

Copper removal from aqueous solution by marine green alga *Ulva reticulata*

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The batch removal of copper (II) ions from aqueous solution under different experimental conditions using *Ulva reticulata* was investigated in this study. The copper (II) uptake was dependent on initial pH and initial copper concentration, with pH 5.5 being the optimum value. The equilibrium data were fitted using Langmuir and Freundlich isotherm model, with the maximum copper (II) uptake of 74.63 mg/g determined at a pH of 5.5. The Freundlich model regression resulted in high correlation coefficients and the model parameters were largely dependent on initial solution pH. At various initial copper (II) concentrations (250 to 1000 mg/L), sorption equilibrium was attained between 30 and 120 min. The copper (II) uptake by *U. reticulata* was best described by Pseudo-second order rate model and the rate constant, the initial sorption rate and the

equilibrium sorption capacity were also reported. The elution efficiency for copper-desorption from *U. reticulata* was determined for 0.1 M HCl, H₂SO₄, HNO₃ and CaCl₂ at various Solid-to-Liquid ratios (S/L). The solution CaCl₂ (0.1 M) in HCl at pH 3 was chosen to be the most suitable copper-desorbing agent. The biomass was also employed in three sorption-desorption cycles with 0.1 M CaCl₂ (in HCl, pH 3) as the elutant.

Heavy metals released into the environment by technological activities tend to persist indefinitely, circulating and eventually accumulating throughout the food chain, becoming a serious threat to the environment. The main sources of heavy metal pollution include electroplating, painting, dying, surface treatment industry,

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etc. These pollutants are toxic and non-biodegradable and probably have health effects. Conventional processes for heavy metal removal often are neither effective nor economical (Volesky and Holan, 1995). Biosorption of heavy metals is one of the most promising technologies involved in removal of toxic metals from industrial waste streams and natural waters (Pagnanelli et al. 2000). Various biomaterials have been examined for their biosorptive properties and different types of biomass have shown levels of metal uptake high enough to warrant further research (Volesky and Holan, 1995). Among the most promising types of biosorbents studied is algal biomass (Figueira et al. 2000). Marine algae proliferate ubiquitously and abundantly in the littoral zones of world oceans, they are rather stable and fast growing (Yang and Volesky, 1999). Most of the metal uptake studies are focused on brown marine algae (Figueira et al. 2000; Cossich et al. 2002), due to its extreme metal adsorbing potential. Among the few studies on green algae, Darnall et al. 1986 inferred that *Chlorella vulgaris* has high affinity for the binding of Au^{3+} , Ag^+ , and Hg^{2+} ions, whereas Holan and Volesky, 1994 inferred that among the algal strains examined, *Codium taylori* showed least affinity for nickel. *Ulva reticulata* is a very common green alga found throughout the Palk bay, and its potential utilization as a metal biosorbent is of interest.

Copper, one of the most widely used heavy metals, is mainly employed in electrical and electroplating industries, and in larger amounts is extremely toxic to living organisms. The presence of copper (II) ions cause serious toxicological concerns, it is usually known to deposit in brain, skin, liver, pancreas and myocardium (Davis et al. 2000). The objective of the present work was to test the ability of *Ulva reticulata* to remove copper (II) ions from aqueous solution. Also basic parameters of copper biosorption equilibrium were determined at various pH values. Copper desorption was also examined.

MATERIALS AND METHODS

Ulva reticulata was collected and sun dried in Mandapam (India). Dry biomass was cut with a knife into irregular shaped particles between 1 and 3 mm in size. The biomass was then washed with distilled water, then filtered and finally dried overnight at 60°C and subsequently used for sorption experiments.

Analytical grades of $CuSO_4 \cdot 5H_2O$, HCl, H_2SO_4 , HNO_3 , NaOH, and $CaCl_2 \cdot 2H_2O$ were purchased from Ranbaxy Fine Chemicals Ltd., India. Cupric (Cu^{2+}) ions were prepared by dissolving its corresponding sulfate salt in distilled water.

Biosorption experiments were performed in a rotary shaker at 150 rpm using 250 ml Erlenmeyer flasks containing 100

ml of different copper concentrations. After 6 hrs contact (according to the preliminary sorption dynamics tests), with 0.2 g *U. reticulata* biomass, equilibrium was reached and the reaction mixture was centrifuged at 3000 rpm for 10 min. The metal content in the supernatant was determined using Atomic Absorption Spectrophotometer (AAS 6VARI0; Analytik Jena, Germany). The amount of metal adsorbed by alga was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$Q = (C_0 - C_f) * V / M \quad (1)$$

where Q is the metal uptake (mg/g); C_0 and C_f are the initial and equilibrium metal concentrations in the solution (mg/L), respectively; V is the solution volume (L); and M is the mass of biosorbent (g). The pH of the solution was adjusted by using 0.1M HCl or 0.1M NaOH.

The Langmuir sorption model was chosen for the estimation of maximum copper sorption by the biosorbent. The Langmuir isotherm can be expressed as,

$$Q = \frac{Q_{max} b C_f}{1 + b C_f} \quad (2)$$

where Q_{max} is the maximum metal uptake (mg/g) and b is the Langmuir equilibrium constant (L/mg). For fitting the experimental data, the Langmuir model was linearized as follows,

$$1/Q = 1/Q_{max} + 1/b Q_{max} C_f \quad (3)$$

The Freundlich model is represented by the equation,

$$Q = K C_f^{1/n} \quad (4)$$

where K (L/g) and n are constants. For fitting the experimental data, the Freundlich model was linearized as follows,

$$\ln Q = \ln K + 1/n \ln C_f \quad (5)$$

The metal-loaded biomass after biosorption was contacted with elutants, 0.1 M HCl, 0.1 M H_2SO_4 , 0.1 M HNO_3 and 0.1 M $CaCl_2$ in 250 ml Erlenmeyer flasks for 3 hrs on a rotary shaker (150 rpm) to study the removal of biosorbed metal ions. The remaining procedure was same as that in the sorption equilibrium experiments. After desorption, the biomass was washed with distilled water, then filtered and finally dried overnight at 60°C. The loss in biomass weight was calculated and the biomass was subsequently used for re-sorption studies.

RESULTS AND DISCUSSION

Effect of pH on copper biosorption

The initial pH of the solution is a very important factor in copper sorption uptake by *U. reticulata*. In general very little or no copper uptake was observed at pH less than 2.0. Working over pH 6.0 was avoided to prevent the possible precipitation of copper hydroxide. The effect of initial pH on the copper biosorption is given in [Figure 1](#). Little copper uptake at low pH values is an indication of competition of excess of protons for the same binding sites on the algal cell wall (Puranik and Paknikar, 1999). The copper uptake increased with increasing pH, to the maximum near pH 5.5, then decreased at higher pH value.

Langmuir and Freundlich sorption models were used to evaluate the sorption behavior of the biosorbent. [Table 1](#) shows the model constants along with correlation coefficients for biosorption of copper on *U. reticulata*. Langmuir sorption model served to estimate the maximum metal uptake values where they could not be reached in the experiments. The constant b represents affinity between the sorbent and sorbate. The Langmuir model parameters were largely dependent on the initial solution pH values. Both the maximum metal uptake Q_{max} and the Langmuir equilibrium constant b increases with increasing initial pH from 3 to 5.5 and decreased, when the pH was increased further. It is worth noting both K and n values also reached their maximum values at pH 5.5, this implies that the binding capacity reaches the highest value and the affinity between the biomass and copper ions was also higher than at other pHs investigated. Langmuir and Freundlich model plots for biosorption of copper are presented in [Figure 2](#) and [Figure 3](#) respectively. At all initial pH values investigated (except at pH 4.5), Freundlich model resulted in higher correlation coefficients than those obtained for Langmuir model fits. A comparison of the maximum copper uptake (Q_{max}) of *U. reticulata* with those of some other biosorbents reported in the literature is given in [Table 2](#). The sorption capacity of *U. reticulata* (74.63 mg/g) was relatively high when compared with other biosorbents.

Kinetic studies

The experimental results of biosorption of copper on *U. reticulata* at various initial concentrations are shown in [Figure 4](#). On changing the initial copper concentration from 250 to 1000 mg/L, the amount sorbed increased from 36.71 to 70.28 mg/g at pH 5.5. But the percent removal of copper decreased from 29.37 to 14.06% as the copper concentration increases from 250 to 1000 mg/L. This is because at lower concentration, the ratio of the initial moles of copper (II) to the available surface area is low and subsequently the fractional sorption becomes independent of initial concentration. However, at higher concentration the available sites of sorption becomes fewer compared to the moles of copper (II) present and hence the percentage

removal of copper (II) is dependent upon the initial Cu^{2+} concentration. To analyze the sorption rates of copper (II) ions onto the biomass, two simple kinetic models were tested.

Pseudo-first-order model. The Pseudo-first order rate expression is generally described by the following equation (Ho and McKay, 1998),

$$dQ_t/dt = K_1 (Q_e - Q_t) \quad (6)$$

where, Q_e is the amount of copper sorbed at equilibrium per unit weight of sorbent (mg/g); Q_t is the amount of copper sorbed at any time (mg/g); and K_1 is the rate constant (min^{-1}).

Integrating and applying boundary conditions, $t = 0$ and $Q_t = 0$ to $t = t$ and $Q_t = Q_t$, equation (6) takes the form:

$$\log (Q_e - Q_t) = \log Q_e - K_1 t / 2.303 \quad (7)$$

In order to obtain the rate constants, the straight-line plots of $\log (Q_e - Q_t)$ against t were made for *U. reticulata* at different initial copper concentrations ([Figure 5](#)). The intercept of the above plot should equal to $\log Q_e$. However, if the intercept does not equal to the equilibrium copper uptake then the reaction is not likely to be first order even this plot has high correlation coefficient with the experimental data (Ho and McKay, 1998). Correlation coefficients were found to be between 0.8349 and 0.9519, but the calculated Q_e is not equal to experimental Q_e , suggesting the insufficiency of Pseudo-first-order model to fit the kinetic data for the initial copper concentrations examined. The rate constants and the correlation coefficients for all concentrations tested have been calculated and summarized in [Table 3](#).

Pseudo-second-order model. The sorption data were also analyzed in terms of a Pseudo-second order mechanism (Ho and McKay, 1998), given by

$$dQ_t/dt = K_2 (Q_e - Q_t)^2 \quad (8)$$

where K_2 is the equilibrium rate constant (g/mg min). Integrating the above equation and applying boundary conditions $t = 0$ and $Q_t = 0$ to $t = t$ and $Q_t = Q_t$, gives

$$t/Q_t = 1/h + 1/Q_e \quad (9)$$

where h is the initial sorption rate. If second order kinetics is applicable, the plot of t/Q_t against t of equation (9) should give a linear relationship from which the constants Q_e , h and K_2 can be determined. Good fits were observed for all initial concentrations ([Figure 6](#)) indicating that sorption reaction can be approximated with the Pseudo-second-order model. Correlation coefficients were found to be between

0.9999 and 1.0000, and were tabulated along with the rate constants in [Table 3](#). The lowest correlation coefficient in this case was 0.9999, which is even better than the first order model. The values of equilibrium sorption capacity, Q_e , were found to increase from 37.04 to 71.43 mg/g, for an increase in the initial concentration from 250 to 1000 mg/L, which also shows good agreement with the experimental equilibrium copper uptake. The very fast sorption kinetics observed with the *U. reticulata* biomass represents an advantageous aspect when effluent treatment systems are designed.

Desorption of copper

The copper-loaded biomass was eluted by various elutants, 0.1 M CaCl₂, 0.1 M HCl, 0.1 M H₂SO₄ and 0.1 M HNO₃. The optimal elutant must be effective, non-damaging to the biomass, non-polluting and cheap. In this work, the effect of 0.1 M CaCl₂ on metal elution was examined at different initial pH conditions. Elution efficiency (E) was determined by the ratio of the metal mass in the solution after desorption to the metal mass initially bound to the biomass (Davis et al. 2000). The elution efficiency of 0.1 M CaCl₂ was strictly pH dependent and maximum desorption performance was observed at initial pH 3. The biomass that was exposed to CaCl₂ has remained soft and appears to be suitable for subsequent cycle. The mineral acids wash of copper-laden biomass released all the metal ions. However, the biomass become more fragile and lost its original color. The biomass weight loss was greater than 35%, when mineral acids are used as elutants. Acid solutions could dissolve some types of polysaccharides that may contain ion-binding sites and the mineral contents of the biomass as well (Kuyucak and Volesky, 1989). Several researchers also observed similar deterioration in the macroscopic appearance of the biosorbent material. For instance, Davis et al. 2000 observed *Sargassum filipendula* biomass become more fragile and the color of the biomass turned from brown to black, when exposed to stronger HCl solution.

An important parameter for metal biosorption is the Solid-to-Liquid ratio (S/L) defined as the mass of metal-laden biosorbent to the volume of the elutant (Davis et al. 2000). Upon elution of the metal from the biosorbent, it is desirable to use the smallest possible eluting volume so as to contain the highest concentration of the metal. At the same time, the volume of the solution should be enough to provide maximum solubility for the metal desorbed. [Figure 7](#) illustrates the effect of S/L ratio on the copper elution efficiency for all the elutants examined. The elution efficiency of 0.1 M CaCl₂ decreased with increasing S/L ratio at all the pH values examined. For instance, 0.1 M CaCl₂ (in HCl, pH 3), at S/L 1 g/L elution efficiency was 90.25% and dropped to 52.88% at S/L 10 g/L. Among the mineral acids examined, the elution efficiency of 0.1 M HCl appeared to be nearly independent of the S/L ratio up

to the examined value of 10 g/L. Elution efficiency of 0.1 M H₂SO₄ and 0.1 M HNO₃ dropped to 92.71% and 95.04% respectively at S/L 10 g/L. It was clear that protons played a major role in desorption. The increase in final pH observed in desorption experiments indicate that copper was displaced from the biomass by protons, showing the probable involvement of ion exchange. The use of *U. reticulata* as a potential biosorbent depends not only on the biosorptive capacity, but also on how well the biomass can be reused. The biomass was used for three sorption-desorption cycles and regenerated using 0.1 M CaCl₂ (in HCl, pH 3) at S/L 1 g/L. At the end of three cycles the sorption capacity of regenerated *U. reticulata* decreased by 13.2% and the weight loss was 15%. The elution efficiency of 0.1 M CaCl₂ (in HCl, pH 3) almost remained constant throughout the three cycles examined. The present experiments revealed 0.1 M CaCl₂ (in HCl, pH 3), appears as an appropriate metal-eluting agent for *U. reticulata*, with its low biomass damage adequate to be employed in continuous operation.

CONCLUDING REMARKS

The present work evaluated the removal of copper (II) from aqueous solution using *U. reticulata* biomass. The sorption capacity of copper on *U. reticulata* increased with increase in pH reaching a maximum at 5.5. The equilibrium sorption data agrees well with Freundlich isotherm with high correlation coefficients. The kinetics of the sorption process was found follow Pseudo-second-order model. The highest copper elution efficiency was 100% for all mineral acids examined at S/L 1g/L. CaCl₂ (in HCl) exhibited a maximum elution efficiency of 90.25% at pH 3 and S/L 1g/L, and decreased as the S/L increases. Low biomass damage and high elution efficiency in the subsequent sorption-desorption cycles favour CaCl₂ (in HCl, pH 3) to be employed as a suitable metal desorbing agent for *U. reticulata*.

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APPENDIX

Tables

Table 1. Langmuir and Freundlich model parameters at different pH conditions.

pH	Langmuir parameters		$R^{2\dagger}$	Freundlich parameters		$R^{2\dagger}$
	Q_{\max} (mg/g)	b (L/mg)		K (L/g)	n	
3.0	45.25	0.00256	0.9869	0.555	1.638	0.9877
3.5	53.48	0.00290	0.9761	0.770	1.682	0.9782
4.0	65.36	0.00361	0.9760	1.275	1.785	0.9772
4.5	69.93	0.00427	0.9863	1.919	1.947	0.9743
5.0	70.92	0.00567	0.9836	2.853	2.146	0.9840
5.5	74.63	0.00804	0.9570	4.268	2.351	0.9828
6.0	72.46	0.00727	0.9616	3.724	2.279	0.9836

[†] Correlation coefficient.

Table 2. Comparison of copper (II) biosorption by different biosorbents on the basis of maximum uptake capacity (Q_{\max}).

Biosorbent	Q_{\max} (mg/g)
<i>Desulfovibrio desulfuricans</i> (Chen et al. 2000)	16.7
<i>Ganoderma lucidum</i> (Muraleedharan et al. 1995)	24
<i>Sargassum filipendula</i> (Davis et al. 2000)	56
<i>Sargassum fluitans</i> (Davis et al. 2000)	51
<i>Sargassum vulgare</i> (Davis et al. 2000)	59
<i>Ulva reticulata</i> (This study)	74.63

Table 3. Kinetic parameters for the effect of initial copper concentration.

Initial concentration (mg/L)	K ₁	Q _e	R ² †	K ₂	Q _e	h	R ² †
250	0.0626	24.13	0.9519	0.0111	37.04	14.98	1.0000
500	0.0438	21.66	0.8349	0.0091	57.80	29.73	1.0000
750	0.0251	27.41	0.8929	0.0035	69.44	16.38	0.9999
1000	0.0209	24.18	0.8671	0.0027	71.43	13.23	0.9999

K₁ (min⁻¹); K₂ (g/mg min); Q_e (mg/g); h (mg/g min); † Correlation coefficient.

Figures

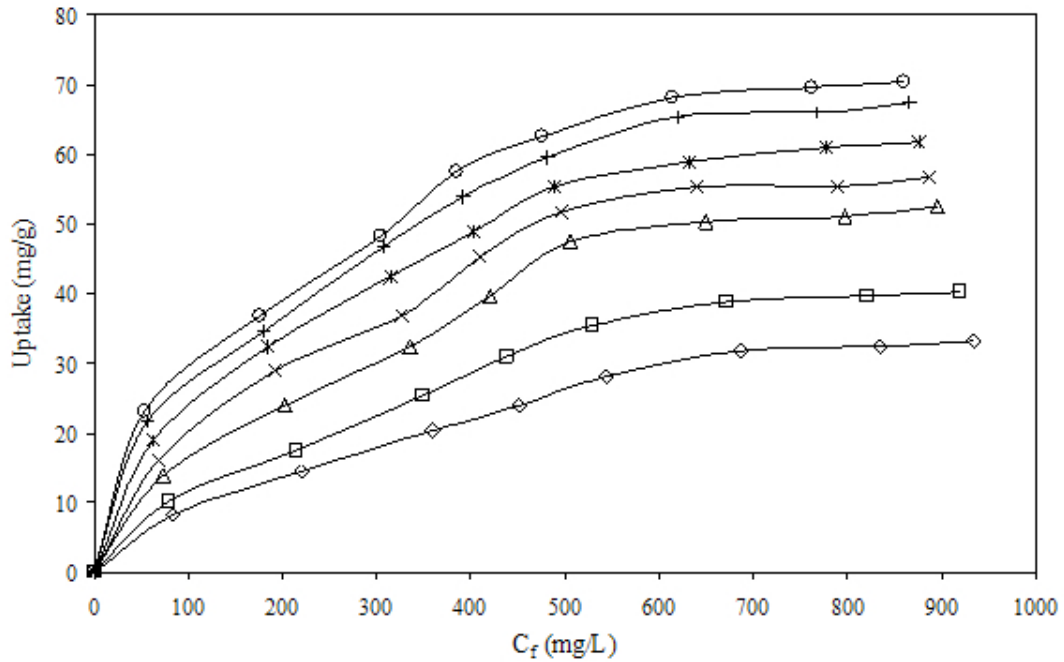


Figure 1. The effect of pH on the biosorptive copper uptake capacity of *U. reticulata* ($M = 2 \text{ g/L}$). Initial solution pH: (\diamond), pH 3.0; (\square), pH 3.5; (Δ), pH 4.0; (\times), pH 4.5; ($*$), pH 5.0; (\circ), pH 5.5; ($+$), pH 6.0.

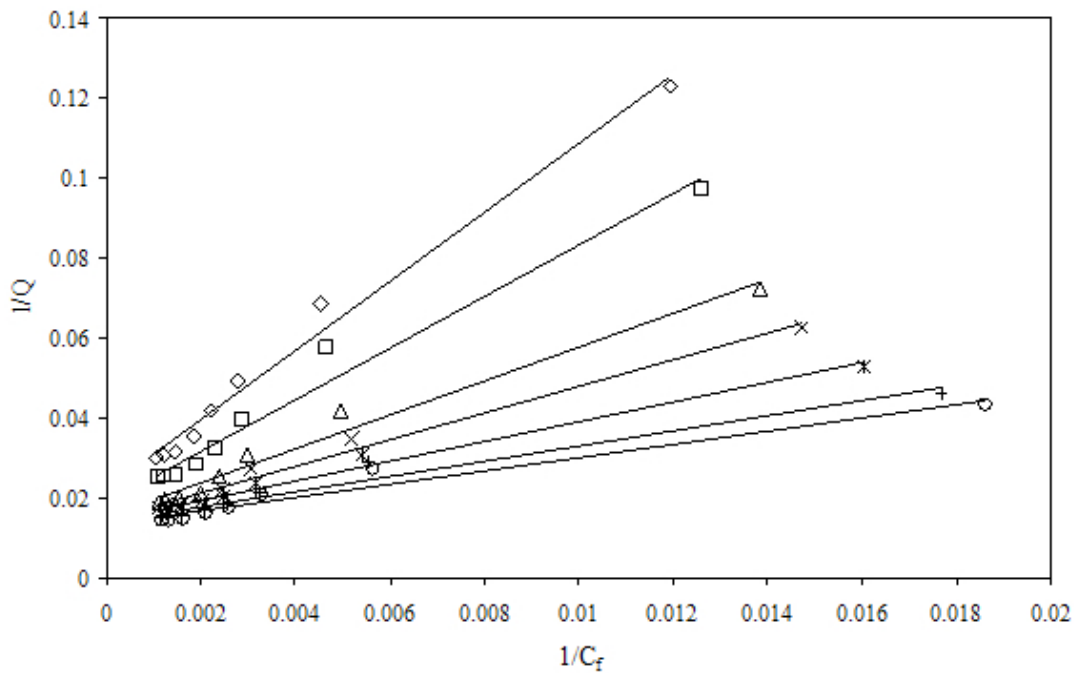


Figure 2. Linearized Langmuir isotherm for copper sorption by *U. reticulata* ($M = 2 \text{ g/L}$). Initial solution pH: (\diamond), pH 3.0; (\square), pH 3.5; (Δ), pH 4.0; (\times), pH 4.5; ($*$), pH 5; (\circ), pH 5.5; ($+$), pH 6.0.

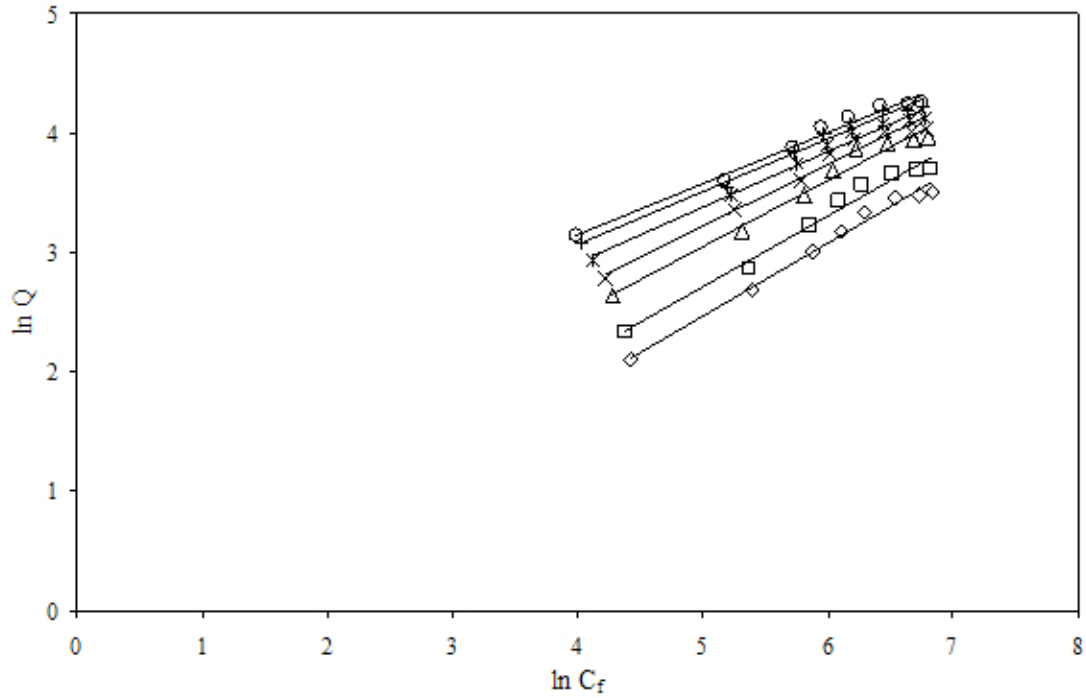


Figure 3. Linearized Freundlich isotherm for copper sorption by *U. reticulata* ($M = 2$ g/L). Initial solution pH: (\diamond) pH 3.0; (\square) pH 3.5; (Δ) pH 4.0; (\times) pH 4.5; ($*$) pH 5; (\circ) pH 5.5; ($+$) pH 6.0.

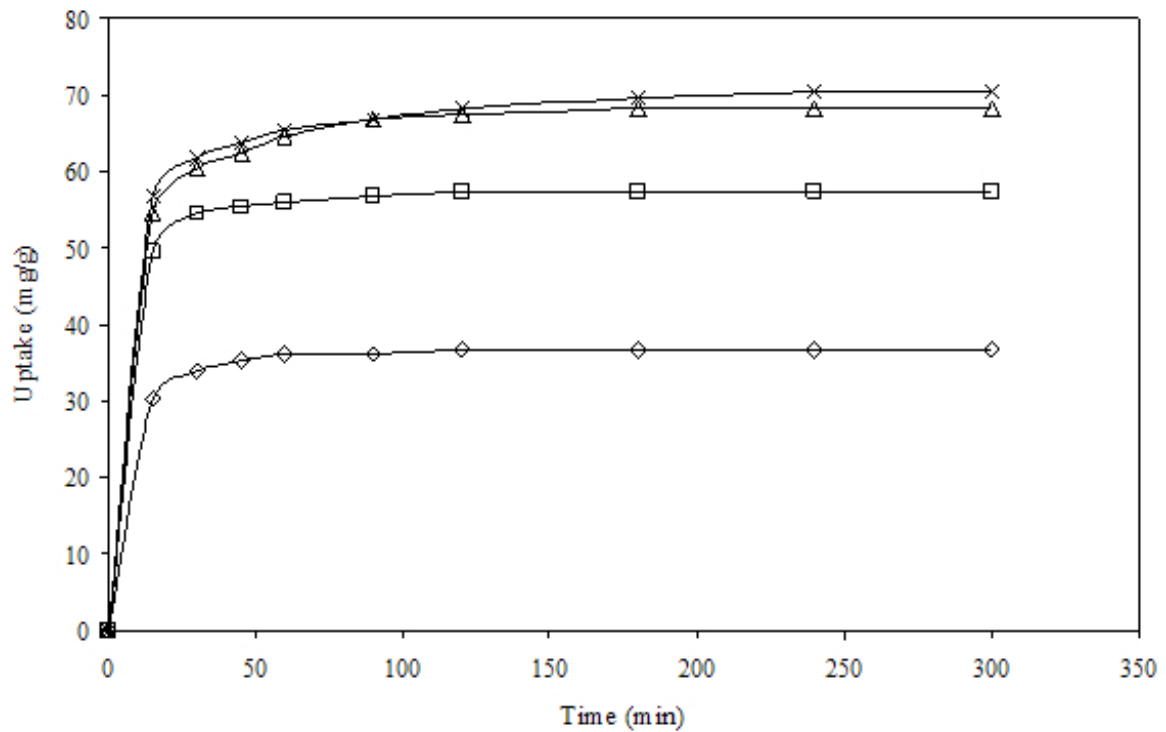


Figure 4. Effect of initial concentration on the sorption of copper onto *U. reticulata* ($M = 2$ g/L, pH 5.5). Initial copper concentration: (\diamond), 250 mg/L; (\square), 500 mg/L; (Δ), 750 mg/L; (\times), 1000 mg/L.

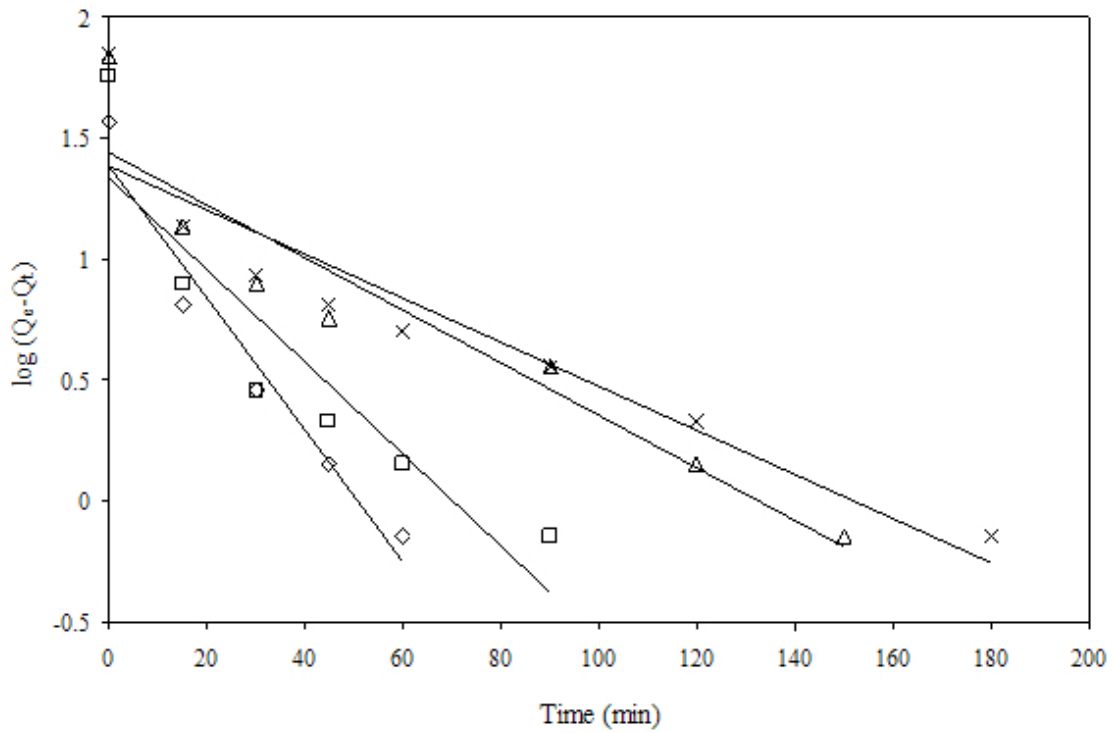


Figure 5. Pseudo-first-order sorption kinetics plot of copper onto *U. reticulata* at various initial concentration (M = 2 g/L, pH 5.5). Initial copper concentration: (◇), 250 mg/L; (□), 500 mg/L; (Δ), 750 mg/L; (×), 1000 mg/L.

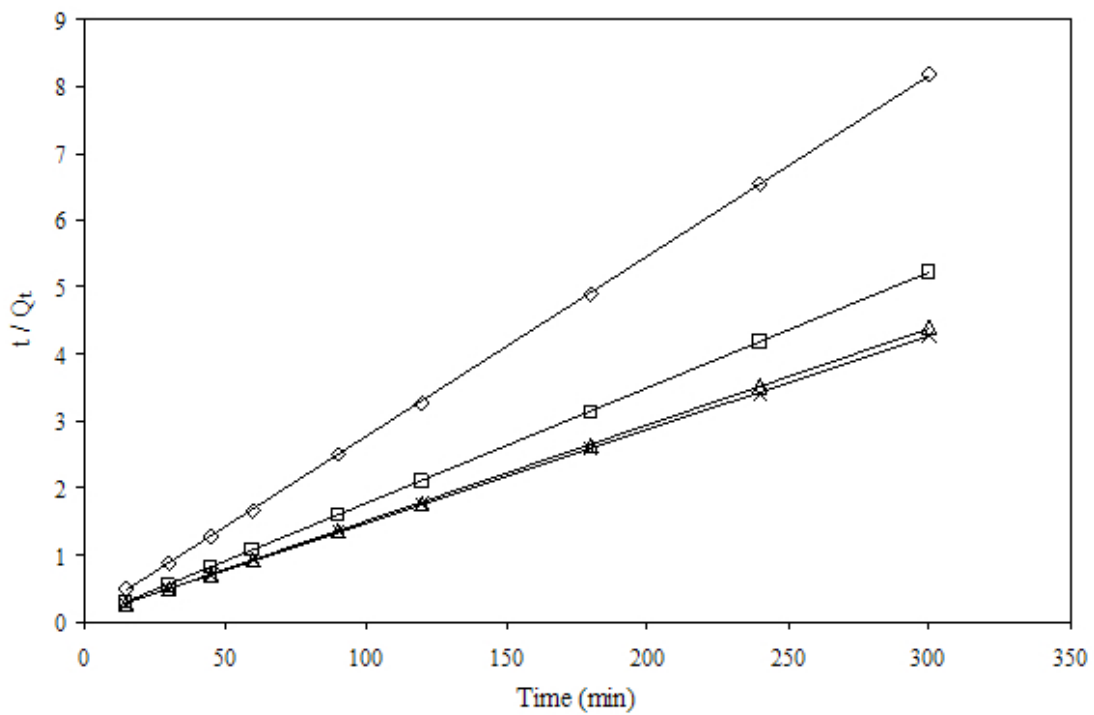


Figure 6. Pseudo-second-order sorption kinetics plot of copper onto *U. reticulata* at different initial concentrations (M = 2 g/L, pH 5.5). Initial copper concentration: (◇), 250 mg/L; (□), 500 mg/L; (Δ), 750 mg/L; (×), 1000 mg/L.

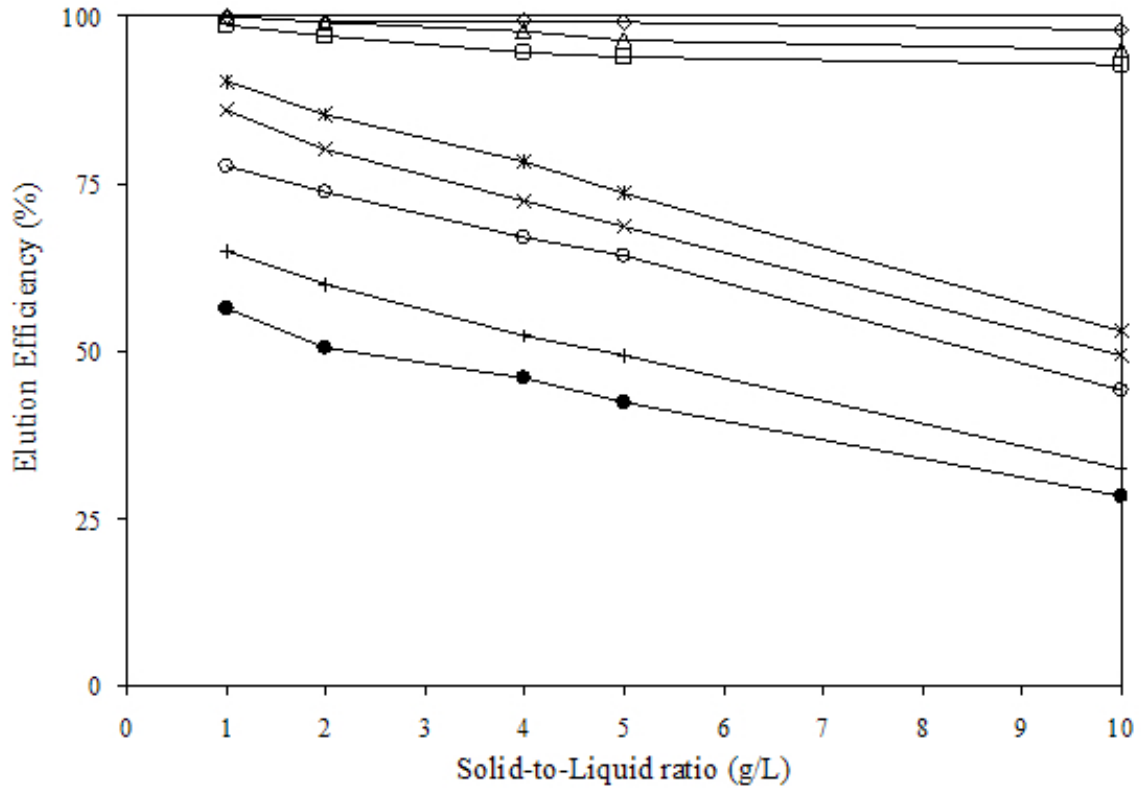


Figure 7. The effect of Solid-to-Liquid ratio (S/L) on copper elution efficiency. Elutants: (×), 0.1 M CaCl₂ (pH 2.5); (*), 0.1 M CaCl₂ (pH 3.0); (○), 0.1 M CaCl₂ (pH 3.5); (+), 0.1 M CaCl₂ (pH 4.0); (●), 0.1 M CaCl₂ (pH 6.0); (◇), 0.1 M HCl; (Δ), 0.1 M HNO₃; (□), 0.1 M H₂SO₄.