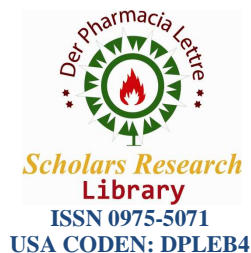




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## Biosorption of Cu (II) from aqueous solutions: Kinetics and characterization studies

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### ABSTRACT

Removal of heavy metals from industrial wastes has been an important environmental research area. In the present study a mixture of two different types of biosorbent for removal of copper from water was investigated. Three types of biosorbents were tested i.e. EG, UA and a combination of both (EG+UA). The batch scale studies were carried out to study the effect of pH, metal concentration and contact time on adsorption capacity. Maximum removal percentage of Cu (II) by EG was about 99% at pH 5 UA and EG+UA got the maximum removal of Cu of about 68%, 74% at pH 8 respectively. In the metal concentration studies EG and UA adsorbed the increased concentration of Cu (II), the combination of adsorbents showed 79.8% adsorption for Cu at 100mg/L and for other concentrations of 200mg/L, 300mg/L, 400mg/L and 500mg/L it showed 68.6%, 67.6%, 58.8 and 57.1% respectively. The maximum Cu (II) removal exhibited by the EG+UA combination was 79.85% obtained for the optimal contact time of 120 min. EG showed Cu (II) removal was maximum up to 99% and UA showed the removal was maximum up to 84% with the contact time 120 min. The morphology characterization of the three adsorbent systems was investigated using the Scanning Electron Microscope (SEM). The Langmuir isotherm was found to be the best-fitting isotherm which indicates the experimental values match with the theoretical reported values. In the kinetic studies the higher R<sup>2</sup> values confirm that the adsorption data are well explained by pseudo second order kinetics.

**Keywords:** Egg shell, heavy metal, Copper, Bio-adsorbents, isotherm models

### INTRODUCTION

Heavy metals are widely distributed in the environment and ecologically important due to their high level of toxicity for living organisms including human beings [1]. Environmental pollution due to the industrial wastes is because of their high content of several heavy metal ions. Copper is one of the major heavy metal ions from the industrial effluent. Copper is essential to human beings as a micronutrient in our diets. The uptake of copper in excess doses may lead to serious kidney failure and liver disease in humans. Water is polluted in many ways like effluent of leather, dye, chemical and electroplating industries. To reduce the environmental pollution due to the heavy metal accumulation, particularly naturally existing element on earth-copper, it is essential to decrease the content of Cu in various situations. Industries and sewage treatment plants release the copper to water and make them polluted. Different methods are available to remove heavy metals before discharging into the environment [2]. Adsorption is one of the cost effective and also eco friendly method for the removal of copper ion from the waste waters even at very low concentration [3, 4].

Egg shells in the form of Calcium Carbonate ( $\text{CaCO}_3$ ) act as an agent in the removal of heavy metals from water and soil. Researchers have shown that derivatives from egg shell waste can be used to effectively remove several divalent metal ions, such as lead, cadmium and copper, from aqueous solution [5, 6]. Egg shell wastes could be used as an alternative to  $\text{CaCO}_3$  for the immobilization of heavy metals in soils [7]. Marine algae could be particularly useful as they are quite abundant in many regions of the world, have metal removal potential [8]. Marine green algae have various functional groups of polysaccharides, proteins and lipids on the surface of cell wall which determined the metal binding capacity [9].

The aim of this work was to evaluate the potential of mixture of two adsorbent namely egg shell and algae as biosorbent for Cu metal ions from aqueous solutions. The adsorption studies were carried out as a function of solution pH, different metal concentration and contact time. The equilibrium data were described by the Freundlich, Langmuir isotherm models and Kinetics studied and compared with experimental data. Atomic absorption spectroscopy (AAS) and scanning electron microscopy (SEM) analysis were performed to elucidate the adsorption mechanism(s).

## MATERIALS AND METHODS

### *Preparation of biosorbent*

The eggshells were collected from a local hatchery waste. They were washed several times with distilled water to remove impurities and dried it in oven at  $105^\circ\text{C}$  for 24 hours. This was followed by soaking the dried eggshells with 0.1N concentration of sulphuric acid for 30 minutes. Then washed with distilled water and again dried in hot air oven at  $180^\circ\text{C}$  after 24 hours. The eggshells were pulverized in mortar and pestle. The eggshell powder was finally ready to use. The second adsorbent was Algae used for the present study. *Ulva* species were collected from the coast of Mandapam (Lat.  $09^\circ 17' \text{N}$ ; Long.  $79^\circ 08' \text{E}$ ), Palk Bay, Tamil Nadu, India. Algae were washed with distilled water and kept it for sun light for complete dry. Dried algae were pulverized in mortar and pestle. The final algae powder was used for the study. The third adsorbent was mixture of one and two in the ratio of 1:1 for the present study. These three biosorbents were named egg shell powder (EG), *Ulva* sp.- marine green alga powder (UA) and a combination of both powder (EG+UA).

### *Preparation of copper solution*

The solution of Cu was prepared by diluting a 1000 ppm stock metal ion solution obtained by dissolving 3.93 g of hydrated copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) in 1000 ml distilled water. All the chemicals used were of analytical grade and distilled water was used to prepare the solutions.

### *Experimental Procedure*

To determine the optimum conditions for biosorption of Cu, the batch biosorption experiments were conducted with EG powder at room temperature in 250 ml Erlenmeyer flasks. The effect of pH on the adsorption capacity was investigated at pH values in the range of 2.0–10.0 by using known volume of 100mg/L (100ppm) Cu solutions.

The desired pH of the solutions were maintained by adding HCl or NaOH at the beginning of the experiment and not controlled afterwards. Adsorbent (EG, UA, 1:1 ratio of EG+UA) 0.25g/100ml was added to medium and the reaction mixture was agitated at room temperature at 200 rpm for 180 min. In the later experiments the pH of the Cu solutions were adjusted to the optimum value ( $5.0 \pm 0.1$ ). The effect of contact time was studied in the time range of 5–360 min. Similarly above, metal solutions with the concentration range of 100–500mg/L (100ppm–500ppm) were used to assess the effect of initial Cu ion concentrations. At the end of the adsorption process adsorbent was separated from the solution, filtered and analyzed for Cu concentration by AAS. Three replicates were used for each Cu biosorption experiments and the results given were the average values.

### *Equilibrium Studies of Cu (II) Adsorption*

Metal solutions with the concentration range of 100–500mg/L (100 ppm–500 ppm) were used to assess the effect of initial Cu ion concentrations. Final Cu concentrations were obtained from AAS. To check the applicability of the Langmuir and Freundlich adsorption isotherms under optimum conditions obtained. Adsorption quantity  $Q_e$  was calculated by equation 1:

$$Q_e = \frac{(C_i - C_f)V}{M} \quad (1)$$

Where  $C_i$  and  $C_f$  (mg/L) are the liquid-phase concentration of copper at initial and final, respectively,  $V$  (L) is the volume of the solution and  $M$  (g) is the mass of dry adsorbent used. The Langmuir and Freundlich isotherms as shown in equation 2 and 3 were chosen for the estimation of metal adsorption.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{K_L Q_m} \quad (2)$$

$$\ln(Q_e) = \ln(K_F) + \frac{1}{n_F} \ln(C_e) \quad (3)$$

Where  $C_e$  = adsorbent concentration at equilibrium ( $\text{mg L}^{-1}$ );  $Q_e$  = equilibrium adsorption capacity ( $\text{mg g}^{-1}$ );  $K_L$  Langmuir adsorption constant ( $\text{L mg}^{-1}$ );  $Q_m$  = maximum adsorption capacity ( $\text{mg g}^{-1}$ );  $K_F$  = Freundlich constant ( $\text{L g}^{-1}$ );  $n_F$  = heterogeneity factor of adsorption sites.

#### **Kinetic Studies of Cu (II) Adsorption**

The kinetic studies were established similar to batch experiments but with various time interval from 5, 10, 15, 30, 60, 120, 180, 240, 300, 360 min.

The linear form of the pseudo first-order rate equation 4 [10] is given.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where,  $q_e$  (mg/g) and  $q_t$  (mg/g) are the amounts of the metal ions biosorbed at equilibrium and time  $t$  (min), respectively, and  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of the equation.  $k_1$  was determined experimentally by plotting of  $\ln(q_e - q_t)$  versus  $t$ .

Experimental data were also tested by the pseudo second-order kinetic model which is given in the equation 5 [11]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \quad (5)$$

where,  $k_2$  ( $\text{g}/(\text{mg min})$ ) is the rate constant of the pseudo second-order equation,  $q_t$  (mg/g) and  $q_e$  the amount of metal ions adsorbed at any time  $t$  and at equilibrium. The linear plot of  $t/q_t$  versus  $t$  for the pseudo second-order model for the biosorption of Cu(II).

#### **SEM**

The morphological investigation on the bare EG sample, EG sample after Cu(II) absorption and EG combined with UA sample after Cu(II) absorption has been examined by a scanning electron microscope (Model:ULTRA55 FESEM).

## **RESULTS AND DISCUSSION**

There have been numerous studies on the sorption of heavy metals from aqueous solutions by egg shells, algae. In the present study the removal of copper ions from aqueous solutions using different biosorbents was investigated. Three types of adsorbents viz. EG, UA and a combination of both (EG+UA) were tested. We observed the result as follows:

#### **Effect of pH**

It is well known that pH can affect the protonation of the functional groups on the biomass as well as the metal chemistry. Figure 1 illustrated that pH obviously influenced the removal efficiency of the copper ions in the aqueous solution. The EG maximum removal percentage of Cu (II) was about 99% at pH 5. The dominant species of copper was free Cu(II) and was mainly involved in the adsorption process when the pH was lower than 5. When the pH greater than 5, copper ions started to precipitate as  $\text{Cu}(\text{OH})_2$ , this had been confirmed [12]. UA showed about 68% removal of copper at pH 8. In case of EG+UA, the maximum removal of Cu was about 74% at pH 8 that might be the reason of precipitation (Figure 1). Effect of pH results showed that EG have more efficient level removal of Cu ion compare with other two biosorbent. The EG+UA getting better removal of Cu ion compare with UA as biosorbent. [13] also reported that pH has an important role in the adsorption of lignosulfonate compounds from egg shell powder.

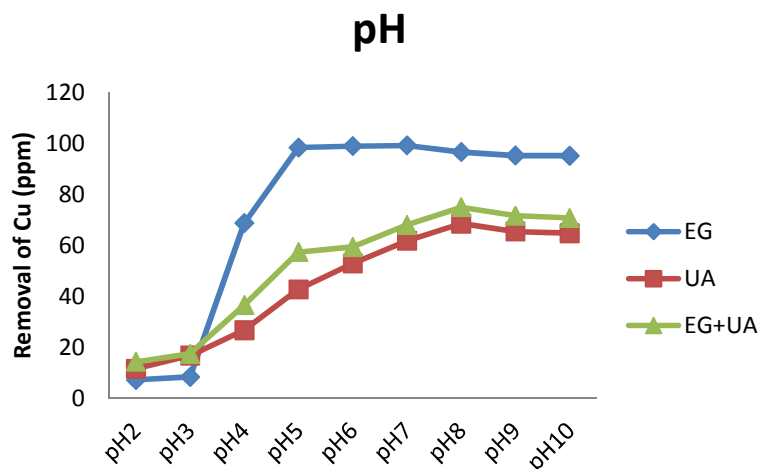


Fig. 1: Effect of pH on % removal of copper ion by bioadsorbent

#### Effect of Concentration

The amounts of copper solutions concentration range of 100–500mg/L (100ppm-500ppm) were used to assess the effect of initial Cu ion concentrations. In the results showed that EG adsorbed the increased concentration and slowly decreased in the percentile level. Cu 100mg/L showed 98.6%, 200mg/L, 300mg/L, 400mg/L and 500mg/L showed 97.2%, 96.5%, 94.6 and 93.7 respectively (Figure 2). UA showed the adsorption for Cu 100mg/L 84.1%, 200mg/L, 300mg/L, 400mg/L and 500mg/L showed 77.4%, 61.9, 59.4 and 54.9 respectively. In the third adsorbent mixture of both (EG+UA) showed the adsorption for Cu 100mg/L 79.8%, 200mg/L, 300mg/L, 400mg/L and 500mg/L showed 68.6%, 67.6%, 58.8 and 57.1% respectively.

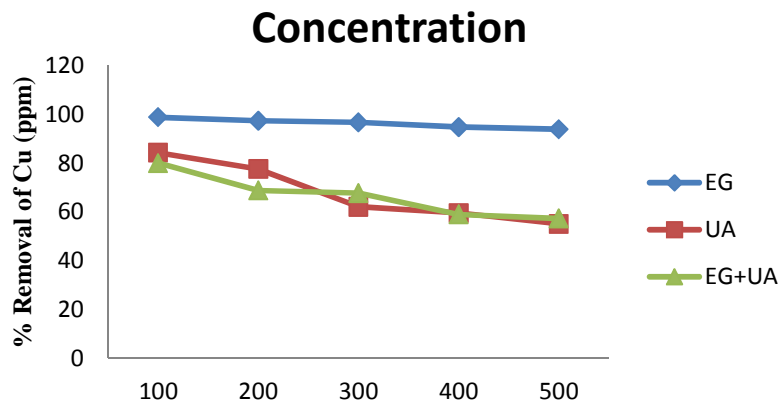


Fig. 2: Effect of Cu concentration on adsorbent

#### Effect of contact time

Results from the figure 3 indicated that the optimum contact time was recorded as 120 min for all the three biosorbents and it is said to have reached equilibrium. Beyond the equilibrium time metal removal showed a decreasing trend. EG showed that percent removal of Cu ions 11-99 % in the contact time of 10-120 min respectively. From 120-360 min, the percentage removal of Cu remains constant (99 %), which showed that equilibrium was reached at 120 min. Thus the results illustrated that the optimum contact time for maximum removal (99 %) of Cu was 120 min. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

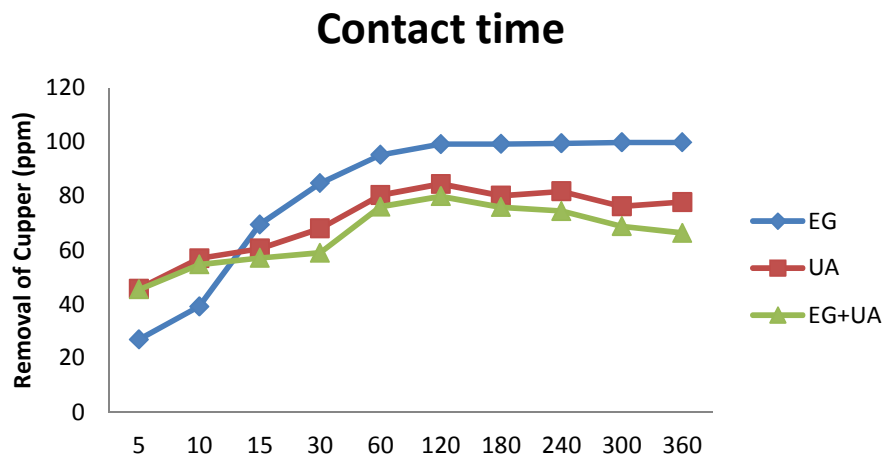


Fig. 3: Effect of Contact time with different adsorbent

In the figure 4, UA showed that Cu removal was increased from 46-84 % with the contact time variation from 10-120 min. From 120-360 min, the percentage removal of Cu decreasing, this showed that equilibrium was reached at 120 min. Thus the results illustrated that the optimum contact time for maximum removal (84.41 %) of Cu at 120 min. The similar results were got in the mixture of EG+UA maximum removal of Cu (79.85 %) in 120 min. The results showed addition of eggshell into algae was inhibited the Cu adsorption. Our results confirmed EG and UA both were got good adsorption when it used separate.

#### SEM analysis

The surface morphology of the selected biosorbents as obtained using Scanning Electron Microscopy (SEM) is shown in Figure 4. Figure 4a and Figure 4b highlights the SEM images obtained for the Egg shell sample before and after Cu adsorption. EG sample has a dense and porous surface texture while after interaction of EG with Cu (II) formation of discrete platelets or flake like deposition is seen on the surface.

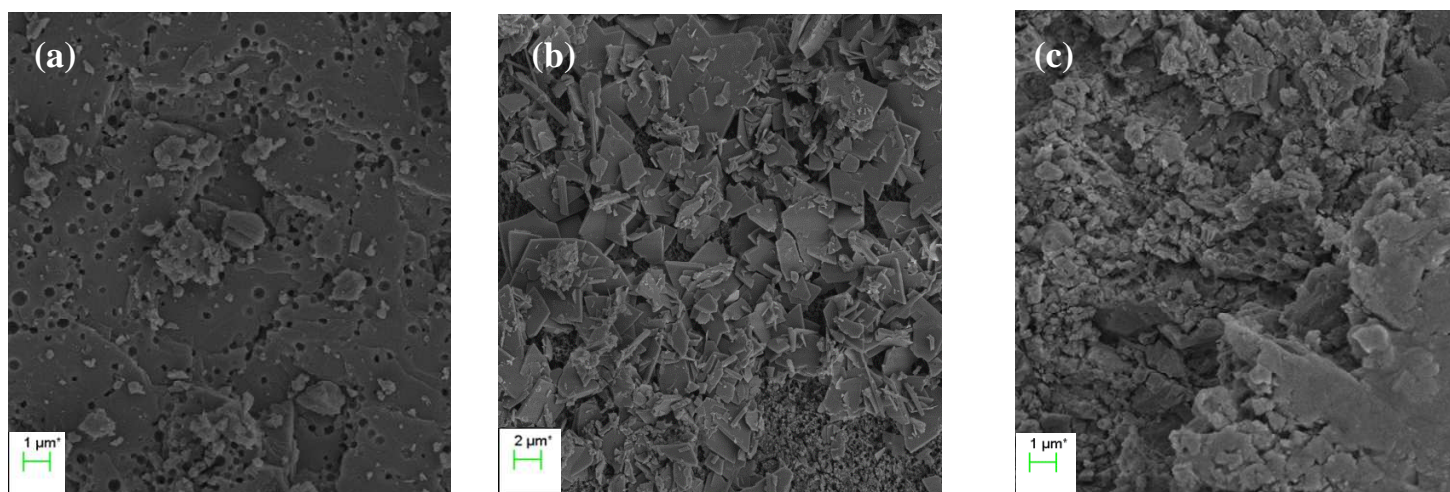


Fig. 4: SEM micrographs for Egg shell (EG) sample before adsorption (a) Egg Shell (EG) sample after Cu (II) adsorption and Egg shell in combination with Ulva-marine green algae (EG+ UA) after adsorption of Cu (II)  
*Biosorption Isotherm*

This result is in accordance with the previous reported work [14]. Moreover the porous structure found on the surface of EG sample totally disappeared. In case of Cu (II) adsorption on EG combined with *Ulva* sp.-marine green alga (Figure 4c), the SEM micrograph depicts the formation of aggregate particles throughout the surface indicating more adhesive appearance of adsorbent ions.

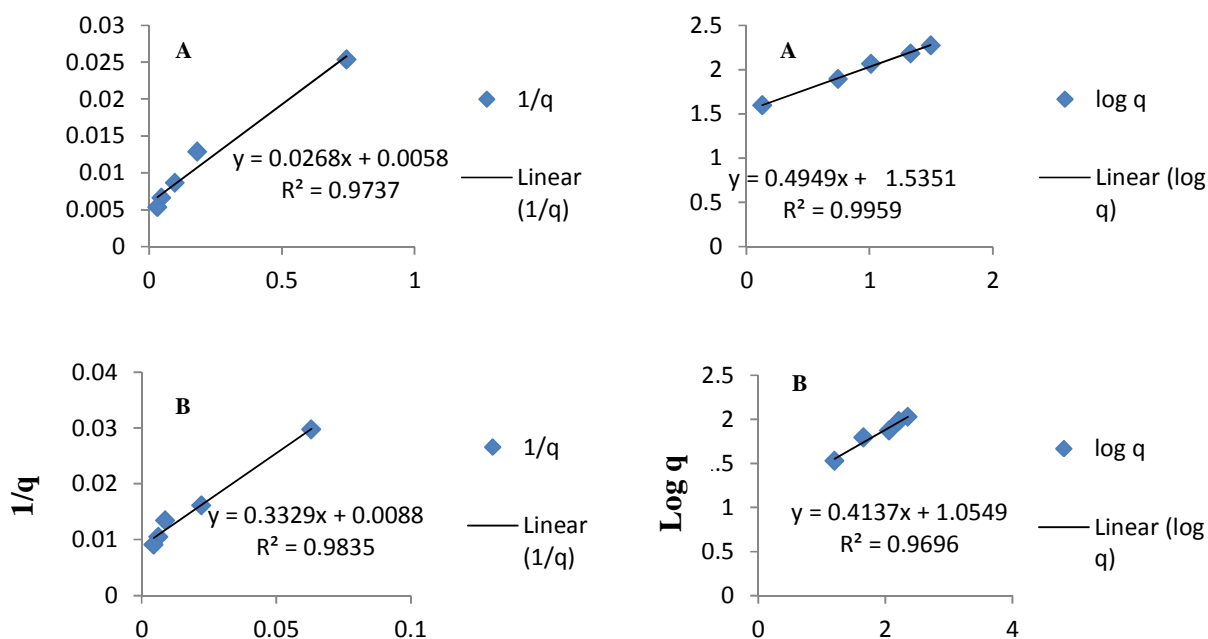
In this study, the experimental results were fitted using two isotherm models (Langmuir and Freundlich), and the best fit isotherm model was selected based on the linear regression correlation coefficients. The Langmuir and Freundlich isotherm models were applied to the experimental equilibrium data for Cu adsorption by three adsorbent. From linear plots using equation 2 and 3, the corresponding linear regression correlation coefficient value,  $R^2$  are given in Table 1 and 2. From Table 1 and 2,  $R^2$  values from Langmuir model were higher, ranging from 0.973-0.995 (Figure 5 and Figure 6). The Langmuir isotherm was then found to be the best-fitting isotherm.

Table 1: Langmuir model for Cu adsorption by different adsorbent

Isotherm Model	Adsorbent	Metal ion	Estimated isotherm parameter		
			$Q_m$ (mg/g)	$K_L$ (L/mg)	$R^2$
Langmuir	EG	Cu	172.41	0.216	0.9737
	UA		113.63	0.024	0.9835
	EG+UA		128.20	0.016	0.9959

Table 2: Freundlich model for Cu adsorption by different adsorbent

Isotherm Model	Adsorbent	Metal ion	Estimated isotherm parameter		
			$n_F$	$K_F$	$R^2$
Freundlich	EG	Cu	2.020	34.284	0.9959
	UA		2.417	11.347	0.9696
	EG+UA		1.854	6.282	0.9861





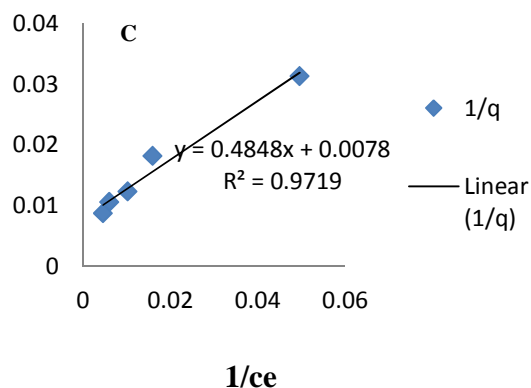


Figure 5: Langmuir isotherm for biosorption of Cu by A) EG B) UA C) EG+UA

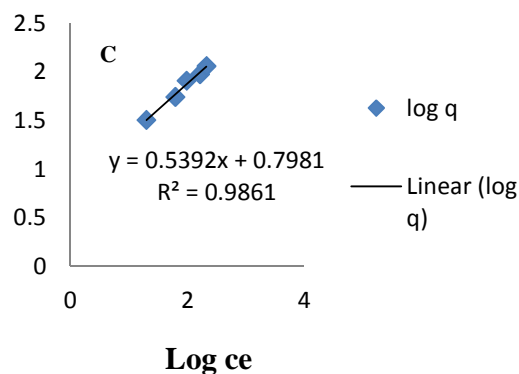


Figure 6: Freundlich isotherm for biosorption of Cu by A) EG B) UA C) EG+UA

**Biosorption Kinetics**

The data from experiments were used to determine R<sup>2</sup> values and rate constant for Pseudo-first order and Pseudo-second order model as shown in Table 3 and Table 4. The good straight line for Pseudo-second order in comparison with Pseudo-first order was shown in Figure 7 and Figure 8. The higher R<sup>2</sup> values confirm that the adsorption data are well explained by second order kinetics.

Table 3: Pseudo- First order kinetics for Cu by different adsorbent

Kinetics model	Adsorbent	Metal ion	q <sub>e</sub> .exp (mg/g)	Pseudo -First order kinetics parameter		
				k <sub>1</sub> (min <sup>-1</sup> )	q <sub>e</sub> .cal (mg/g)	R <sup>2</sup>
Pseudo-First order	EG	Cu	39.68	-0.0525	33.4041	0.9722
	UA		33.76	-0.0391	18.0218	0.9854
	EG+UA		31.94	-0.0373	17.0844	0.9264

Table 4: Pseudo -Second order kinetics for Cu by different adsorbent

Kinetics model	Adsorbent	Metal ion	q <sub>e</sub> exp (mg/g)	Pseudo-second order kinetics parameter		
				k <sub>2</sub> (min <sup>-1</sup> )	q <sub>e</sub> cal (mg/g)	R <sup>2</sup>
Pseudo-second order	EG	Cu	39.68	0.0107	51.5463	0.9704
	UA		33.76	0.0049	34.6020	0.9951
	EG+UA		31.94	0.0052	32.2580	0.9817

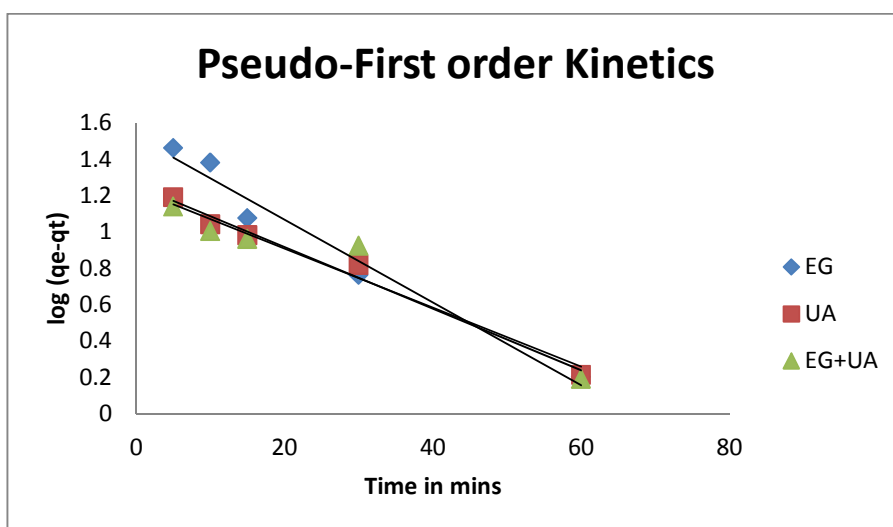


Fig. 7: Pseudo First order kinetics

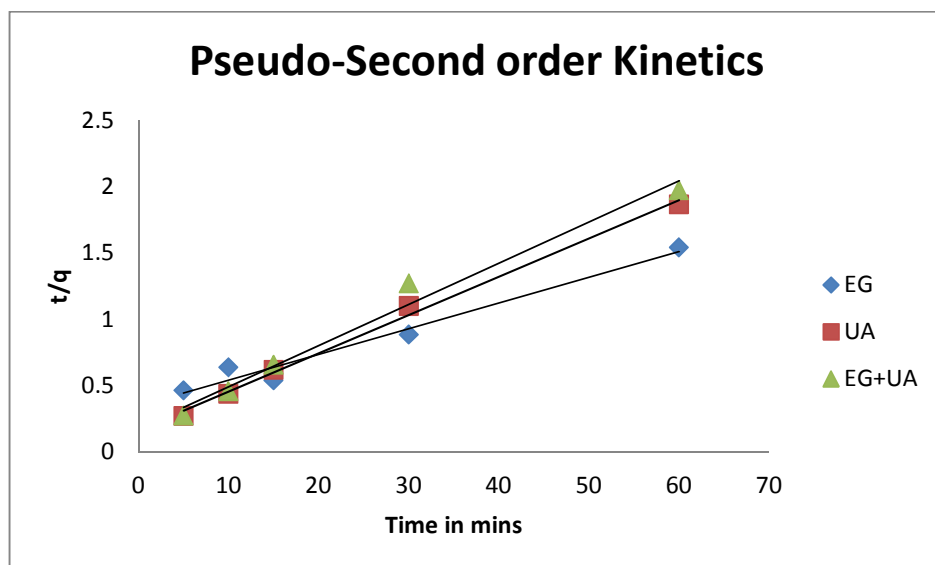


Fig. 8: Pseudo-second order kinetics

### CONCLUSION

The effectiveness of the EG, UA and EG+UA as biosorbent of Cu ions was confirmed. The effect of parameters like pH, contact time and initial concentration of biosorption process was studied. The optimum pH for biosorption of copper was found to be 5.0. Any further increase in pH resulted in a decrease in percent removal which might be due to the precipitation of the metal at higher hydrogen ion concentration. The optimum contact time was recorded as 120 min for all the three biosorbents and it is said to have reached equilibrium. Beyond the equilibrium time metal removal showed a decreasing trend. The morphology characterization of the three biosorbents was investigated using the Scanning Electron Microscope (SEM). The Langmuir isotherm was found to be the best-fitting isotherm because Langmuir model showed higher  $R^2$  value, ranging from 0.973-0.995 than the Freundlich isotherm model. In the kinetic studies the higher  $R^2$  values confirm that the adsorption data followed pseudo second order kinetics. The pseudo second order kinetics showed higher  $R^2$  value, ranging from 0.9704- 0.9951 than the pseudo first order kinetics. Among the three biosorbents EG showed higher removal of Cu ions than other two biosorbents. UA showed better results than the mixture of both (EG+UA). This difference in the percent removal of these biosorbents may be due to the masking of the active metal binding sites when used in combination i.e. (EG+UA). Future research is in progress to study the mechanism involved during the biosorption process.

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