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Biosorption of Cu(II) from aqueous solution onto immobilized *Ficus religiosa* branch powder in a fixed bed column: Breakthrough curves and mathematical modeling

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Abstract−We investigated the adsorption potential of powdered branches from *Ficus religiosa*, an abundantly available plant, for the removal of Cu(II) from aqueous solution via column studies. Biomass was used as silica immobilized form and characterized using available techniques, including Fourier transformed infrared spectroscopy (FTIR) and scanning electron microscope (SEM). Breakthrough curve approach was used to explain removal capacity of biomass in a continuous flow mode, using different operating parameters like bed height (5-30 cm), inlet metal concentration (100-300 mg/L) and pH (3-5) of the solution, at a fixed flow rate of 2 mL/min. Biosorption of Cu(II) favored with increased service time (breakthrough and exhaust time) of the column with an increase in pH of inlet solution. Maximum biosorption capacity (17.5 mg/g) for Cu(II) was achieved at 5 cm bed height, pH 5 and 300 mg/L influent Cu(II) concentration. Findings suggested that *Ficus religiosa* branch powder takes less service time and thus triggers fast removal of metal ions. Bed depth service time (BDST), Thomas and Yoon-Nelson models were effectively applied to the breakthrough data. The study indicated that the immobilized powdered branches could be used for the effective removal of Cu(II) ions in a continuous flow mode.

Keywords: *Ficus religiosa*, Copper, Breakthrough Curve, Biosorption, Fixed Bed, BDST Model

INTRODUCTION

Copper, an important micronutrient for living organism, is an essential trace element needed to catalyze various physiochemical reactions in the human body. With amounts above the permissible/safe limits, it can cause certain diseases such as Alzheimer's, Parkinson, Wilson, and Menkes. It also causes reproductive, immunological and cardiovascular disorders at high concentrations [1,2]. Consumption of copper-contaminated water is one major reason for higher amounts in the body. Naturally, copper occurs in the form of ores like azurite, malachite and chalcopyrite. Copper mostly gets into water reservoirs through the effluents from processes like electroplating, metallurgy, mining, smelting, petroleum, and refining. The Environmental Protection Agency (EPA) established the standard permissible limit for Cu(II) to be less than 1.0 mg/L for industrial effluents prior to their discharge into water reservoirs. So, water bodies are under serious risk of copper-poisoning due to the disposal of poorly-treated industrial effluents directly to them. Being non-biodegradable, copper is capable to be accumulated in these reservoirs as well as in the food chain. This scenario is chronically deteriorating the biosphere and posing a serious threat to the environment as well as human life.

The use of agricultural ligno-cellulosic materials for the treatment of Cu(II) contaminated water is a possible eco-friendly method, being developed as *biosorption*. Recently, a large amount of work has been reported on copper biosorption in batch mode. The optimized parameters provide mechanistic information about the kinetics and equilibrium of the biosorption processes. A number of studies have been reported on biosorption of Cu(II) in the batch mode, including the use of *Cystoseira crinitophylla* [3], *Acacia leucocephala* [4], *Thuja orientalis* [5], *Cymbopogon citratus* [6], *Musa paradisiaca* [7], pine cone shell [8], black gram husk and *Adenanthera pavonina* [9]. For the treatment of contaminated water at a large scale, such as municipal and industrial wastewater, continuous flow process provides relatively apt information about contact time and equilibrium as compared to the batch process [10]. This continuous flow process is more feasible since it drives constant influent of metal ions (e.g., Cu(II)) solution in the column and throws the *treated* water from the other end of column [11]. Moreover, the bulk volume of industrial effluents can be continuously treated by the measured quantity of biomass packed in the fixed-bed column. Recycling of the biomass is also possible in continuous mode, making it a cost-effective and sustainable process. There are fewer research studies for fixed bed column biosorption of Cu(II) ions (Table 1). Breakthrough curves are used to evaluate column biosorption efficiency, by calculating the breakthrough time (time to reach a significant outflow concentration 't_b') and exhaustion time (time to reach the enrichment of the packed bed column 't_e') values.

The present research was designed for the continuous removal of Cu(II) in a fixed bed column by powdered branches of *Ficus religiosa*, locally known as Peepal. *Ficus religiosa* is a well-known medicinal plant, used to treat various diseases, e.g., heart diseases, diarrhea, diabetes, jaundice, rheumatic pain, and asthma. It is also antimicrobial and an antidote for certain poisons [12]. This biomass is com-

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Table 1. Different plant materials (biosorbent) used for the remedy of Cu(II) metal ion

Biosorbents	Cu(II) Concentration (mg/L)	Exhaust time (min)	Bed depth (cm)	Flow rate (mL/min)	Biosorption capacity (mg/g)	*Model	References
Palm oil boiler mill fly ash (POFA)	20	395	2.0	5.0	21.93	T, Y-N, B	[39]
Coconut shell	10	5400	20	10	7.25	Y-N, B, C	[40]
Rice husk	10	109	9	10	6.33	B	[41]
Sunflower shell	60	150	5.0	5.0	26.22	A	[42]
Pine cone shell	50	260	14.3	2	9.38	S	[8]
Kenaf Fibers	100	2220	30	6.0	47.27	T, B	[1]
Triticum sativum	100	370	200	300	12.2	T, B, Y	[33]
Chitosan-Coated Bentonite	200	540	2.0	0.4	12.14	T, Y-N, B	[43]
Ficus religiosa	300	30	5	2	17.50	B	Present work

*Yan=Y, Thomas=T, Bed depth service time (Bohart-Adams) model=B, Yoon-Nelson=Y-N, Clark=C, Artificial neural network=A, Sip=S

posed of hemicelluloses, lignin, pectin, and cellulose. It also contains nitro, carboxylic, hydroxyl, carbonyl and amino groups. These groups serve as the active sites for binding for Cu(II). Leaves of *Ficus religiosa* have been reported for batch biosorption of Pb(II), Cd(II), Ni(II), Cr(VI) and Co(II) [10,13-17]. The powdered branches of *Ficus religiosa* were reported for batch biosorption of Pb(II) and Cd(II), showing good biosorption capacity [18]. To the best of our knowledge, no studies about the use of powdered branches for Cu(II) removal in continuous flow mode have been reported so far in the literature.

In the present study, the dried powdered branches of *Ficus religiosa* were immobilized and packed in a glass column. Column biosorption studies were performed to explore the effects of the amount of biomass in the column, the pH of the metal solution and concentration of the inlet solution. The conditions were optimized regarding these factors at a constant flow rate. The breakthrough curves were drawn and the data was used to provide an insight into the biosorption behavior of *Ficus religiosa* powdered branches (FRBP) using various models like bed depth service time model (BDST), Thomas model and Yoon-Nelson model.

MATERIALS AND METHODS

1. Materials

Ficus religiosa (peepal) branches were collected from Punjab University Lahore (31.582 °N, 74.329 °E) during March 2016, thoroughly washed with water and oven dried till constant mass. These branches of *Ficus religiosa* were ground in a blender (Kenwood) and sieved to separate the fraction of particles (with an average size of <177 μm) for the column experiments. The required fraction of biomass was then washed with water, dried in the oven until constant mass and kept in airtight plastic recipients. Stock solution of Cu(II) metal was prepared (1,000 mg/L) using A.R. grade copper sulfate. Other dilutions and solutions were prepared as per requirement using analytical grade reagents.

2. Immobilization of Biomass

Biomass was silica-immobilized to enhance its density and to ease the packing of the column, using the process described in the literature [19]. Briefly, 2% solution of H_2SO_4 (300 mL) was added into a beaker (1,000 mL) with 20 grams of simple biosorbent with constant stirring. A saturated solution of $Na_2Si_3O_7$ (Merck) was added dropwise into a mixture of biosorbent and H_2SO_4 till pH 2; stirred the whole mixture for 20 minutes. Subsequently, a pH of 7 was attained after addition of sodium silicate solution. Mixture was further stirred for 10 min and filtered. Immobilized biomass was washed, oven-dried and stored in the plastic recipient, labeled as immobilized *Ficus religiosa* (IMFR).

Powdered branches of *Ficus religiosa* were characterized by pH_{pzc}, Fourier transformed infrared spectroscopy (FTIR), scanning electron microscope (SEM), BET surface area and quantification of acidic and basic groups by the standard methods [20,21].

3. Continuous Biosorption Studies

For continuous flow studies, a glass column of 15 mm internal diameter and 500 mm length was packed with the required quantity of biosorbent to a specific bed height, 5, 15 and 30 cm (as per requirement). During column packing, glass wool was placed at

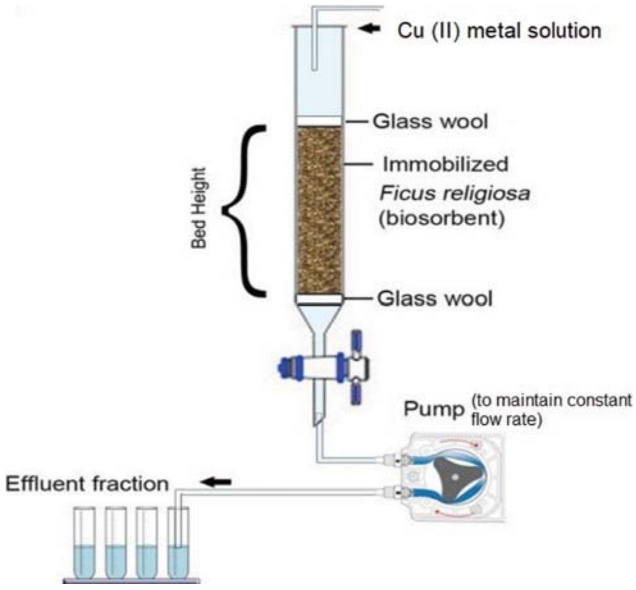

Fig. 1. Graphical illustration of fixed bed column biosorption process.

Table 2. Summary of models used to evaluate breakthrough curves

Model	Linear equations	Description	Reference
Bed depth service time (BDST) model	$t=\frac{N_oZ}{C_ov_1}-\frac{1}{K_aC_o}\ln\left(\frac{C_o}{C_b}-1\right)$	BDST model explains direct relationship between time 't' and bed height 'Z', K_a (L/mg min) rate constant) and N_o (mg/L) biosorption capacity of bed) calculated from intercept and slope of the equation. v_l is the linear flow rate (cm/min)	[19,23]
Thomas	$\ln\left(\frac{C_e}{C_o-C_e}\right)=\frac{C_oK_T}{r}V-\frac{K_Tqm}{r}$	A straight line plot be $\ln(C_e/(C_0-C_e))$ vs V, K_T=rate constant (mL/min·mg), q=metal uptake by sorbent (mg/g)	[24,44,45]
Yoon-Nelson	$\ln\left(\frac{C_t}{C_o-C_t}\right)=k_{YN}t-\tau k_{YN}$	Model evaluates the direct relationship of $\ln\left(\frac{C_e}{C_o-C_e}\right)$ vs t, k_{YN}=rate constant (min^{-1}), τ=time require for 50% effluent concentration (min)	[25,46]

the bottom and top of desired bed height to attain even distribution of solution throughout the column and to avoid the disturbance of the packed bed. The setup of continuous biosorption is shown in Fig. 1.

Performance of fixed bed column for biosorption of Cu(II) onto *Ficus religiosa* was investigated at various bed heights (5 to 30 cm) at various concentrations (C_o=100 to 300 mg/L) and pH (3 to 5) at 2 mL/min flow rate (linear velocity ~1.13 cm/min). The continuous flow rate of the column was maintained using Fisher medium flow pump. The fractions of effluent Cu(II) were collected after fixed intervals of time and analyzed using atomic absorption spectrophotometer (Perkin Elmer AAnalyst 100), to determine the effluent concentration (C_e, mg/L). Since the flow rate was fixed, the volume of treated Cu(II) solution could be easily calculated. The dimensionless concentration (C_e/C_o) was used to plot the breakthrough curves. Breakthrough curves expressed the relationship between the ratio of effluent to influent concentration (C_e/C_o) and time [22]. A similar method was followed to study the effects of other parameters like a variation of bed height, concentration of Cu(II) ions and pH of Cu(II) solution. The results provided are the mean values of triplicate experimental results. No detectable Cu(II) adsorption was observed by the glassware during the course of experiments.

4. Breakthrough Curve Analysis

Performance of continuous flow experiments was evaluated by the obtained S-shape breakthrough curves, which provided valuable information about breakthrough time (t_b) and exhaust time (t_e). The times at which Cu(II) concentration ratio (C_e/C_o) was 0.1 and 0.9 were expressed as breakthrough and exhaust times, respectively. At column enrichment point, the influent and effluent concentration became almost equal. The total mass of metal adsorbed q_{total} (mg) was calculated by Eq. (1).

$$q_{total}=\frac{F}{1000}\int_{t=0}^{t=t_{total}}C_{ad}dt \quad (1)$$

where C_{ad} (mg/L, C_o–C_e) is a concentration of metal adsorbed and F (mL/min) is the flow rate. Copper uptake capacity q_e is the ratio of the masses of metal adsorbed 'q_{total}' to the biomass 'm' given by Eq. (2).

$$q_e=\frac{q_{total}}{m} \quad (2)$$

Biosorption capacity for Cu(II), q_e (mg/g) and R% (percentage metal removal efficiency) were calculated using breakthrough data (breakthrough time, exhaust time, effluent volume, and mass of biomass) at 10 and 90% of initial concentration. R% (Eq. (3)) is the percent ratio of q_{total} (total mass of metal Cu(II) adsorbed) and m_{total} (amount of metal fed into the column).

$$R\%=\frac{q_{total}}{m_{total}}\times 100 \quad (3)$$

5. Dynamic Model Studies

For continuous flow studies, it is important to evaluate the breakthrough curves that provide information about the dynamic models. A number of mathematical models have been developed for column biosorption. Bed depth service time (BDST), Thomas and Yoon-Nelson models were used to evaluate the experimental data of continuous flow studies. Linear equations of these models are given in Table 2.

Bed depth service time (BDST) model equation was proposed by Bohart and Adams [23]. It provides information about the adsorption rate of metal, controlled by a surface process on adsorbate and about the unused adsorbent capacity. BDST model explains the linear relationship between service time and the bed height of the column.

Thomas model is widely used to evaluate breakthrough curves predicting the adsorption efficiency of the column. The model follows the Langmuir type adsorption-desorption process with negligible axial dispersion [24], while rate driving force is second-order reversible kinetics.

Yoon-Nelson model assumes that the probability of a decrease in biosorption capacity is proportional to the probability of adsorbate-biosorption and sorbate-breakthrough on the sorbent [25]. The time required for 50% adsorption-breakthrough is expressed as τ (min).

RESULTS AND DISCUSSION

1. Characterization of Powdered Branches

Functional groups (binding sites) present on the powder biomass surface were identified using FTIR spectrophotometer (Cary 630-Agilent) in ATR mode (on a ZnSe crystal). An FTIR spectrum of biomass is given in Fig. 2(a). Phenolic (O-H) and (C-O) stretching vibration of carbohydrate groups of the material show their existence at 1,235 cm^{-1} and 1,032 cm^{-1} respectively. A broadband at

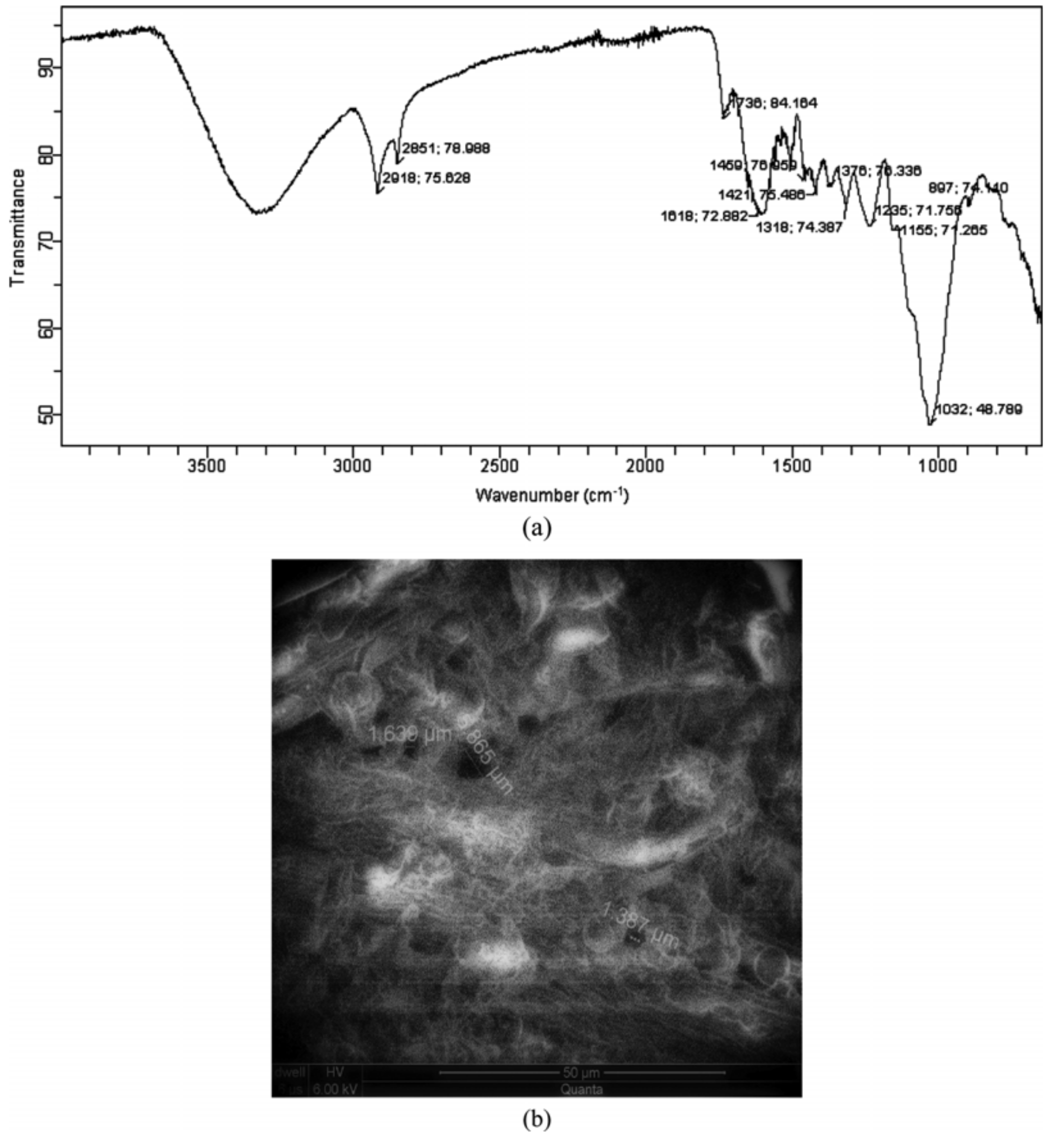

Fig. 2. Characterization of powdered *branches of Ficus religiosa* by (a) FTIR, (b) SEM.

1,318 cm^{-1} reveals the existence of cellulosic (C-H) group. The peak at 1,618 cm^{-1} depicts the stretching vibration of alkenes (C=C). The absorption band at 1,736 cm^{-1} indicates the existence of stretching vibration of carbonyl (C=O) groups, such as aldehyde and ketones of lactones and quinines. The broad bands at 2,918 cm^{-1} and 2,815 cm^{-1} reveal the presence of C-H and O-H groups on the biosorbent surface [26]. The N-H groups show peaks around 3,500-3,200 cm^{-1}. These sharp lines are usually buried underneath the broad O-H peaks and thus difficult to observe. This does not show their absence [16,17,27,28]. This indicated that the biomass was rich in O and N containing groups.

The topography and surface features of the biomass were elucidated using scanning electron microscopy (SEM). The SEM micrograph of simple *Ficus religiosa* was obtained on Nova Nano 450 (Fig. 2(b)). The SEM shows that the surface of biomass is irregular and coarse and is porous. A material with a porous and irregular surface having N and O containing functional groups is usually a good biosorbent [29].

Boehm titrations (potentiometric titration) were performed for the quantification of strong as well as weak acidic and basic active sites present on *Ficus religiosa* biomass. Titration results provide that the concentration of total acidic groups was 12.25 mmol/g (phenolic 8.25 mmol/g and carboxylic-lactonic groups 4.0 mmol/g), and total basic groups were 4.3 mmol/g [30]. More acidic sites indicate that the material is likely to behave as a negative surface after dissociation of acidic sites. This would be attracting the positively charged metal ions more towards it, facilitating the removal process.

For adsorption purposes, the surface area of the materials is very important. A high surface area indicates a high adsorption capacity. Brunauer Emmet Teller (BET) surface area was found to be 653.15 m^2/g. The surface area is relatively high enough to compete for most of the activated carbons synthesized from plant materials [31]. Such a high surface area shows the high adsorption characteristics of the material. Some other physical properties such as bulk density, ash contents, particle size, moisture contents and surface area of the biomass are given in Table 3. Very small

Table 3. Characterization of powdered *Ficus religiosa*

Physical properties (unit)	Powdered FR
Bulk density (g/mL)	0.12
Moisture contents (%)	5.4
Ash contents (%)	58
Particle size (μm)	<177
BET Surface area (m^2/g)	653.515
Monolayer volume (cm^3/g)	150.123
Total acid group (mmol/g)	12.25
(i) Phenolic groups	8.25
(ii) Lactones and carboxylic groups	4.0
Total basic group (mmol/g)	4.3

moisture content indicates that the material used is dry enough. A small bulk density value justifies the need of silica-immobilization of the material before packing of the column. The bulk density of the silica immobilized material was found to be 0.24 g/cm^3. The moisture content decreased to 5.0% and the ash content increased from 65%. The silica immobilization was not found to change the properties significantly. Overall, the characterization indicates that the powdered branches are capable to attract/adsorb/remove positively charged copper ions.

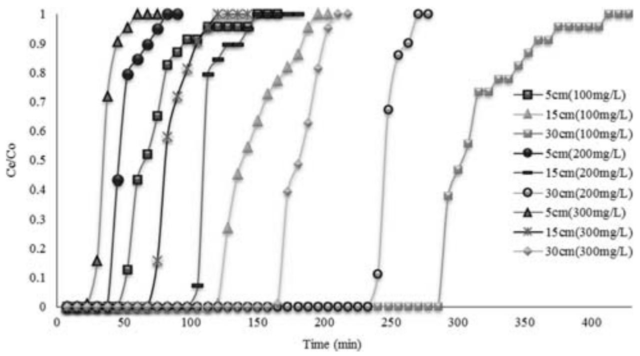

Fig. 3. Breakthrough curves of Cu(II) biosorption on different bed heights (5-30 cm) and concentrations (100-300 mg/L).

2. Fixed Bed Column Studies

2-1. Effect of Concentration on Cu(II) Biosorption

The effect of variation in the Cu(II) concentration was studied to explore the capacity of the biomass while in the continuous mode. This is surely helpful in the upgrading of the process at a larger scale. Biosorption capacity of biomass was found to change with the variation in initial concentration of Cu(II) for a particular amount of material. Fixed bed column biosorption was studied on various concentrations of Cu(II) (100, 200, and 300 mg/L) and different bed heights 5, 15 and 30 cm at a flow rate of 2 mL/min. Experimental results revealed that the breakthrough time (t_b) of 5 cm bed height decreased from 52.5 to 42.5 min as concentration increased from 100 to 200 mg/L (Fig. 3). The breakthrough time was decreased by 19.05% when the concentration increased from 100 to 200 mg/L. A further decrease of 29.41% was observed by increasing the concentration from 200 to 300 mg/L. There was 42.85% decrease in t_b while the concentration was increased three-times the original concentration. A similar trend was observed on further increase in concentration as well as bed heights. At 100 mg/L, exhaust time (t_e) increase from 97.5 to 360 min as bed height increases from 5 to 30 cm. Breakthrough and exhaust time disclosed a direct relation with column bed height and inverse trend with the concentration of the metal solution.

Biosorption capacity q_e and removal efficiency R% of biomass were calculated using Eqs. (2) and (3), respectively (Table 4). Removal efficiency also increased from 86.66% to 95.34% as bed height of the column increased from 5 to 30 cm at 100 mg/L concentration of Cu(II). Moreover, with an increase in concentration from 100 to 300 at 15 cm bed height, the value of R% fell from 95.83 to 93.33 because of prompt enrichment of binding sites [32].

2-2. Effect of Bed Height on Biosorption of Cu(II)

An increase in bed height is expected to increase the removal efficiency due to the increase in the amount of packed material. Biosorption of Cu(II) was found to have a linear relationship with a bed height of the column. As bed height increased from 5 cm to 30 cm, the amount of biosorbent packed in a column also increased from 1.8 g to 9.1 g. Similarly, as the biomass quantity increased, biosorption capacity and breakthrough time (Fig. 3) were also improved. Breakthrough time of column increased from 52.5 to 124.5 min as

Table 4. Breakthrough parameters for biosorption of Cu(II)

Concentration of Cu(II) mg/L	Bed depth cm	Service time (min)		R %		q_e mg/g	
		0.1 C_0	0.9 C_0	0.1 C_0	0.9 C_0	0.1 C_0	0.9 C_0
100	5	52.5	97.5	46.66	86.66	5.83	10.83
	15	124.5	187.5	62.5	95.83	5.08	7.65
	30	290	360	74.41	95.34	6.37	7.91
200	5	42.5	75	54.54	90.90	9.44	16.66
	15	107.5	142.5	66.66	88.88	8.78	11.63
	30	240	272.5	84	96	10.55	11.98
300	5	30	52.5	57.14	85.71	10	17.5
	15	75	105	66.66	93.33	9.18	12.85
	30	175	205	78.26	95.65	11.54	13.52

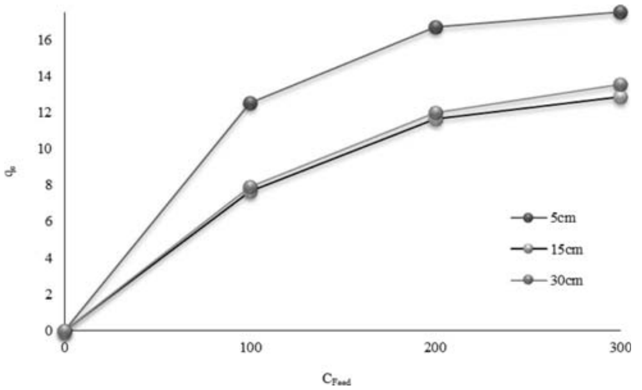

Fig. 4. Dynamic isotherms of concentrations (100-300 mg/L) vs sorption capacity on different bed heights (5, 15 and 30 cm).

the bed height increased from 5 to 15 cm at 100 mg/L concentration. The same trend was observed by a further increase in the bed height. The capacity was not found to vary linearly with increase in bed height, although the amount of material was increased. This might be because the capacity was calculated by dividing the adsorbed concentration by the amount of biomass. The maldistribution of solution and induction of channeling in bed of column were also reasons for nonlinear behavior of bed height and capacity [33]. Thus, there was a decrease in the biosorption capacity with an increase in the bed height. A similar trend was reported by some researchers [34-36]. The relationship of concentration with biosorption capacity was graphically described as isotherms (Fig. 4). The isotherm for 5-30 cm bed height and 100-300 mg/L concentration exhibit a linear behavior with q_e until the saturation point reach. The maximum biosorption capacity (17.5 mg/g) was found at 300 mg/L of Cu(II) at 5 cm bed height.

2-3. Effect of pH on Biosorption

The surface charge of the biomass is dependent on the solution pH. Powdered branches were found to have more acidic functional groups than the basic groups, so the pH dependency of the surface charge was obvious. A very low pH would result in the positive surface due to protonation of the biomass [30]. However, a very high pH would cause the metal ions to precipitate forming the hydroxides. So the pH studies were performed in a narrow pH range: 3 to 5. The pH of the metal solution has a direct relation with the biosorption capacity of column [37].

In the present study, the effect of initial pH for Cu(II) solution

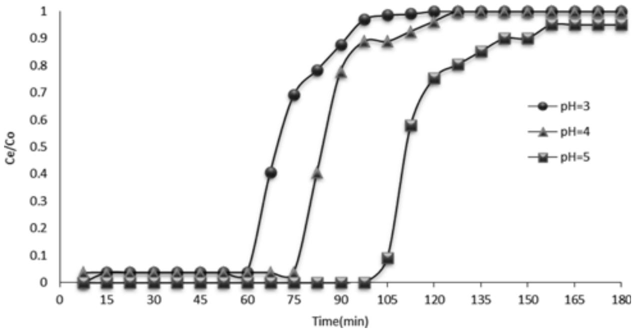

Fig. 5. Breakthrough curves of Cu(II) at various pH.

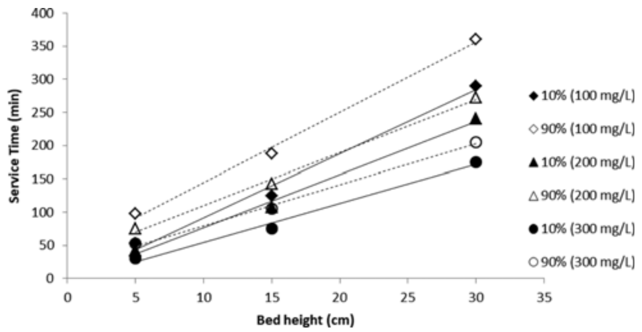

Fig. 6. BDST model for Cu(II) by immobilized *Ficus religiosa* (C_o= 100-300 mg/L and flow rate 2 ml/min).

(200 mg/L) was investigated on 15 cm bed height. As the pH of the metal solution increased from 3 to 5, the value of breakthrough time also increased from 62 to 107.5 min (Fig. 5). The metal solution became turbid above pH 5, indicative of the precipitation of metal ions. This result is in accordance with the literature that, mostly, metal ions show maximum removal at around pH 5 [19,30].

3. Mathematical Modeling

3-1. Bed Depth Service Time (BDST) Model

In continuous flow studies, the BDST model was applied to the experimental data. A linear plot of bed height against service time of column was obtained on 10% and 90% service times. The model was applied on various bed heights 5-30 cm and for various initial metal ion concentration (100-300 mg/L) at 2 mL/min flow rate. As shown in Fig. 6, the curves were linear for a breakthrough as well as exhaust concentrations ($0.1C_0$ and $0.9C_0$ respectively). The values of coefficients of determination indicated the validity of the BDST model. These values and other BDST parameters like rate constant (K_a) and capacity of column (N_o) were calculated using intercept and slope of the equations, respectively, given in Table 5.

The BDST column capacity N_o was found to increase with initial concentration at 10% breakthrough time. The value of N_0 almost doubled (from 1087.18 to 1989.39 mg/L) when the metal ion concentration was increased from 100 to 300 mg/L. In general, the BDST capacity value increased when service time increased from 10% to 90% of C_0. As given in Table 5, the rate constant was higher at 10% breakthrough time than at 90% time. This was due to the availability of greater vacant sites at the initial stages of attachment onto the biomass surface. The linear fitting of the model equations indicated that the breakthrough data could be explained by the BDST model.

3-2. Thomas Model

Thomas model parameters were determined on various bed heights (5-30 cm) and concentrations (100-300 mg/L) over a con-

Table 5. BDST parameters values for Cu(II) biosorption at 10% breakthrough concentration

Initial concentration (mg/L)	BDST equation for Cu(II)	R^2	N_o (mg/L)	K_a (L/mg min)
100	$t=9.6211Z-4.6842$	0.9883	1087.18	4.69×10^{-3}
200	$t=7.9737Z-2.8947$	0.9936	1802.06	3.80×10^{-3}
300	$t=5.8684Z-4.4737$	0.9899	1989.39	1.64×10^{-3}

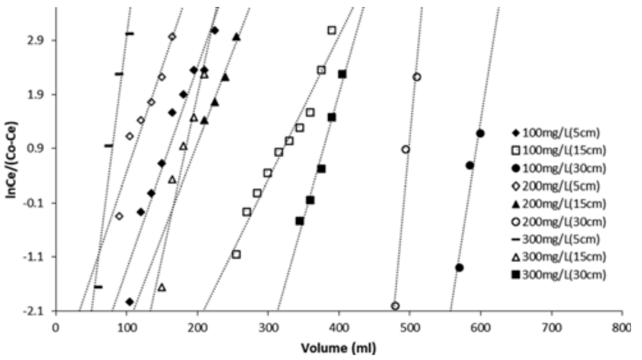

Fig. 7. Thomas model applied on various bed height (5-30 cm), concentration 100-300 mg/L and 2 ml/min flow rate.

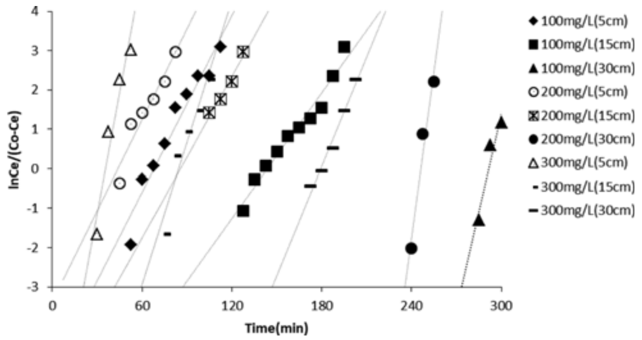

Fig. 8. Yoon-Nelson model applied on various bed height (5-30 cm), Concentration 100-300 mg/L and 2 mL/min flow rate.

stant flow rate of 2 mL/min. Linear plots for $\ln(C_e/C_o-C_e)$ *vs* V on different bed heights and concentration were applied to calculate the values of K_T and q using slope and intercept of the plot (Fig. 7). The values of the parameters are given in Table 6. The value of q was found to decrease (from 7.562 to 6.406 mg/g) as bed height of the column increased from 5 to 30 cm at 100 mg/L concentration. At the same concentration, the value of K_T changed from 0.750 to 1.652 mL/min.mg with increasing bed height (5 to 30 cm). The coefficients of determination values were less than 0.98 for all sets of data. The Thomas constant values were in accordance with those found in the literature [38]. The linear fitting could only be accepted if R^2 was found to be greater than 0.98. Hence, the Thomas model was unable to explain the obtained breakthrough data for Cu(II) removal by powdered branches.

3-3. Yoon-Nelson Model

In the existing study, Yoon-Nelson model parameters (k_{YN} and τ) were also calculated from the linear plots (Fig. 8). The enrichment time of the column with Cu(II) ions was equal to 2τ. The R^2 values were found to be smaller than 0.98 for all the linear fitting. The value of K_{YN} (0.075 to 0.1651 min^{-1}) decreased with an increase in bed height (5 to 30 cm). On the other hand, the calculated τ values (68.1 to 291.6 min) increased as bed height increased from 5-30 cm. Increase in bed height provided more binding sites for Cu(II) biosorption, which indicated a direct relation with τ (time required for 50% effluent concentration). The difference between the experimental and model τ values was calculated as D (%) $(=100^*(\tau_{cal}-\tau_{exp})/\tau_{exp})$. The D% values are given in Table 6. The negative sign just shows that the calculated/model values were smaller than the experimental values. In most of the cases, D% was quite insignificant, indicating that Yoon-Nelson model could be applied for the modeling of the data. The difference between experimental and calculated τ values indicated the linear model fitting, but R^2 values were contradicting this linear fitting. This contradiction pointed to the fact that the Yoon-Nelson model could not be applied to explain the breakthrough data. So, it could be inferred that for the modeling of the Cu(II)-fixed bed studies, the BDST model was the best fit at the breakthrough concentration.

CONCLUSION

In the present study, the utilization of an eco-friendly biosorbent (branches of *Ficus religiosa*) for the removal of Cu(II) ions from synthetic contaminated solutions using column biosorption was discussed. The material was characterized to find the feasibility and potential use for the purpose. The fixed bed column mode is relatively economical and technically viable for its use at an industrial scale. Metal removal efficiency was evaluated by the breakthrough curve (breakthrough time and exhaust time) and column design parameters such as column bed height, the initial concen-

Table 6. Thomas and Yoon-Nelson model parameters for Cu(II) biosorption

Cu(II) conc. (mg/L)	Bed height (cm)	Thomas model			Yoon-Nelson model				
		k_T (mL/min mg)	q_m (mg/g)	R^2	k_{YN} (1/min)	R^2	Calculated τ (min)	Experimental τ (min)	D (%)
100	5	0.750	7.562	0.9377	0.0750	0.9377	68.1	67.5	0.82
	15	0.532	5.859	0.9662	0.0531	0.9662	143.8	142.5	0.92
	30	1.652	6.406	0.9168	0.1651	0.9168	291.6	303.5	−3.91
200	5	0.386	9.772	0.9253	0.0770	0.9253	44.1	49.5	−10.93
	15	0.342	6.987	0.9695	0.0683	0.9695	85.7	110	−22.08
	30	1.411	10.826	0.9574	0.2823	0.9574	246.2	248	−0.72
300	5	0.683	11.896	0.9297	0.2050	0.9297	35.7	41.5	−14.01
	15	0.401	10.338	0.9194	0.1204	0.9194	84.4	80.5	4.88
	30	0.309	11.825	0.9744	0.0926	0.9744	179.3	190	−5.61

tration of Cu(II) solution and pH. A linear relationship for the breakthrough times with bed height and pH was found. The times decreased with an increase in the initial concentration of Cu(II) solution. The breakthrough data was analyzed using BDST, Yoon Nelson, and Thomas model. Yoon Nelson and BDST models were not found to successfully explain the biosorption process. The bed depth service time model was found to best fit at the breakthrough times and concentration. The results suggested that degradable biomass (FR) possessed significant potential for the detoxification of Cu(II) contaminated waters from industrial effluent in continuous flow mode.

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