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BATCH AND COLUMN SORPTION OF HEAVY METAL FROM AQUEOUS SOLUTION USING A MARINE ALGA *SARGASSUM TENERRIMUM*

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ABSTRACT: Batch and continuous sorption studies to remove copper (II) from aqueous solution was tested using marine alga, *Sargassum tenerrimum*. Maximum copper uptake of 174.23 mg/g was observed according to the Langmuir model at an initial pH of 6. The copper loaded biomass was eluted using 0.1 M HCl and no damage to the biosorbent was caused. Effects of operating parameters such as bed height and flow rate were studied in a packed column and the metal uptake decreased with increase in flow rate. The Bed Depth Service Time and Thomas models were used to analyze the experimental data and the model parameters were estimated. During regeneration experiments, a loss of sorption performance was observed during seven cycles of sorption-desorption indicated by a shortened breakthrough time and a broadened mass transfer zone.
Keywords: Biosorption, marine alga, isotherm, packed column.

INTRODUCTION

Disposal of heavy metals pose serious threats to the environment due to immense toxicity and tendency to intrude in the web of living organisms. Wastewaters emanated from industries like electroplating, painting and dying units are the major cause of heavy metal pollution. Conventional methods like coagulation-flocculation, oxidation, filtration, electrochemical methods etc., are inadequate to cater to the need of effective disposal of the pollutants. Hence alternative methods which are inexpensive and easy to apply in heavy metals wastes are necessary. Adsorption processes have been investigated as an efficient and effective method to remove heavy metals from wastewater. Biosorption is one such technique wherein the heavy metals are adsorbed and assimilated by biomaterials which occur in nature. The effectiveness of metal removal depends on the sorptive characters of the biosorbent and properties and quantum of the effluent.

Algal biomass has proved to be the best choice[1] for this task as the carboxylic, sulfonic and hydroxyl groups in the polysaccharides present in the algae can easily uptake the heavy metals[2-4]. The sorptive properties of the algae are enabled by the presence of macroscopic structures in them which synthesize the biosorbent particles for the adsorption process. Several investigators reported that packed bed column proved to be more effective in the heavy metal removal by using biosorbents as the packing medium. Volesky et al[5] employed a column of 2.5 cm ID packed with 38 g of dry *Sargassum filipendula* to remove copper. Vijayaragavan et al[6] used a glass column of 2 cm ID and 35 cm length with *Turbinaria ornata* as the biomaterial for copper removal. The concentration difference that prevails in the packed column serves as the driving force for heavy metal sorption and this phenomenon has been exploited for the metal removal using column[7-9].

In the present investigation a marine algae, *Sargassum tenerrimum* has been used as the biosorbent for the sorption process of copper from aqueous solution. The investigation includes batch equilibrium studies to determine the optimum working conditions in terms of pH and the sorption capacity of the algae. In addition, the present study employed an up-flow packed column to investigate copper removal as a function of bed height and flow rate.

MATERIALS AND METHODS

Preparation of Sargassum tenerrimum and Chemicals

The marine alga, *Sargassum tenerrimum*, was collected in Mandapam (Tamilnadu, India) and then sun-dried. It was then grounded to an average particle size of 0.76 mm. The sieved biomass was soaked in 0.1 M HCl for 4 h in order to protonate it. The alga was then washed in distilled water and dried at 60º C overnight. A weight loss of approximately 15% was observed. All chemicals including $CuSO_4.6H_2O$ obtained from Sd fine chemicals Ltd. (India) were of analytical grade. In the sorption equilibrium experiments, a borate buffer solution prepared by dissolving NaOH and 0.1M HCl was used to maintain the pH.

Batch experiments

The Batch studies were conducted in Erlenmeyer flasks by adding 0.25 g of *Sargassum tenerrimum* biomass to 100 ml of copper solutions of different concentrations (50–1000 mg/l). After shaking the flasks at 250 rpm for 12 h in a rotary shaker, the algal biomass was separated from copper solution by centrifugation at 3000 rpm for 10 min. The final concentration of copper solutions in the supernatant of each sample was determined using Atomic Absorption Spectrophotometer (Perkin Elmer, Model AAS - 300). The equipment was initially calibrated using standardized copper solution. The samples were diluted with distilled water before analysis whenever required. The amount of copper adsorbed by algae was calculated from the differences between the amount added to the biomass and the copper content after adsorption using the following equation:

$Q=V(C_o-C_f)/M$ ---------------- (1)

where Q is the copper uptake (mg/g), C_0 and C_f are the initial and final copper concentrations in the solution respectively (mg/l), V, the solution volume (l) and M is the mass of biosorbent (g).

The biomass along with the adsorbed copper was eluted with 0.1 M HCl in 500 ml Erlenmeyer flasks for 4 h by agitating in a rotary shaker at a speed of 50 rpm to desorb the copper ions from the algal mass. The biomass was then washed with distilled water, filtered and dried at 60ºC overnight and weighed to determine the loss. The regenerated biomass was again used for the adsorption studies.

Column experiments

A packed bed column made of acrylic with an internal diameter of 3 cm and a height of 40 cm is used for the study. To enable a uniform inlet flow of the solution into the column glass beads of 1.5 mm diameter were placed to attain a height of 2 cm. An adjustable plunger was held in position at the top of the column with a 0.5 mm stainless sieve. A 0.5 mm stainless sieve followed by glass wool was provided at the bottom of the column to support the packing. A known quantity of biomass was placed in the column to yield the desired sorbent bed height. Copper (II) solutions of initial concentration 100 mg/l (pH 6) were fed upward inside the column by a peristaltic pump (pp60, Miclins) to get the desired flow rates. Copper solutions of relatively lower concentrations are used to obtain gentle breakthrough curve as industrial effluents posses copper concentration in this range[10]. Copper concentrations of the effluent at the column exit collected at different time intervals were analyzed and the column was operated till the effluent metal concentration reached a value of 99.5 mg/l or higher.

The biomass loaded with copper ions was regenerated with 0.1 M HCl (Flow rate 5 ml/min) after exhaustion. The bed was washed with distilled water after elution till the pH of the wash effluent reached 7. The sorption and desorption studies were conducted again by feeding the copper solution and this cycle studies were carried out for seven times and the sorption capacity was evaluated. The biomass was washed with distilled water and dried at 60º C to determine the loss in weight after seven cycles. All the batch and column experiments were carried out in duplicates and the deviations were within 5%.

Analysis of Column data

The amount of metal adsorbed by the biomass (m_{ad}) is obtained by multiplying the area above the breakthrough curve and the flow rate. The uptake capacity (Q) of the sorbent is calculated as the ratio of metal mass (m_{ad}) and the bisorbent mass (M)[7]. To establish the overall sorption zone (Δt) two parameters are evaluated. They are the breakthrough time (t_b)and the exhaustion time (t_e)[5] defined as times at which the copper concentration in the effluent reached 1 mg/l and exceeded 99.5 mg/l respectively.

$\Delta t = t_e-t_b$ ---------------------(2)

The critical bed height which is also termed as the height of the mass transfer zone (Z_m) is related to bed height, breakthrough and exhaustion times[5] and is determined using

$Z_m=Z(1-(t_b-t_e))$ --------------- (3)

where Z is the bed height (cm).

The other parameters involved in the analysis of column studies are effluent volume (V_{eff}), quantity of copper ions sent to the column (m_{total}) and the percentage copper removed (η) which are calculated as follows[7]:

$V_{eff}=Ft_e$ --(4)

$m_{total}= C_0Ft_e/1000$ ---------------(5)

$\eta(\%)= m_{ad}*100/m_{total}$ ---------(6)

Elution efficiency (E) is calculated as follows[5]:
$E(\%) = m_d*100 / m_{ad}$ ---------(7)
where, F is the volumetric flow rate (ml/min) and m_d is mass of metal desorbed which was calculated from the elution curve (C Vs t).

RESULTS AND DISCUSSION

Batch Studies

In the batch study the effect of pH on the biosorption of copper was initially analyzed to obtain sorption isotherms for different initial concentrations (50 – 1000 mg/l) of copper solution. The pH values were selected from 3.0 to 6.0 to maintain acidic range as most of the effluents containing heavy metals are acidic[11]. The effect of pH on copper uptake by *Sargassum tenerrimum* is shown in Fig. 1 from which it can be seen that uptake of copper at low pH values are relatively small and increases with increasing pH reaching a maximum at 6.0. Reduced copper uptake at low pH values is an indication of competition of protons for the same binding sites on the algal cell wall[6]. Batch studies over pH 6.0 were avoided to prevent the probable precipitation of copper.

The experimental data obtained from the batch studies were modeled using various simple adsorption models such as Langmuir (Eq.(8)), Freundlich (Eq.(9)) and Redlich Peterson(Eq.(10)) and shown in Fig 2.

$Q = Q_{max}bC_f / (1+bC_f)$ -------(8)

$Q = K(C_f^{(1/n)})$ ------------------(9)

$Q = K_{RP}C_f / (1+a_{RP}(C_f^{\beta}))$ ------(10)

where C_f is the final copper concentration (mg/l), Q_{max} is the maximum copper uptake (mg/g), b the Langmuir equilibrium constant (l/mg), k the Freundlich constant$(l/g)^{1/n}$,n the Freundlich constant , K_{RP} the Redlich-peterson isotherm constant(l/g), a_{RP} the Redlich-peterson isotherm constant $(l/mg)^{\beta}$ and β the exponent, which lies between 0 and 1. All the parameters in the adsorption model equations are evaluated for different pH conditions and reported in Table1. From the correlation coefficients of each of the models it is clear that the Langmuir isotherm (R^2=0.985) proves to be the best fit compared to the Freundlich (R^2=0.962) and Redlich-Peterson (R^2=0.960) isotherms. All the model parameters were evaluated by non-linear regression using MATLAB software.

The parameters in the Langmuir sorption model[12] (Q_{max} and b) characterize the sorptive properties and their values depend mainly on the pH conditions. Both the parameters show increasing trend with increasing initial solution pH. The constant b is a measure of the attraction between the sorbent and sorbate. This can be inferred by the higher values of b (steep initial slope) in sorption isotherm showing higher affinity between the sorbate and sorbent. Hence the desirable properties of good biosorbents are higher Q_{max} and b values[3]. The peak values for Q_{max} and b are found to be 174.23 mg/g and 0.0053 l/mg respectively, for the pH of 6.0 respectively (Table 1). The most significant feature of the Langmuir sorption model is its ability to predict the maximum uptake values that cannot be reached in experiments. The Freundlich equation[13] is the best suited isotherm to fit the heterogeneous systems. The Freundlich constants (k and n) showed a similar trend like Langmuir constants and reached their maximum values at pH 6. This is an implication that the binding capacity reaches the highest value in this pH (like the affinity between the biomass and the copper ions) when compared to other pH ranges. The Redlich Peterson model[14] serves as a compromise between the above said two models. The parameters of this model (K_{RP} and β) too showed the similar trend and increase with increasing pH and reached their maximum values at pH 6. But the constant a_{RP} decreases with increasing pH (Table 1).

The copper adsorbed by the *S.tenerrimum* was washed using 0.1M HCl and the elution efficiency (E) can be determined from the ratio of the mass of copper desorbed from the solution to the mass of copper in the sorbent present initially[15]. The elution given by HCl, washed off the copper ions and was found that the biomass was not damaged by eluting with the acid solution. The algae *S. tenerrimum* is of high potential because in addition to its immense absorptive capacity it has the merit of being reused. The same biomass was used for seven sorption-desorption cycles by regenerating with 0.1 M HCl and proved to have sustained copper uptake capacity for the entire seven cycles examined. The elutant HCl proved to be very effective in desorbing the biosorbed metal ions. The loss in weight of dry biomass is less than 3% after 7 cycles and no significant reduction in biosorption capacity was observed after 7 cycles.

Column studies

Effect of bed height

The adsorption of metal in the packed bed column is greatly influenced by the amount of biosorbent used. The study was conducted for three different bed heights 15, 20 and 25 cm using 11.35, 14.12 and 18.25 g of biomass respectively. A flow rate of 5 ml/min of copper solution with an initial concentration of 100 mg/l was fixed as the feed conditions for the column studies. Fig. 3 represents the breakthrough curves for the adsorption of copper by *S. tenerrimum* obtained for the various bed heights from 15 to 25 cm. It can be seen that the breakthrough time and exhaustion times increased with increasing bed height. This is due to the reasons that the adsorption regime available for mass transfer is increased and the quantum of binding sites is enhanced facilitating more sorption. It was found that 67.53, 68.32 and 68.57 mg/g of copper uptake were obtained by the biomass for 15, 20and 25 cm of column height, respectively were obtained .This corresponds to total copper removal percentages of 56.96, 60.82 and 62.56% for bed heights of 15, 20and 25 cm respectively showing an increasing trend with respect to the bed height.

The column data can be modeled by establishing a term named service time which is defined as the time required for the effluent copper concentration to reach 1 mg/l. The bed height (Z) and service time (t) holds a linear relationship which is given by BDST (Bed Depth Service Time) model which is expressed as follows[16]:

$t = (N_oZ/C_ov) – (1/K_aC_o)\ln((C_o-C_b)-1)$ -----(11)

Where C_b is the breakthrough metal ion concentration (mg/l),

N_0 the sorption capacity of bed (mg/l),

v the linear velocity (cm/h) and

K_a the rate constant (lit/mg h).

Fig. 4 indicates the linearity between the service time and bed height with a correlation coefficient of 1 for the flow rate of 5 ml/min and hence the BDST model holds good for the present system. Initial concentration C_0 and linear velocity v, were held constant during the column operation. The sorption capacity of the bed per unit bed volume, N_0 and the rate constant K_a were computed from the slope and intercept of BDST plot and are found to be 3819.42 mg/l and 0.0919 mg/h respectively. The rate constant K_a which is a measure of the rate of transfer of solute from the fluid phase to the solid phase[17] largely influences the breakthrough phenomenon in the column study. For smaller value of K_a relatively longer bed is required to avoid breakthrough whereas the breakthrough can be eliminated even in smaller bed heights when the value of K_a is high[17]. BDST model parameters can be used for scaling up of the process for other flow rates without further experiment runs.

Effect of flow rate

Most of the industrial scale treatments of heavy metal removal from effluents are accomplished in continuous mode and hence the study of effect of flow rate on sorptive characters becomes an important criterion[18]. In the present work the sorption capacity of *S. tenerrimum* is studied for various flow rates in the range of 5 to 20 ml/min for the initial copper concentration of 100 mg/l and bed height of 25 cm. Fig. 5 represents the trend of the variation in the effluent copper concentration against time for the flow rates 5, 10 and 20 ml/min. Also it can be inferred that the copper uptake dropped as the flow rate is increased. An earlier breakthrough and exhaustion times were observed in the plot for the flow rate of 20 ml/min. The values are reported as 68.57, 63.37 and 50.42 mg/g for the flow rates 5, 10 and 20 ml/min respectively, which shows that the flow rate largely affects the sorption capacity. The total copper removal percentages 5, 10 and 20 ml/min are found to be 62.59, 60.13 and 46.92% The reduction in the copper uptake capacity at higher flow rates is due to the unavailability of sufficient retention time for solute to interact with the sorbent and the limited diffusivity of solute into the sorptive sites or pores of the biomass caused thereby.

The important feature in the design of fixed bed adsorption column is the prediction of concentration time profile or the breakthrough curve for the effluent and a mathematical model to fit them. One of the simple and generally used models[7,19] reported by many researchers is the famous Thomas model which is expressed in linear form as

$\ln((C_o-C)-1) = (k_{Th}Q_oM/F) - (k_{Th}C_o)V/F$ ---(12)

where k_{Th} is the Thomas model constant (lit/mg hr), Q_0 the maximum solid phase concentration of solute (mg/g) and V the throughput volume (l). A plot of ln [(C_0/C)-1] against t (where t = V/F) for a given flow rate[7] can be used to determine the model constants. Fig.5 show the linear nature of the model yielding a good fit for the experimental data at all flow rates with correlation coefficients greater than 0.983. The parameters of the Thomas model evaluated at the three flow rates were reported in Table 2.

Regeneration

The concept of regeneration of biosorbents is important in industrial applications for the removal of metal from waste water. Reusability of sorbent can be evaluated by comparing the sorption potential of regenerated biomass with the original biomass[18]. In the present study seven sorption – desorption cycles were carried out in the packed column with 18.25 g of the biomass yielding an initial bed height of 25 cm, bed volume of 87.6 ml and a packing density of 208.33 g/l. The analysis was made for a period of 21 days continuously with 129.823 liters of copper solution having the initial concentration of 100 mg/l. The elution process was carried out with 15.511 of 0.1 M HCl

Table 3 summarizes the values for breakthrough time, exhaustion time and copper uptake for the seven cycles. 13.90 g of dry biomass was left in the column at the end of seventh cycle, indicating a weight loss of 23.84%. The bed height dropped to 22.5 cm from 25 cm and the bed volume got reduced to 80.3 ml. The packing density was found to be 173.2 g/l after seven sorption –desorption cycles. Fig. 6 represents the breakthrough curves for the regeneration cycles wherein it can be observed that breakthrough time showed decreasing trend whereas the exhaustion time increased progressively.

The cycles were run till the exhaust limit reached 99.8 mg/l of copper to avoid the time delay that normally occurs for full bed saturation. The actual length of the bed and the slope of the successive breakthrough curves decreased during the course of the regeneration cycles. The loss of sorption performance is not mainly due to biomass damage but rather because of sorbing sites, whose accessibility becomes difficult as the cycles progressed[5]. The loss of sorption performance was not reflected in the biosorption capacity, as it remained reasonably consistent irrespective of the number of cycles. The uptake also strongly depended on the previous elution step, since prolonged elution may destroy the binding sited or inadequate elution may allow metal ions to remain in the sites[6]. After seven sorption-desorption cycles, it was found that *Sargassum tenerrimum* biomass exhibited a consistently high copper uptake of 63.43 mg/g, which shows the ability of *S tenerrimum* to retain its bisorption capacity and withstand extreme conditions.

In regeneration operations the activity of biosorbents are estimated in terms of "life factors". The life factors are dependent on the minimum bed height (Z_m) or the critical bed height which is defined as the height required to obtain the breakthrough time t_b at t=0. The life factor was calculated in terms of the critical bed height using linear regression given by

$$Z_m = Z_{m,0} + k_L x \text{ --------------(13)}$$

where x is the cycle number, $Z_{m,0}$ the initial critical bed height (cm) and k_L the corresponding life factor (cm/cycle). The plot of Z_m versus x (fig. 7) gives the values of $Z_{m,0}$ and k_L as 14.081 cm and 0.5727 cm/cycle, respectively. The desorption process and agents for continuous operations should be selected in such a way that they are not only effective but also should not damage the sorbents. In all the seven cycles the elution curves showed a similar fashion with a sharp increase in the start of operations followed by a gradual decrease (fig. 8). The elution efficiencies were always greater than 99.214% throughout the experiment. The elution process was carried till the effluent copper concentration reaches 5 mg/L and on an average of 7.1 h cycles.

In Figs. 9 and 10 the pH profiles of sorption and elution process for cycles 1, 4 and 7 are shown. In brown algae the metal binding mainly occurs by the ion exchange mechanism due to the presence of carboxylic and sulfonic groups as the two key functional groups[3,20]. In the present investigation the protonated biomass when brought in contact with copper solution, Cu^{2+} exchanged with H^+ ions to occupy the binding sites, due to which the pH dropped. In all the sorption cycles effluent pH continuously decreased as the saturation of the bed progressed and finally stabilized near 3.0. The pH profiles and elution curves showed a similar trend and it was inferred that the pH shoots up in the initial stages and decreased gradually. This is due to the exchange of the H^+ ions provided by the elutant (0.1 M HCl) with the Cu^{2+} ions in occupying the sites, wherein the pH of the solution increased up to the point where the copper concentration reached the peak in the effluent. Further when the effluent copper concentration decreased, the effluent pH also decreased and eventually reached the influent pH. Thus the pH profiles of the sorption and elution cycles ascertain that the mechanism involved in biosorption of copper by the alginophyte *S. tenerimmum* is ion exchange.

CONCLUSION

This study showed that the marine alga *S. tenerimmum* could be used as an efficient biosorbent for the removal of Copper ions from aqueous solutions. Batch studies showed that this alga can adsorb Copper based on Langmuir model with a maximum uptake of 174.23 mg/g at an initial pH of 6.Column studies also proved the suitability of this algae and its potential to withstand extreme conditions without losing its metal sorption capacity.

Table 1: Parameters in Langmuir, Freundlich and Redlich-Peterson models at different pH:

pH	Langmuir model			Freundlich model			Redlich–Peterson model			
	Q_{max}(mg/g)	b(l/g)	R^{2*}	$K(l/g)^{1/n}$	n	R^{2*}	K_{RP}(l/g)	$a_{RP}(l/g)^{\beta}$	β	R^{2*}
3.0	45.04	0.0011	0.929	0.175	1.198	0.903	0.117	0.300	0.192	0.935
3.5	116.27	0.0012	0.989	0.292	1.213	0.973	0.149	0.294	0.216	0.969
4.0	158.73	0.0014	0.984	0.600	1.239	0.958	0.215	0.059	0.466	0.959
4.5	163.93	0.0015	0.985	0.533	1.291	0.957	0.245	0.036	0.516	0.947
5.0	169.49	0.0022	0.988	1.297	1.443	0.970	0.480	0.022	0.600	0.964
5.5	170.90	0.0036	0.985	2.498	1.593	0.956	0.684	0.020	0.613	0.914
6.0	174.43	0.0053	0.985	4.461	1.802	0.962	0.833	0.016	0.616	0.960

* Correlation coefficient

Table 2: Thomas model parameters

Flow rate(ml/min)	k_{Th} (l/mg h)	Q_0 (mg/g)
5	0.0022	69.292
10	0.0060	56.437
20	0.0091	51.254

Table 3: Sorption and elution process parameters for seven sorption-elution cycles

Cycle No.	Uptake (mg/g)	t_b (h)	t_e (h)	Δt (h)	dc/dt (mg/l h)	Z (cm)	Z_m (cm)	V_{eff} (l)	Copper removal %	Elution efficiency %
1	68.57	23.1	57.9	34.8	3.181	25.0	15.025	17.37	62.596	99.450
2	69.95	22.6	60.1	37.5	2.791	24.6	15.349	18.03	61.492	99.214
3	69.78	21.7	60.5	38.8	2.601	24.0	15.391	18.15	60.937	99.749
4	66.42	20.0	62.9	42.9	2.450	23.6	16.096	18.87	55.789	99.626
5	72.34	17.9	63.6	45.7	2.221	23.2	16.670	19.08	60.093	99.416
6	65.01	14.6	64.1	49.5	2.012	22.9	17.684	19.23	53.583	99.725
7	63.43	11.9	65.1	53.2	1.932	22.5	18.387	19.53	51.477	99.806

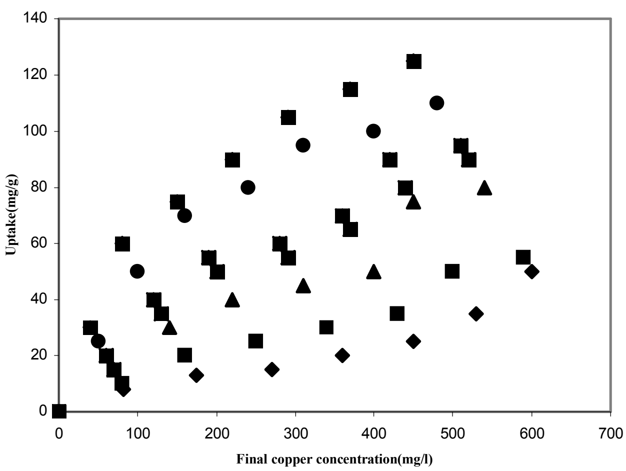

Fig 1.Effect of pH on copper biosorption by *S.tenerrimum* (biomass dosage=2.5 g/l) Initial solution pH:

◆pH 3.0 ■pH 3.5 ▲pH 4.0 ■pH 4.5 ■pH 5.0 ●pH 5.5 ■pH 6.0

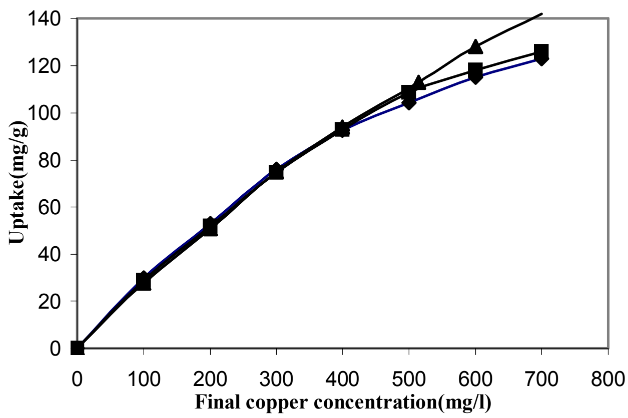

Fig 2. Applications of models to experimental isotherm data at pH=6 and biosorbent dosage = 2.5 g/l.

◆ Langmuir model ■ Freundlich model ▲ Redlich-Peterson model

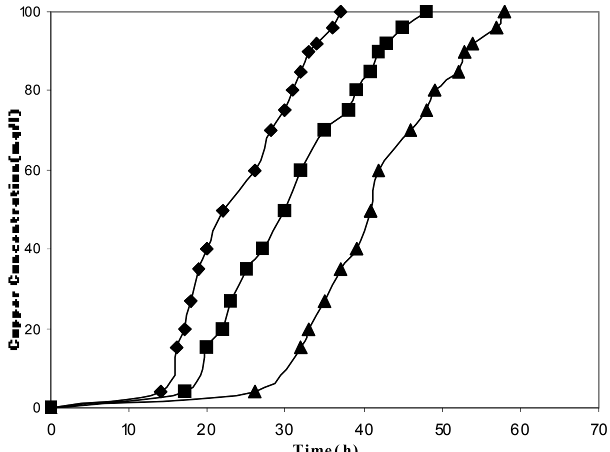

Fig 3.Breakthrough curves for copper biosorption onto *S.tenerrimum* at different bed heights (flow rate=5 ml/min, intial copper concentration= 100mg/l, pH=6)

—◆— 15 cm —■— 20 cm —▲— 25 cm

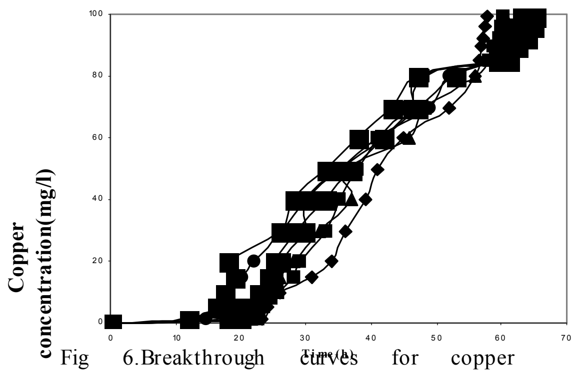

Fig 6.Breakthrough curves for copper concentration onto *S.tenerrimum* biomass during regeneration cycles(initial bed height=25 cm,flow rate=5 ml/min, initial copper concentraion=100 mg/l, pH=6). Sorption cycles:

—◆— 1 cycle —■— 2 cycle —▲— 3 cycle —■— 4 cycle —■— 5 cycle —●— 6 cycle —■— 7 cycle

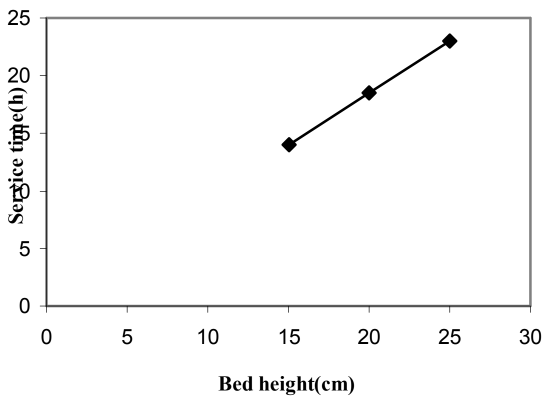

Fig 4.BDST model plot for copper biosorption by *S.tenerrimum* (flow rate=5 ml/min, initial copper concentration=100 mg/l, pH=6)

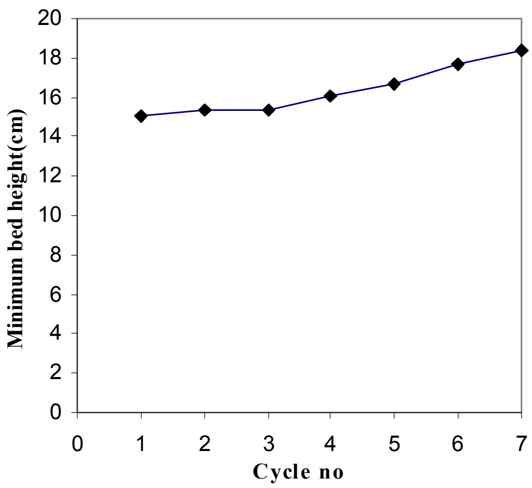

Fig 7.Life factor chart

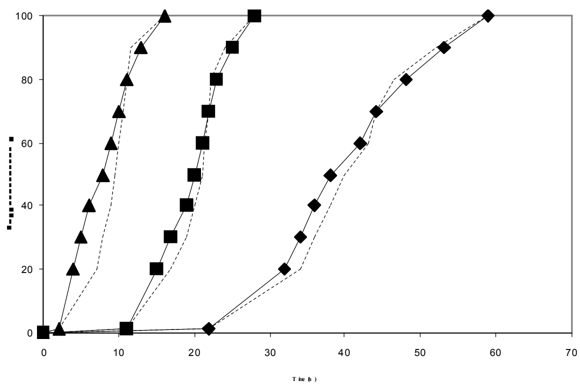

Fig 5.Breakthrough curves for copper biosorption onto *S.tenerrimum* at different flow rates(bed height=25 cm,intial copper concentration=100 mg/l,pH=6)......predicted from Thomas model.Flow rates:

—◆— 5 ml/min —■— 10 ml/min —▲— 20 ml/min

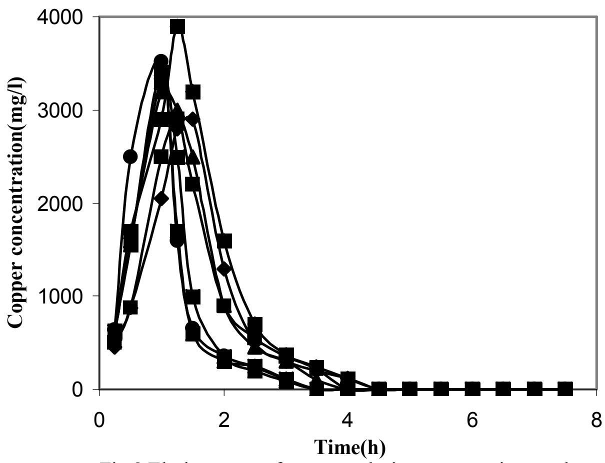

Fig 8.Elution curves for copper during regeneration cycles (flow rate=5 ml/min, elutant=.1 M HCl).

Elution cycles: —◆— 1 cycle —■— 2 cycle —▲— 3 cycle —■— 4 cycle —■— 5 cycle —●— 6 cycle

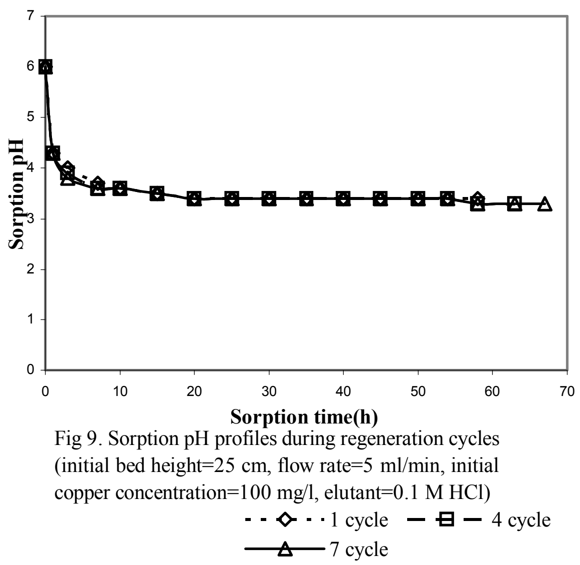

Fig 9. Sorption pH profiles during regeneration cycles (initial bed height=25 cm, flow rate=5 ml/min, initial copper concentration=100 mg/l, elutant=0.1 M HCl)

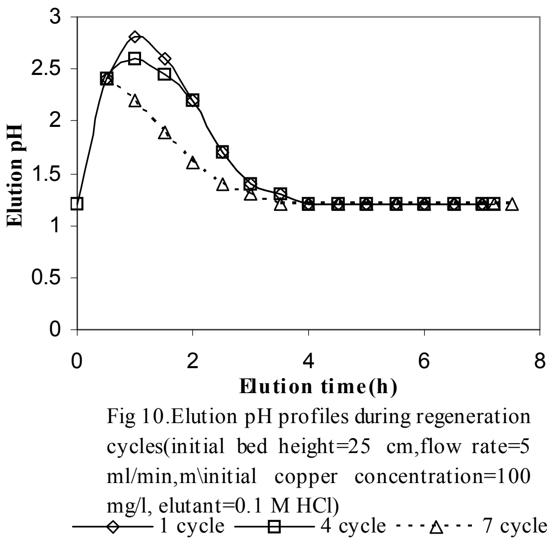

Fig 10.Elution pH profiles during regeneration cycles(initial bed height=25 cm,flow rate=5 ml/min,m\initial copper concentration=100 mg/l, elutant=0.1 M HCl)

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