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Adsorption Studies of Cu^{2+} using Tea Leaves and Tea Fibre (*Camellia Sinensis*) as Adsorbents

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Abstract: *Pollution of aquatic environments is in geometric increase and it is becoming a serious environmental problem, this pollution however includes heavy metal and they tend to threatens aquatic ecosystems, aquaculture, and directly or indirectly human health. These tend to pose danger due to their relatively high and persistent nature and accumulation and bio magnifications along the aquatic food chain. Thus this research work focuses on the removal of Cu^{2+} from aqueous solution using Tea Leaves and Tea Fibre (Camellia Sinensis) as Adsorbents. From the result of this experiment, the above named adsorbent is very efficient as it tend to 99.9% removal of the heavy metal; however it is found that the variation of pH has a negligible effect in the % removal of Cu^{2+} and at a very high adsorbent dosage, % removal of Cu^{2+} decreases. Due to the high removal of Cu^{2+} from aqueous solution using tea fiber and leaves, it clearly shows that tea fibre and tea leaves are good adsorbent for the removal of Cu^{2+} from aqueous solution. Therefore tea fibre and tea leaves can be employed in treatment of waste water containing Cu^{2+} for effective removal.*

1. Introduction

Pollution of aquatic environments is in geometric increase and it is becoming a serious environmental problem, this pollution however includes heavy metal and they tend to threatens aquatic ecosystems, aquaculture, and directly or indirectly human health (Etim *et al.*, 2019a,b). These tend to pose danger due to their relatively high and persistent nature and accumulation and bio magnifications along the aquatic food chain (Fu *et al*., 2014). The term “heavy metals” is often used when addressing stable and potentially toxic metals with an atomic density greater than 4g/cm³ (Etim *et al.*, 2019c,d; Adelagun *et al*., 2021; Etim et al., 2017).

Biosorption in recent times are known to be an alternative technique for the uptake of toxic metals including Cu^{2+} from wastewater (Babarinde *et al.*, 2008). However, it is a relatively new technology that has important use in the removal of low-level concentration of toxic metal (Akhtar *et al*., 2004). Biosorption is a new technology that can be employ in the removal of metal ions from aqueous solutions, and this serve to replace the old conventional methods such as reduction or oxidation, ion exchange, filtration, electrochemical treatment, membrane technology, evaporation recovery, chemical precipitation, chemical lime coagulation and solvent extraction (Anayurt, 2009). The mechanism of the biosorption process has been explained in terms of the reaction between anionic groups present in the biomasses and the cationic metal ions (Etim *et al.*, 2019a,c).

The tea plant is the species of plant whose leaves and leaf buds are used to produce tea. It is termed as a low cost adsorbent since it requires little processing, it is abundant in nature, and a by-product from tea processing as stated by (Etim *et al*., 2022; Bajpai *et al*., 201; Itodo and Etim, 20150). In this research work, the tea fibre and tea leaves from tea plant are used as an absorbent.

This research work focus on the removal of Cu^{2+} from aqueous solution using tea fibre and tea leaves as an absorbent.

2. METHODOLOGY

2.1. Sample Collection and Preparation

The tea leaves (*Camellia Sinensis*) for this research work was collected from Kakara High Land Tea, Sardauna L.G.A., Taraba State, Nigeria. They were collected into in the early hours of the day and then washed properly to remove moist and dirt, after which they were rinsed with distilled water. The sample was then properly dried at room temperature after which the sample was pulverized and sieved with 150mm micron.

2.2. Preparation of Stock Solution

Copper (II) oxide of 0.1M concentration was prepared and used all through the experimental work. 7.95g of copper (II) oxide powder were dissolved in 1000 mL of the stock solution.

2.3. Preparation of Different Concentrations of Metal Solutions

In this research work, a total of 4 different concentrations of copper (II) oxide solutions were prepared: 20mg/l, 30mg/l, 40mg/l and 50mg/l. Subsequently, the copper solutions with different concentrations and 2g of biosorbent materials were put into an orbital shaker at different temperatures (between 40ºc - 70ºc). The rotational speed of shaker in all the experiments was kept constant at 220rpm. This experiment was performed in duplicate and the best result was used. Lastly, the solution was filtered to prepare samples for the measurements of the metal ion concentration (Etim *et al.*, 2022 and Asuquo *et al., 2019*)

2.4. Effect of Initial Concentration

Metal solution of 50mL, containing different concentrations; 20mg/l, 30mg/l, 40mg/l and 50mg/l were measured into different conical flasks. 2g of the biosorbent were dispersed in each of them, the flasks were corked and the mixture agitated with the aid of a shaker for 1hour to attain equilibrium, the slurries were then filtered using whatman filter paper and a plastic funnel, the filtrate were kept in well labeled containers and thereafter the concentrations of the resulting filtrate were determined using Atomic absorption spectrometer. (Etim *et al.*, 2022) and (Entezari, *et al.*, 2009)

2.5. Effect of pH

The effects of pH on the biosorption of metal ions were carried out within the range that would not be influenced by the metal precipitated (Pavasant, *et al*., 2006). Experiments were conducted at 30ºC to study the effect of initial solution pH on the biosorption of copper (II) oxide by contacting 2g of the *camellia sinensis* with 50mL of the metal ion solution in a glass tube. The pH of each of the solutions were adjusted to the desired value with 0.1M sodium hydroxide and /or 0.1M nitric acid. The studies were conducted at pH values of 2, 3, 5 and 7. The glass tubes containing the mixture were left in a water bath for 24 h. The biomass were removed from the solution by decantation and the residual the metal concentration in the solution were analyzed

2.6. Effect of Biosorbent Dosage

Biosorbent of 1g, 2g, 3g, and 4g were weighed into different conical flasks. 50ml of metal solution were measured into each of the conical flasks and labeled. The flasks were corked and the mixture agitated with the aid of a shaker for 1hour to attain equilibrium, the slurries were then filtered using Whatman filter paper and a plastic funnel, the filtrate were kept in well labeled containers and thereafter the concentrations of the resulting filtrate were determined using Atomic absorption spectrometer. (Reddad, *et al*., 2002 and Etim, *et al*., 2022)

2.7. Isotherms Studies of Biosorption

The experimental data will be fitted using Langmuir and Freundlich (Hall et al. 1966)

Freundlich Isotherm

Freundlich isotherm describes an empirical relationship that exists between the adsorption of solute and the surface of the adsorbent. The empirical equation proposed by Freundlich is:

$$\log q_e = \log K_f + \frac{1}{n}\log C \quad (2.1)$$

Where,

K_f and n are coefficients;

q_e is the weight adsorbed per unit weight of adsorbent

C is the concentration of the metal solution

taking logarithm and rearranging: $\log q_e$

$$q = K_f C^{1/n} \quad (2.2)$$

The constant K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption (Voudrias et al. 2002).

Langmuir Isotherm

The Langmuir isotherm equation is written as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (2.3)$$

Where,

C_e is the equilibrium concentration of adsorbate,

q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium.

q_m and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The values of q_m and b were calculated from the slope and intercept of the Langmuir plot of C_e versus C_e/q_e (Langmuir 1918).

3. RESULTS AND DISCUSSION

3.1. Effect of Initial Concentration in the Removal of Cu^{2+} from Aqueous Solution using Tea Fibre and Tea Leaves

Table 3.1 and 3.2 shows clearly the effect of Initial concentration in the removal of Cu^{2+} from aqueous solution using tea fibre and tea leaves respectively. It was obseved that as the initial concentration increases, the % removal of Cu^{2+} also increases when tea fibre and tea leaves were used as adsorbent, this shows clearly that the more the initial concentration of an aqueous solution, the more Cu^{2+} can be removed using the above named adsorbent.

In similar manner, figure 3.1 and 3.2 is a graph showing the effect of concentration in the removal of Cu^{2+} from aqueous solution using tea fibre and tea leaves respectively

Table3.1. *Initial concentration values for the removal of Cu^{2+} from aqueous solution using tea fibre*

Initial conc. (C_i)	Final conc. Mg/L (C_f)	% Removal (%R)	Metal uptake (q_e)
20.00	0.01418	99.929	0.49965
30.00	0.01365	99.954	0.74965
40.00	0.01391	99.965	0.99965
50.00	0.01364	99.973	1.24966

Table3.2. *Initial cconcentration values for the removal of Cu^{2+} from aqueous solution using tea leaves*

Initial conc. (C_i)	Final conc. Mg/L (C_f)	% Removal (%R)	Metal uptake (q_e)
20.00	0.01445	99.927	0.49963
30. 00	0.01364	99.954	0.74966
40.00	0.01418	99.964	0.99965
50.00	0.01377	99.972	1.24965

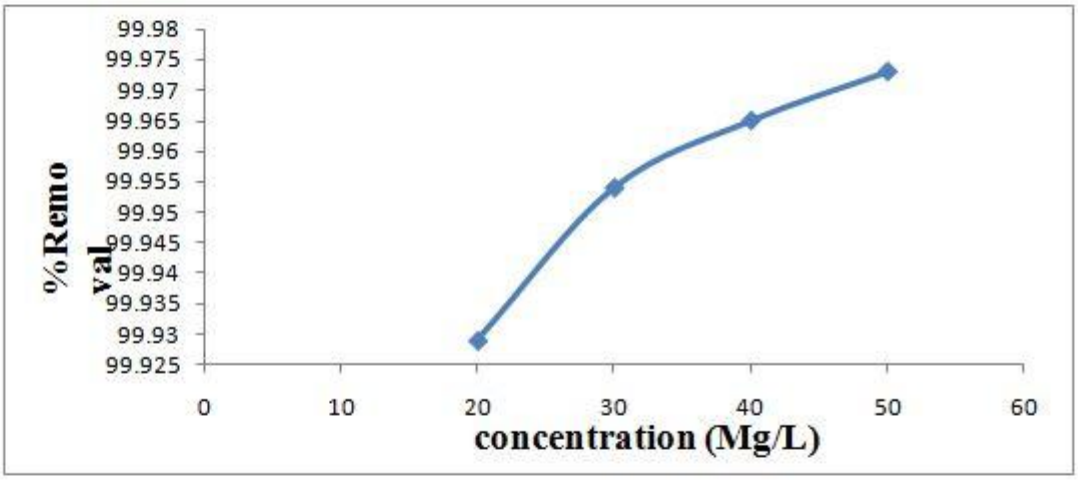

Figure3.1. *Graph of initial concentration showing the % removal of Cu^{2+} using tea fibre*

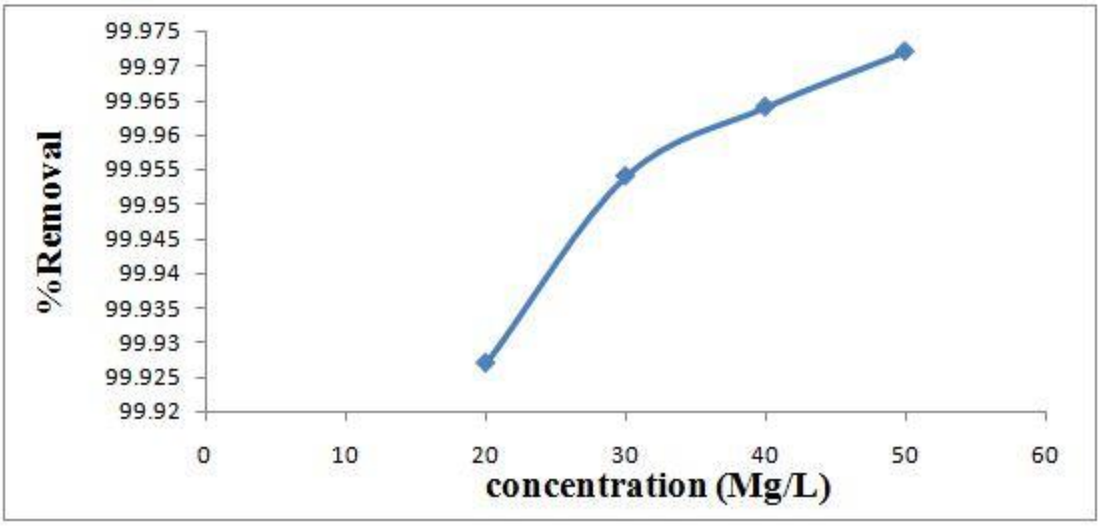

Figure3.2. *Graph of initial concentration showing the % removal of Cu^{2+} using tea leaves*

3.2. Effect of pH in the Removal of Cu^{2+} from Aqueous Solution using Tea Fibre and Tea Leaves

Table 3.3 and 3.4 shows the effect of pH in the removal of Cu^{2+} from aqueous solution using tea fibre and tea leaves respectively. It was obseved that the pH of the aqueous solution have negligible effect in the % removal of Cu^{2+} when tea fibre and tea leaves were used as adsorbent, this shows clearly that the pH of an aqueous solution may not affect the % removal of Cu^{2+} using the above named adsorbent**.**

Similarly, figure 3.3 and 3.4 is a graph showing the effect of pH in the removal of Cu^{2+} from aqueous solution using tea fibre and tea leaves respectively

Table3.3. *pH values for the removal of Cu^{2+} from aqueous solution using tea fibre*

pH	Initial conc. (C_i)	Final conc. Mg/L (C_f)	% Removal (%R)	Metal uptake (q_e)
2.00	40.00	0.01445	99.964	0.99963
3.00	40.00	0.01377	99.965	0.99965
5.00	40.00	0.01377	99.965	0.99965
7.00	40.00	0.01431	99.964	0.99964

Table3.4. *pH values for the removal of Cu^{2+} from aqueous solution using tea leaves*

pH	Initial conc. (C_i)	Final conc. Mg/L (C_f)	% Removal (%R)	Metal uptake (q_e)
2.00	40.00	0.01404	99.965	0.99965
3.00	40.00	0.01377	99.965	0.99966
5.00	40.00	0.01445	99.964	0.99964
7.00	40.00	0.01404	99.965	0.99965

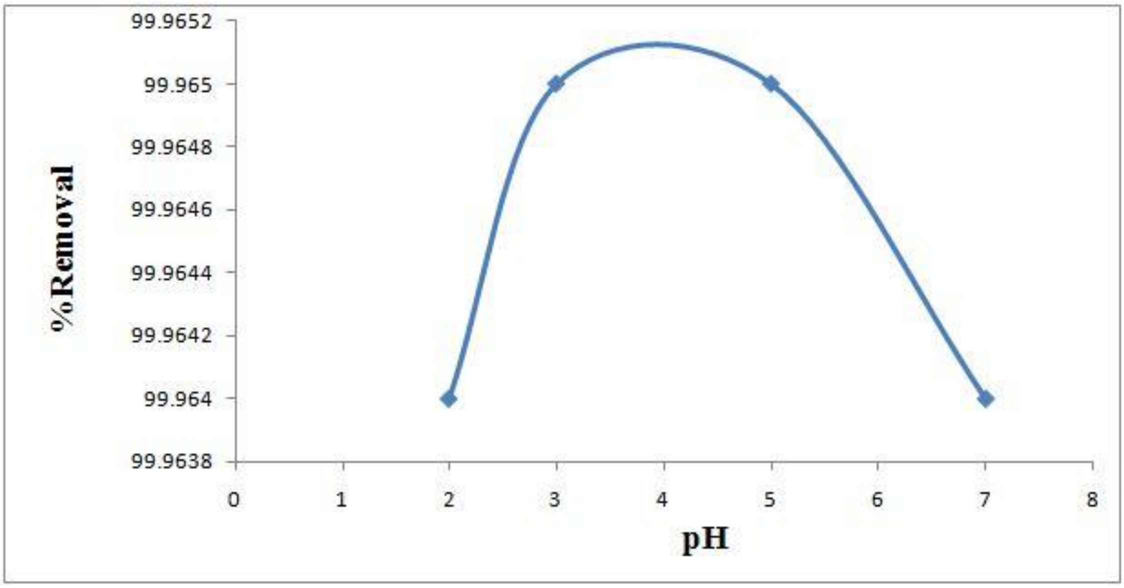

Figure3.3. *Graph of pH indicatin % removal of copper using tea fibre (Camellia Sinensis).*

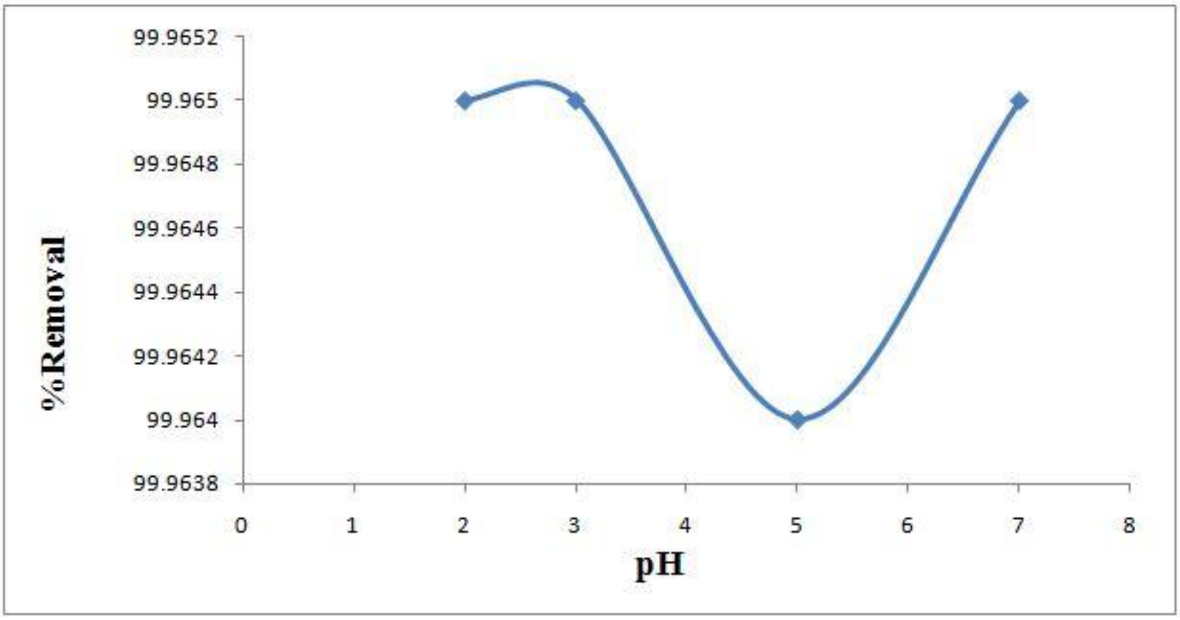

Figure3.4. *Graph of pH indicating % removal of copper using tea leaves*

3.3. Effect of Adsorbent Dosage in the Removal of Cu^{2+} from Aqueous Solution using Tea Fibre Tea Leaves

Table 3.5 and 3.6 shows the effect of adsorbent dosage in the removal of Cu^{2+} from aqueous solution using tea fibre and tea leaves respectively. A decrease of % removal was obseved at a high adsorbent dosage when tea fibre and tea leaves were used as adsorbent, this shows clearly that at high adsorbent dosage, the % removal of Cu^{2+} will be reduced using the above named adsorbent**.**

Similarly, figure 3.5 and 3.6 is a graph showing the effect of adsorbent dosage in the removal of Cu^{2+} from aqueous solution using tea fibre and tea leaves respectively

Table3.5. *Adsorbent dosage data for the removal of Cu^{2+} from aqueous solution using tea fibre*

Adsorbent dosage(g)	Initial conc. (C_i)	Final conc. Mg/L (C_f)	% Removal (%R)	Metal uptake (q_e)
1.00	40.00	0.01377	99.966	1.99931
2.00	40.00	0.01404	99.965	0.99965
3.00	40.00	0.01377	99.966	0.66644
4.00	40.00	0.01526	99.962	0.49981

Table3.6. *Adsorbent dosage data for the removal of Cu^{2+} from aqueous solution using tea leaves*

Adsorbent dosage(g)	Initial conc. (C_i)	Final conc. Mg/L (C_f)	% Removal (%R)	Metal uptake (q_e)
1.00	40.00	0.01364	99.966	1.99932
2.00	40.00	0.01364	99.966	0.99966
3.00	40.00	0.01431	99.964	0.66643
4.00	40.00	0.01364	99.966	0.49983

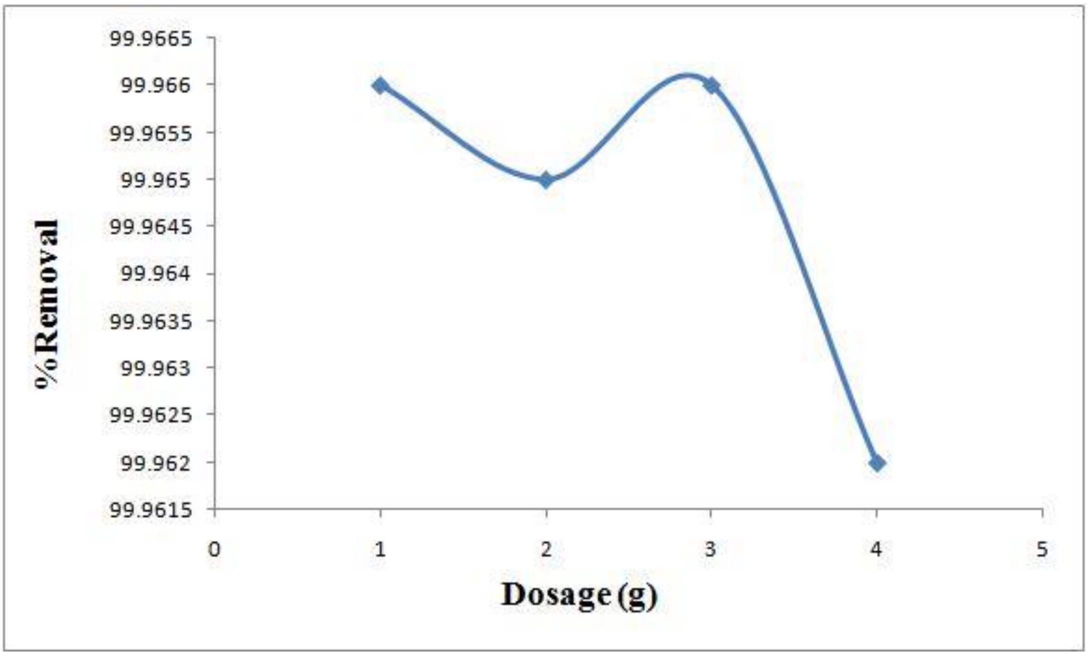

Figure3.5. *Graph showing adsorbent dosage for % removal of Cu^{2+} using tea fibre*

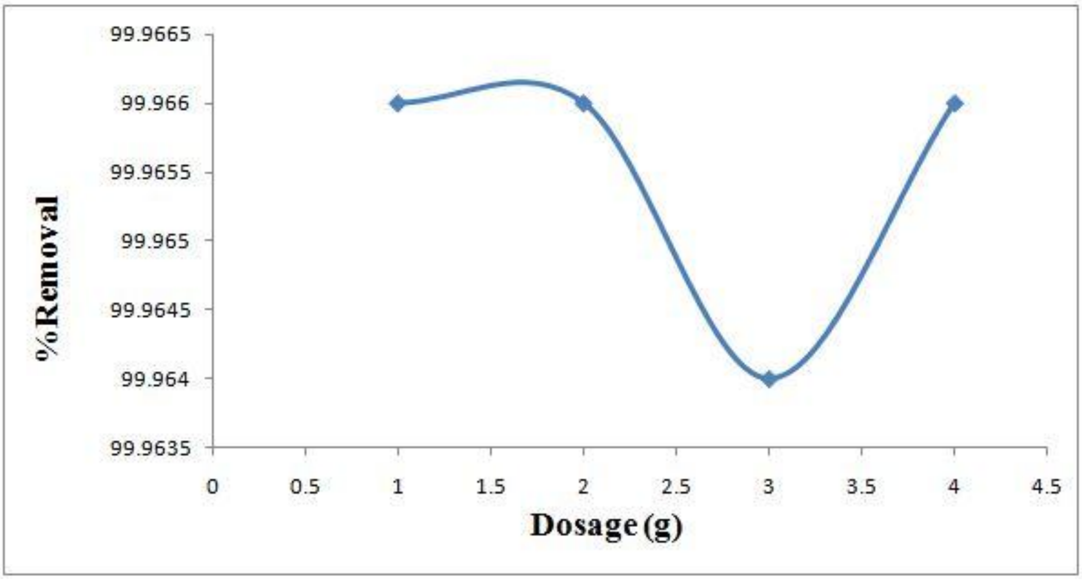

Figure3.6. *Graph showing adsorbent dosag for % removal of copper using tea leaves*

3.4. Freundlich Isotherm and Langmuir Isotherm

The adsorption constants and the correlation coefficients for the two isotherm models are presented in table 3.7 and 3.8 where K_L and K_f is the adsorption capacity and q_{max} and 1/n the adsorption intensity. This indicate the relative distribution of energy and heterogeneity of adsorbate sites for Langmuir and Freundlich model and considering the distribution, the Langmuir model described the adsorption process better than Freundlich model. The R^2 values for the two models also indicate Langmuir to be better. The R_L values which are called the separation factor explain the adsorption to be irreversible.

Table3.7. *Freundlich isotherm data for tea leaves and fibre*

Conc. (Mg/L)	$logC_e$ (leaves)	$logq_e$ (leaves)	$logC_e$ (fibre)	$logq_e$ (fibre)
20	-1.8401	-0.3013	-1.8483	-0.3013
30	-1.8652	-0.1251	-1.8652	-0.1251
40	-1.8483	-0.0002	-1.8567	-0.0002
50	-1.8611	0.0968	-1.8652	0.0968

Table3.8. *Langmuir isotherm data for tea leaves and fibre*

Conc. (Mg/L)	C_e/ q_e (leaves)	C_e (leaves)	C_e/ q_e (fibre)	C_e (fibre)
20	0.029	0.01445	0.028	0.01418
30	0.018	0.01364	0.018	0.01364
40	0.014	0.01418	0.014	0.01391
50	0.011	0.01377	0.012	0.01364

Table3.9. *Isotherm parameters for the adsorption of Cu^{2+} using tea fibre and leave at different concentrations*

Isotherm	Parameters	Biosorbent
Langmuir	q_{max} 21.549 K_L -0.2803 R^2 0.6124 R_L 0.9962	**Fibre**
Freundlich	1/n -15.259 K_f -28.446 R^2 0.5165	
Langmuir	q_{max} 14.005 K_L 0.1782 R^2 0.4397 R_L 0.9961	**Leave**
Freundlich	1/n -8.3968 K_f -15.647 R^2 0.3192	

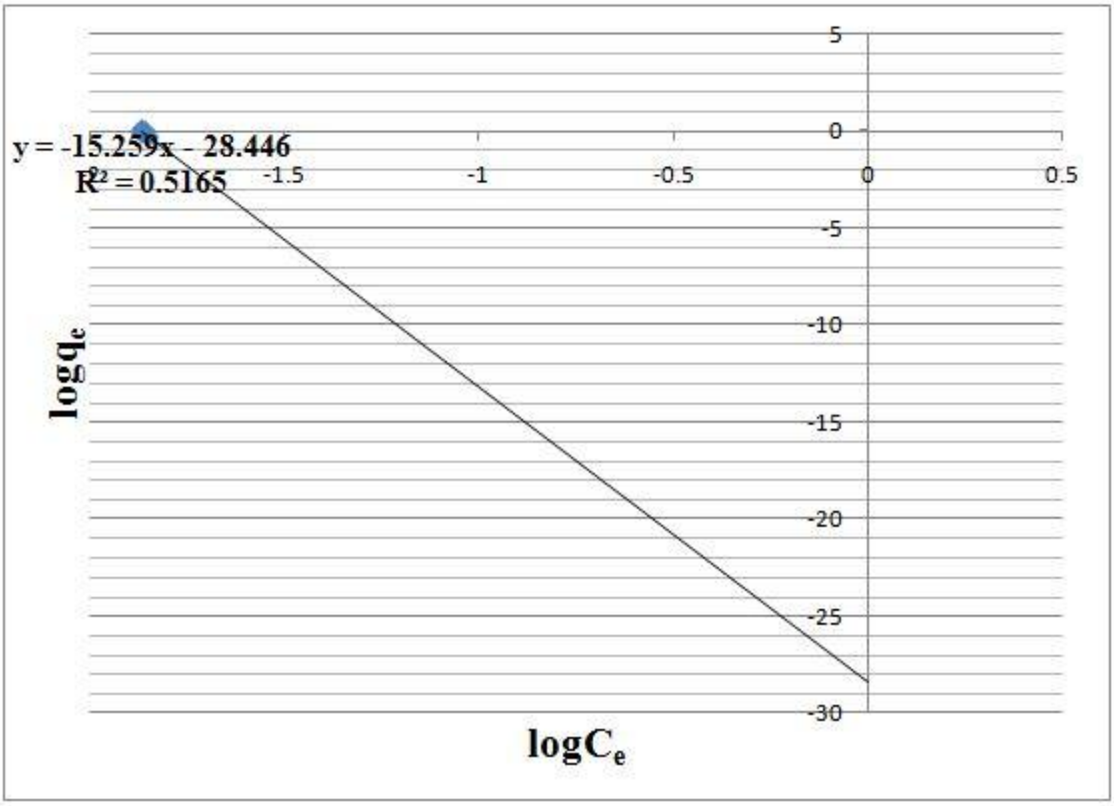

Figure3.7. *Freundlich isotherm graph for tea fibre*

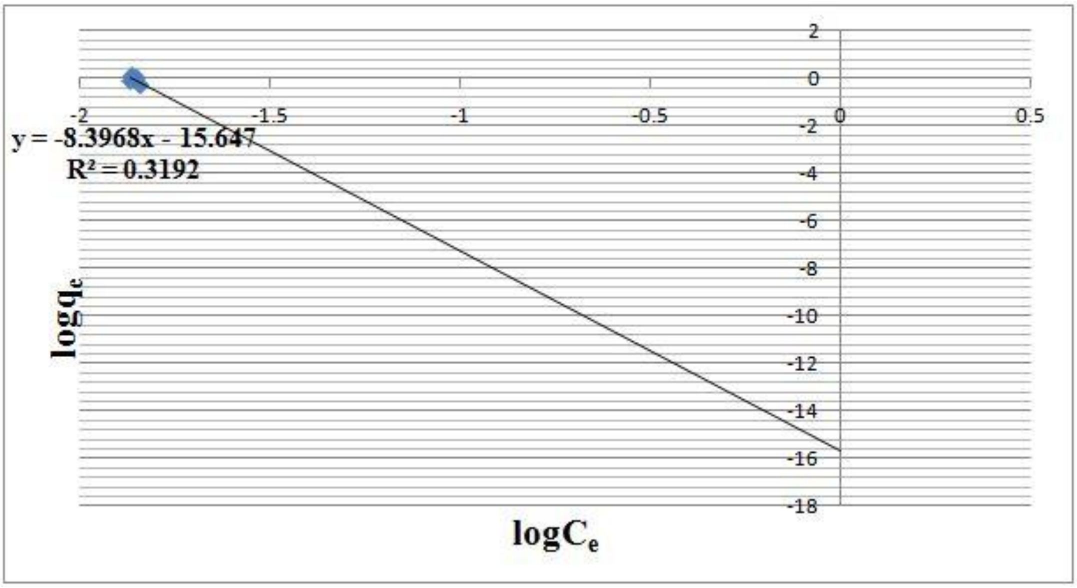

Figure3.8. *Freundlich isotherm graph for tea leave*

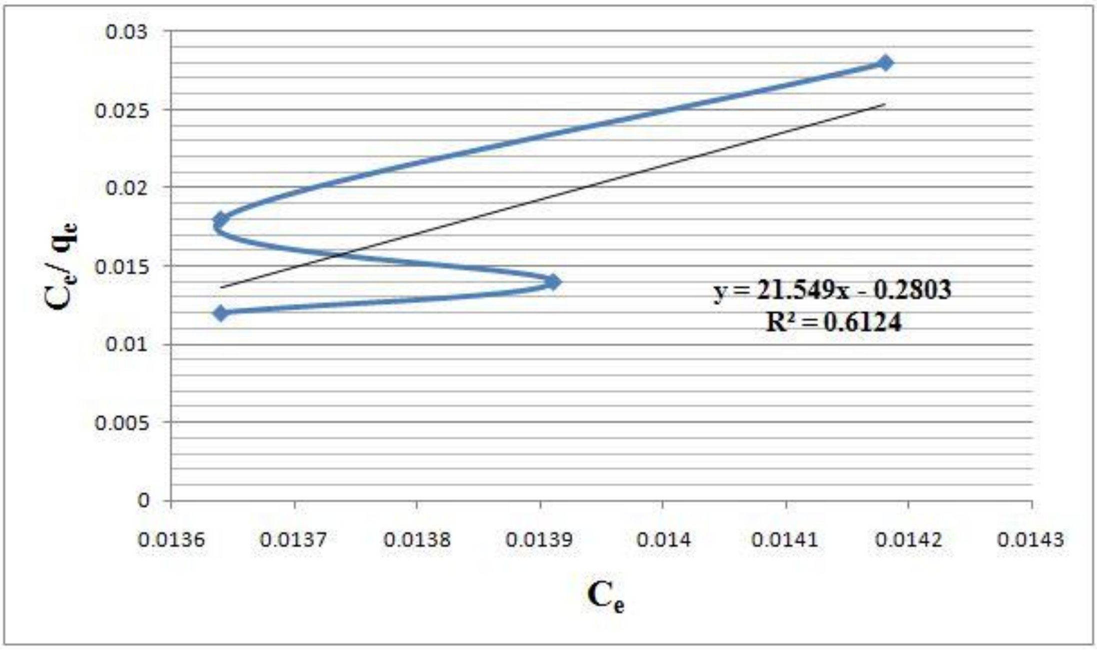

Figure3.9. *Langmuir isotherm graph for tea fibre*

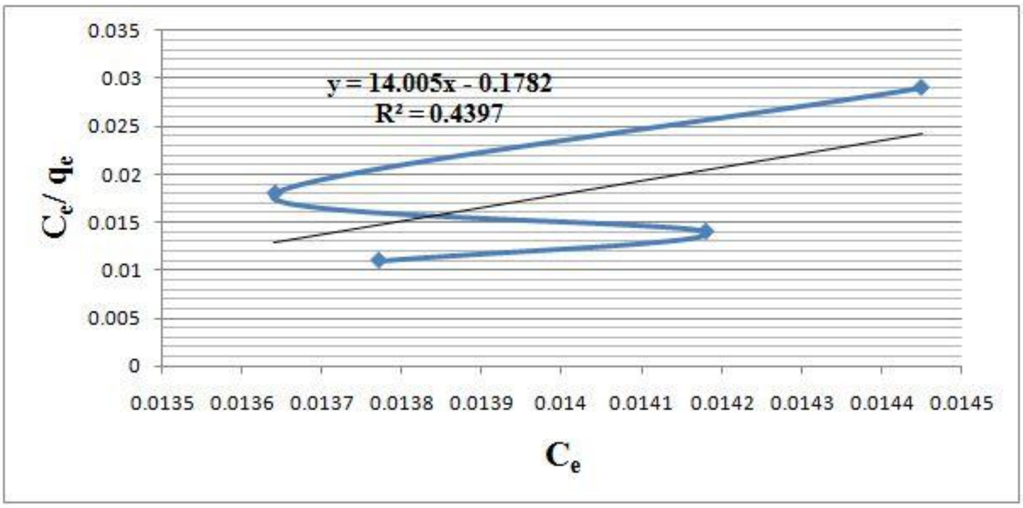

Figure3.10. *Langmuir isotherm graph for tea leave*

4. Conclusion

From the results obtained in this show that tea fibre and tea leaves can be used can good adsorbents for the removal of Cu^{2+} in the treatment of domestic wastewaters and industrial effluents.

The maximum percentage removal of Cu^{2+} was found to 99.97% in both adsorbents. This further attests to the high the high accuracy and efficiency of the adsorbent used. In conclusion, since both the tea fibre and tea leaves are found to be good biosorbents which are occur naturally and are environmentally friendly, these adsorbents should be adopted in the treatment of wastewaters and industrial effluents.

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