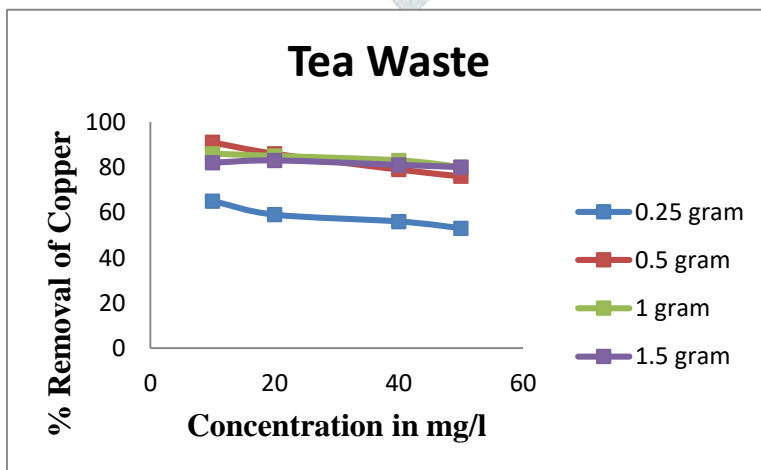


Fig 3.4: Effect of concentration on % removal of copper ion by tea waste

### 3.5 Adsorption Isotherm

Adsorption process is generally considered through graphs known as adsorption isotherm. Adsorption isotherms were used to fit the equilibrium data and their relevance was judged with correlation coefficient ( $R^2$ ).

#### 3.5.1 Langmuir Isotherm

The linear plot of Langmuir Isotherm for Copper adsorption is shown in Figure 3.5. Calculated parameters along with regression coefficients are illustrated in table below. The batch equilibrium data has perfectly fitted in the Langmuir model, with a correlation coefficient  $R^2 = 0.9805$  for tea waste. It can be inferred that the value of  $R_L$  lie in between 0 and 1 indicating the adsorbents prepared are favorable for adsorption of the metal ions under conditions used in the study.

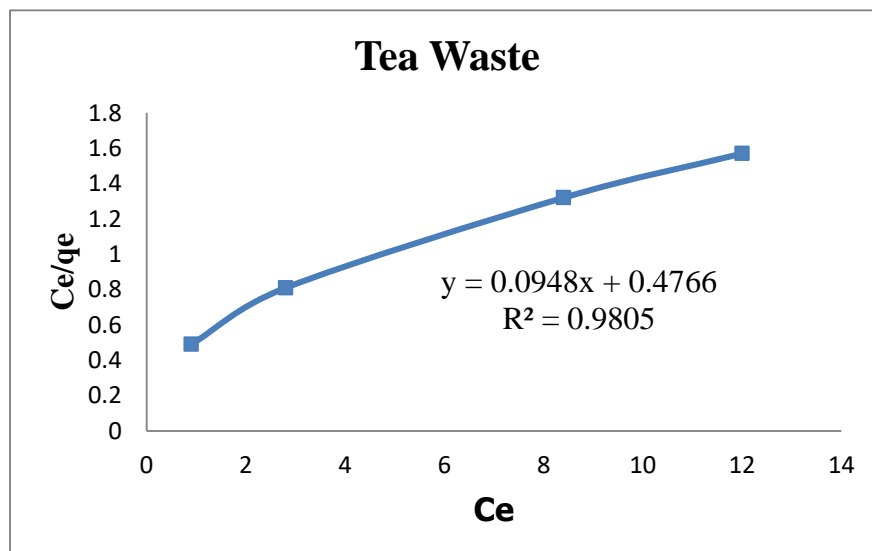


Fig 3.5: Langmuir Adsorption Isotherm for Cu by using tea waste

Table 3.1– Calculated Langmuir parameters for Cu Adsorption by Tea waste

$q_m$ (mg/g)	$b$	$R^2$
10.5	0.19	0.9805

Table 3.2 - Values of  $R_L$  for removal of copper ions by Tea waste

Concentration of copper (ppm)	$R_L$ value of Copper
10	0.34
20	0.20
40	0.11
50	0.09

#### 3.5.2 Freundlich Isotherm

The linear plot of Freundlich Isotherm for Copper adsorption is shown in figure 3.6. The batch equilibrium data has perfectly fitted in the Freundlich model. Calculated parameters along with regression coefficients are illustrated in table below. The batch equilibrium data has perfectly fitted in the Freundlich model, with a correlation coefficient  $R^2 = 0.99$  for tea waste. It can be inferred that the value of 'n' is in between 1 and 10, so it indicates a favorable adsorption.

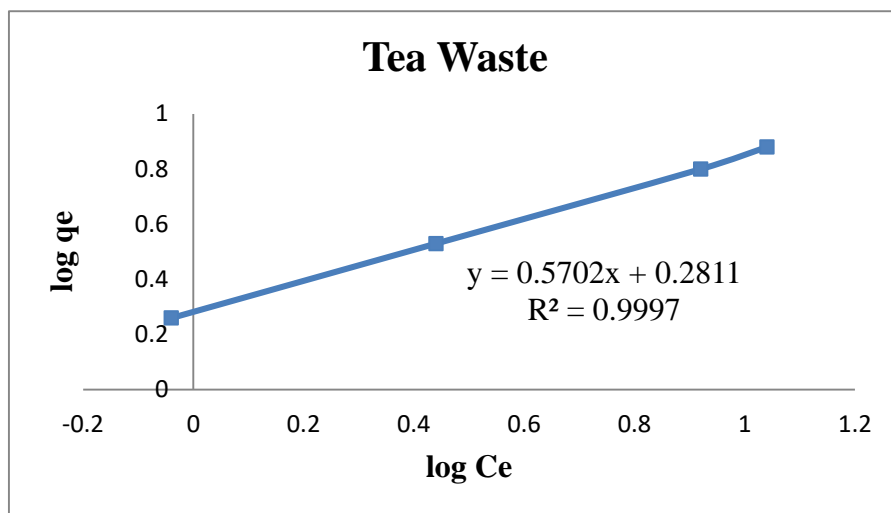


Fig 3.6: Freundlich Adsorption Isotherm for Cu by using tea waste

Table 3.3 – Calculated Freundlich parameters for Cu adsorption by tea waste

$K_F$	$1/n$	$R^2$
1.91	0.5702	0.99

3.6

**Adsorption Kinetics**

The kinetics study was carried out by pseudo – first order, pseudo-second order kinetics model.

**3.6.1 Pseudo- first order model**

The experimental outcomes of the first order rate constants are illustrated in Fig 3.7. The adsorption data have a low regression coefficient  $R^2 = 0.7538$  which suggests that the adsorption of copper on tea waste does not follow the pseudo-first order adsorption kinetics. The calculated  $q_e$  is not close to  $q_e$  experimental, so the calculations for pseudo second order kinetics is to be carried out.

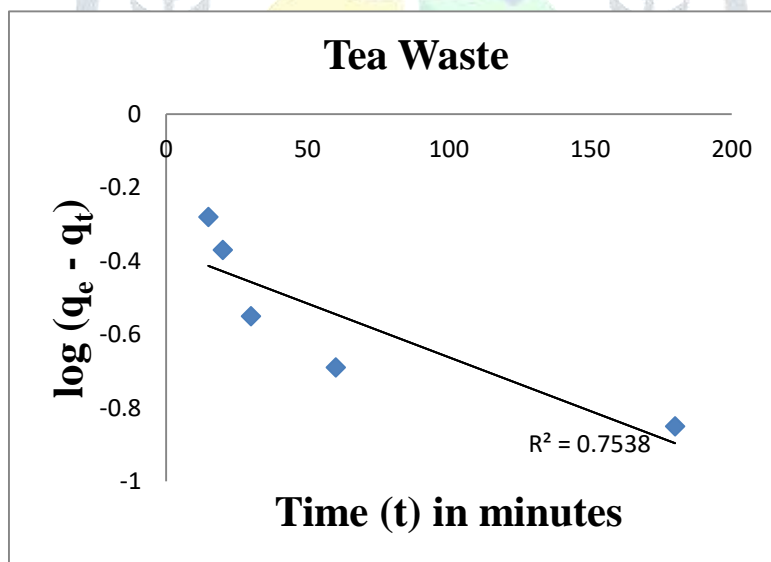


Fig 3.7: Pseudo-first order kinetics for Cu by using tea waste

**3.6.2 Pseudo-second order model**

The experimental outcomes of the pseudo second order rate constants are illustrated in Fig 3.8. The adsorption data have regression coefficient  $R^2 = 0.996$  close to unity which recommends that the adsorption of copper on tea waste follow the pseudo-second order adsorption kinetics. The calculated  $q_e$  is close to  $q_e$  experimental. So, the pseudo second order equation fitted the experimental data well.

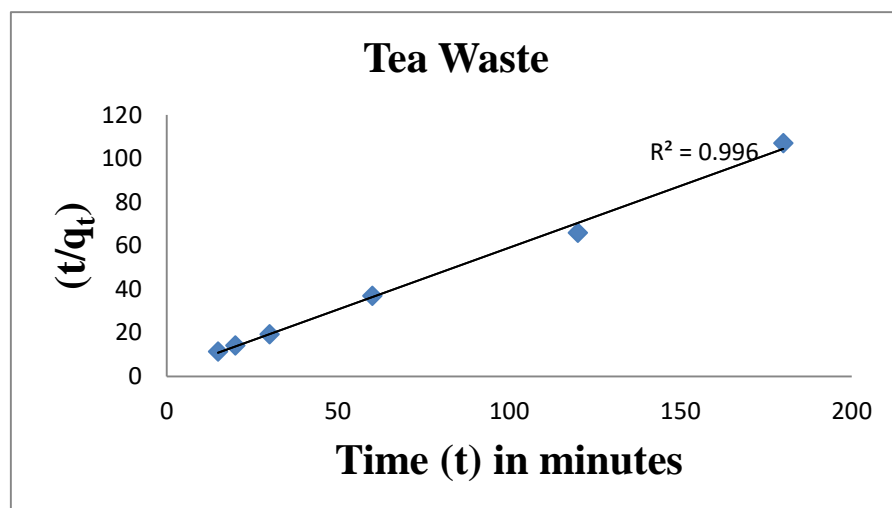


Fig 3.8: Pseudo-second order kinetics for Cu by using tea waste

Table 3.4- Adsorption Kinetics Model

Model	Parameter	Value	R <sup>2</sup>
Pseudo- first order	K <sub>1</sub>	0.0667	0.75
	q <sub>e</sub> calculated	0.40	
Pseudo-Second order	K <sub>2</sub>	0.24	0.99
	q <sub>e</sub> calculated	1.76	

#### 4. CONCLUSION

Tea waste is a cheap and effective adsorbent for the removal of copper (II) ions from aqueous solution. Experiment result showed that Tea waste is capable for expelling Copper from aqueous solution to an extent of 91 % at ideal state of pH 5, contact time 120 minutes, initial conc. of 10 ppm and 0.5 gram /100 ml adsorbent dose. The equilibrium data obtained from this study was best fitted to the Freundlich model with correlation coefficient  $R^2 = 0.99$ . In order to correlate metal uptake concentration and kinetic studies of adsorption revealed that the adsorption process follow a pseudo second with correlation coefficient  $R^2 = 0.99$ . Therefore, Tea waste can be used for the removal of Cu from waste water without any pre-treatment.

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