Copper biosorption in a column of pretreated *Aspergillus niger* biomass

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Abstract

In this study, biosorption of Cu(II) was investigated in a column of pretreated *Aspergillus niger* biomass. The breakthrough was measured as a function of influent flow rate and bed height for a feed solution at 10 mg/l metal ion concentration. Biosorption was evaluated in terms of the equilibrium capacity of the column and the amount of metal loading on the *A. niger* surface. It has been observed that pretreatment of the biomass enhanced the activity of the surface reactive groups and hence the uptake. The breakthrough data obtained was described by bed depth service time (BDST) and Thomas models. The amount of copper adsorbed per gram of pretreated *A. niger* was 13.4 ± 0.60 mg/g. The sorbed copper was eluted from the column using 0.1N HCl in five consecutive sorption–desorption cycles. For the same initial metal ion concentration, a packed column reactor shows more uptake of Cu(II) in comparison to a batch reactor.
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1. Introduction

Biosorption can be used as an alternative method for removal of heavy metals from wastewater [1]. The removal of traces of toxic copper metal ions by biosorption from wastewater has gained interest in recent years [2]. Batch studies provide insight into the effectiveness of copper removal by biomass. However, the continuous operation of a reactor is a more efficient mode of operation in comparison to a batch process. Hence there is the need to perform column studies. The cost of production of the biomass is a factor which determines the suitability of a biomass for industrial biosorption applications. It would obviously be effective to use the same biomass for multiple sorption-desorption cycles.

Different types of reactors including fluidized bed columns and continuous stirred tank reactors can be used for column studies. However, packed bed sorption has a number of advantages including the possibility of achieving a reasonably high sorption capacity with very low effluent concentrations. Adsorption takes place from the inlet of the column and proceeds to the exit and a high degree of purification can be achieved in a single process step [3].

Several reports of batch biosorption studies have been communicated by various groups [4,5]. However, relatively few reports exist of column studies for biosorption of metals. Kapoor and Viraraghavan [6] studied column operation for the removal of copper by immobilized *Aspergillus niger*. Volesky et al. [7] reported sorption of copper by a packed bed of *Sargassum filipendula* biomass. Vijayaraghavan et al. [8] reported on the operation of a column for sorption of copper by *Turbinaria ornate* biomass.

Recent batch studies have identified the potential for copper biosorption by pretreated *A. niger* biomass [9]. In this study, removal of copper by pretreated *A. niger* has been studied in a packed bed column. Important design parameters such as column bed height and flow rate of metal solution into the column have been identified. The breakthrough profile for the sorption of copper is analyzed using bed depth service time (BDST) and Thomas models and mass transfer parameters are determined from the models. The column is regenerated and reused in five cycle operations towards evaluating the biomass for its effective use in industrial applications.

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2. Materials and methods

2.1. Growth of culture

The fungus *A. niger* strain NCIM 618 (ATCC 10594), was obtained from NCIM, Pune, India and used for the sorption studies. The laboratory strain of *A. niger* was propagated in potato dextrose agar (PDA) consisting of 39 g/l PDA and 0.1 g/l of yeast extract. The culture was maintained on slants and was incubated for 5–7 days at $33 \pm 2\,°C$. The growth medium used had the following composition (g/l): dextrose, 30; peptone, 10; $(NH_4)_2HPO_4$, 0.4; KH_2PO_4, 0.2; $MgSO_4·7H_2O$, 0.2. All reagents were from Himedia or Merck (Mumbai, India). The pH of the growth medium was adjusted to 5.8–6.0 by the addition of 0.1N HCl prior to autoclaving. Once inoculated, flasks were shaken at 200 rpm for 5 days at $33 \pm 2\,°C$. After harvest, the biomass was transferred to a 1% formalin solution for 24 h. The biomass was then dried at $60\,°C$ for 20–24 h and powdered in a mortar. The powdered biomass residue was sieved and in the range of 0.75–1.0 mm particle size was used for further studies.

2.2. Column experiment

The sorption studies were carried out in a glass column of 1.5 cm outside diameter with 0.3 cm wall thickness and 11 cm (total height 22 cm) length. Packed bed experiments were carried out at $33\,°C$. A perforated polymeric plate was fitted at the top and bottom of the column for better flow distribution of the metal solution and to support the biomass during the studies. Experiments were conducted to study the effect of bed height, flow rate of the influent metal solution at a fixed initial concentration of metal in influent.

Pretreated biomass of 1, 2 and 3 g were packed in the glass column and the sorption experiment was performed corresponding to 2.1, 3.1 and 4.1 cm of initial height of the column. The sorption was conducted at flow rates between 1.6 and 9.8 ml/min. Cu(II) solution of concentration 10 mg/l, was fed from the top of the column. Effluent samples were collected at different times from the bottom of the column. Column effluent samples were analyzed by atomic absorption spectroscopy (AAS-SL 173, EIL, India).

In the desorption process, 0.1N HCl was used as an eluting agent. The flow rate was varied between 1.2 and 1.6 ml/min. Sorption studies were also carried out after regeneration of the biomass. The adsorption–desorption process was continued for five consecutive cycles to investigate the adsorption capacity of the biomass.

2.3. Modeling and analysis of column data

The breakthrough data was modeled using the BDST model [10] and the linearized Thomas model [11]. BDST is a simple model for predicting the relationship between the bed depth (h), and service time (t), in terms of process concentrations and adsorption parameters. This model has been used by many researchers for column studies of metal sorption [8,12]. Hutchins [13] proposed a linear relationship between the bed depth and service time as

$$t = \frac{N_0}{C_0 F/A} H - \frac{1}{K_b C_0} \ln \left(\frac{C_0}{C} - 1 \right) \tag{1}$$

C is the effluent copper concentration (mg/l), C_0 the influent copper concentration (mg/l), F the volumetric flow rate in cm^3/h, N_0 the adsorption capacity (mg/l), K_b the rate constant in BDST model (l/mg h), t time (h) and H is the bed depth of the column in cm. Eq. (1) can be represented in the form of a straight line:

$$t = mh - C_x \tag{2}$$

The slope of the BDST model (m) represents the time required for the sorption zone to travel a unit length through the adsorbent [14] and can be used to predict the performance of the bed at different initial metal ion concentrations.

The Thomas model [15] has been used in studies of metal sorption by column experiment [6,16]. The Thomas model is presented in the following equation:

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(k_t/F(q_0 M - C_0 V)\right)} \tag{3}$$

C is the effluent copper concentration (mg/l), C_0 the influent copper concentration (mg/l), k_t the Thomas rate constant (ml/min mg), q_0 the maximum copper adsorbed in biomass (mg/g), M the weight of the biomass, V is the throughput volume (l) and F is the volumetric flow rate (ml/min). A linearized Thomas equation (Eq. (4)) is actually used for the fitting of the experimental data:

$$\ln \left(\frac{C_0}{C} - 1 \right) = \frac{k_t q_0 M}{F} - \frac{k_t C_0 V}{F} \tag{4}$$

The amount of copper adsorbed (m_{ad}) in the bed is represented by the area above the breakthrough curve (C vs. t) and can be obtained by numerical integration [17]. The breakthrough time is defined as the time when the effluent concentration of copper reaches 0.5 mg copper/l. The bed exhaustion time t_e represents the time when a copper concentration of 9.9 mg/l is observed in the effluent. The time difference between t_b to t_e (i.e. Δt) is related to the length of the sorption zone. The length of this zone can be calculated from the following equation [18]:

$$H_m = H \left(1 - \frac{t_b}{t_e} \right) \tag{5}$$

H is the total length of the sorption bed and H_m is the length of the sorption zone (the critical bed length). This length signifies the minimum bed height required to obtain the breakthrough time at zero.

The amount of metal desorbed (m_d) from the bed by elution is calculated by integrating the elution curve as

$$m_d = \int C \, dV \tag{6}$$

The ratio of m_d, metal desorbed to the metal sorbed in the previous cycle is the elution efficiency (E). The regeneration parameters t_p (peak time, h), c_p (peak concentration, mg/l) and
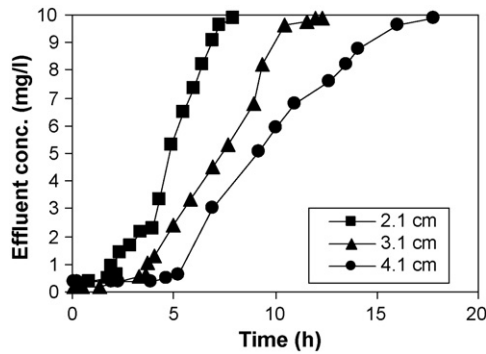
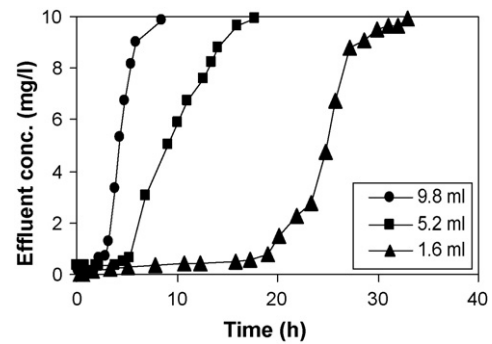Fig. 1. Effect of bed height on the breakthrough profile for sorption of copper ($F = 5.2$ ml/min, $C_0 = 10$ mg/l).
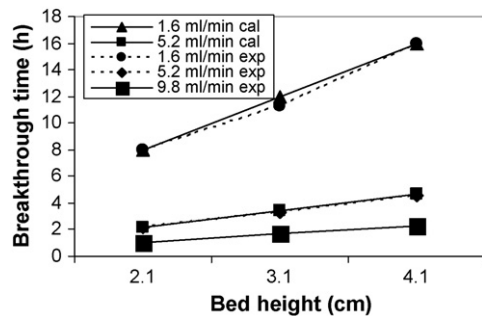

Fig. 2. Effect of bed height by the bed depth service time (BDST) model for sorption of copper ion.

concentration factor (CF) for the copper sorption process are calculated after each sorption–desorption cycle [7].

$$CF = \frac{c_p}{C_0} \quad (7)$$

3. Results and discussion

3.1. Column performance

Sorption of copper by pretreated *A. niger* biomass is presented in the form of a breakthrough curve where effluent concen-

Fig. 3. Effect of flow rate on breakthrough capacity at different flow rates for sorption of copper ion (bed height: 4.1 cm).

tration *C* is plotted against time. It has been reported that the breakthrough curves exhibit an S-shaped due to mass transfer effects [7]. Fig. 1 shows the breakthrough profile of copper biosorption at different bed heights for a given flow rate. The metal uptake capacity increased with increasing bed height, from 2.1 to 4.1 cm. In the column experiment, the increase in the uptake capacity with the bed height is due to the increase in the available binding sites for the adsorption. The breakthrough and exhaustion times were observed to increase with the bed height.

The simplicity of the BDST model is that it can predict the slope for any unknown flow rates with a known slope at a given flow rate. The breakthrough time against the bed height at different flow rates for the sorption as shown in Fig. 2. The nature of the plots was linear indicating the validity of the BDST model for the pretreated *A. niger* biomass at all flow rates employed. Table 1 shows the slope and intercepts calculated using a flow rate of 9.8 ml/min. BDST model parameters are calculated for flow rates of 1.6 and 5.2 ml/min. It can be seen that the calculated and experimental values are in good agreement with intercept values varying slightly. The advantage of the BDST model is that any experimental data can be scaled up to other flow rates without further experimental data and analysis [12]. Table 2 shows the estimated parameter of the BDST model (N_0, the adsorption capacity; rate constant K_b; the critical bed depth H_m) for

Table 1
Experimental and calculated bed depth service time (BDST) parameters for sorption of copper

Metal	Flow rate (ml/min)	Analysis	Slope m (h/cm)	Intercept C_x (h)	Correlation coefficient
Copper	1.6	Experimental	3.95	−0.52	0.99
	1.6	Calculated	3.96	−0.29	1.00
	5.2	Experimental	1.22	−0.40	0.99
	5.2	Calculated	1.22	−0.34	1.00
	9.8	Experimental	0.65	−0.32	0.99

Table 2
Bed depth service time (BDST) parameters for sorption of copper

Metal	Flow rate (ml/min)	Linear flow rate (m/h)	N_0 ($\times 10^3$ mg/l)	K_b (l/mg h)	H_m (cm)
Copper	1.6	0.02	5.96	0.48	0.13
	5.2	0.05	5.96	0.67	0.33
	9.8	0.09	5.96	0.84	0.49

Table 3
Thomas model equation parameters for sorption of copper

Metal	Bed height (cm)	Flow rate (ml/min)	Uptake (mg/g)	k_t (ml/min mg)	t_b (h)	t_e (h)	Δt (h)	Total removal (%)
Copper	2.1	1.6	13.74	1.01	8.00	19.00	11.00	70.45
	2.1	5.2	13.38	1.69	2.18	7.91	5.73	83.96
	2.1	9.8	12.74	3.08	1.01	4.43	3.42	81.77
	3.1	9.8	12.92	2.46	1.74	6.50	4.76	79.02
	4.1	9.8	13.11	1.89	2.30	8.40	6.10	76.90

Table 4
Column characteristics of different biomasses for Cu(II) removal

| Adsorbent	Source	Initial metal concentration (mg/l)	Column diameter (mm)	Column height (mm)	Flow rate (ml/min)	Bed height (mm)	Uptake (mg/g)	Reference
Aspergillus niger (pretreated)	Fungi	10	12	220	9.8	41	13.11	This study
A. niger (immobilized)	Fungi	10	12.7	300	3	245	2.9	[6]
Sargassum filipendula	Raw seaweed	35	25	500	15	410	38.2	[7]
Ulva reticulate	Marine green alga	100	20	350	5	250	56.3	[8]
Turbinaria oranta	Brown marine algae	100	20	350	5	250	68.76	[19]
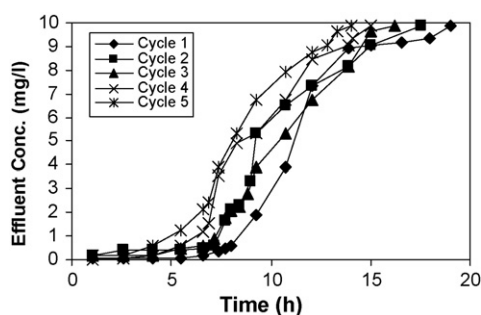
Fig. 4. Breakthrough curves for biosorption of copper by *Aspergillus niger* biomass for five sorption cycle (bed height: 2.1 cm, flow rate 1.2–1.6 ml/min).
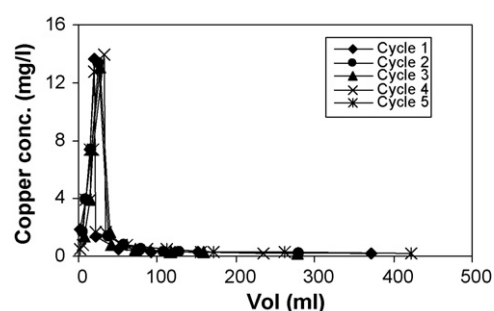

Fig. 5. Elution curves for copper in 0.1N HCl for five regeneration cycles.

copper biosorption by the *A. niger* system. These BDST model parameters can be useful in scaling up the process.

The effect of flow rate on breakthrough capacity is indicated in Fig. 3. As the flow rate increases, the breakthrough time decreases. A similar decrease in breakthrough capacity is reported in the literature for sorption by the fungus *Pycnoporus sanguineus* [12]. This is due to the low residence times that result at a high flow rate, and also possibly due to leaching of copper from the biomass at such flow rates. The column data is fitted to the linearized form of the Thomas model. The parameters k_t and q_0 are estimated and presented in Table 3. The linearized Thomas

equation is found to describe the system well. A compilation of column characteristics of the prepared biomass with other adsorbents discussed in the literature is presented in Table 4.

3.2. Regeneration studies

In a previous study, we have reported the biosorption of Cu(II) on pretreated *A. niger* in a batch reactor [2,20,21]. We now discuss the effect of regeneration by multiple sorption–desorption cycles on copper biosorption by *A. niger* biomass. The primary objective of regeneration is to retain the sorption capacity of exhausted biomass; a secondary objective is to recover

Table 5
Breakthrough parameters for five sorption–desorption cycle of copper biosorption process

Break-through no.	Uptake (mg/g)	t_b (h)	t_e (h)	Δt (h)	k_t (ml/min mg)	Bed height (cm)	Minimum bed height (cm)	Total removal (%)
1	13.74	8.00	19.00	11.00	1.01	2.1	1.22	70.40
2	13.46	7.15	17.54	10.39	1.21	2.1	1.24	62.54
3	13.25	6.58	16.24	9.66	0.74	2.0	1.19	67.99
4	12.79	5.50	15.04	9.54	1.24	2.0	1.27	64.06
5	12.59	4.08	14.01	9.93	1.05	1.9	1.35	65.65

Table 6
Regeneration parameters for five sorption–desorption cycle of copper biosorption process

Elution no.	Flow rate (ml/min)	Time of elution (h)	t_p (h)	c_p (mg/l)	CF	% E
1	1.6	4.6	1.16	13.62	1.36	98.7
2	1.6	4.9	1.0	13.33	1.33	97.8
3	1.2	5.1	1.05	13.05	1.30	98.6
4	1.6	4.5	1.05	13.91	1.39	97.4
5	1.2	5.5	0.89	12.76	1.28	93.3

bound copper. Reported data supports three to seven consecutive sorptions–desorption cycles for regeneration studies for different biosorbents [8,12,19]. Five sorption and desorption cycles breakthrough curves for copper biosorption with pretreated *A. niger* biomass are presented in Fig. 4. As shown in the figure decreased breakthrough and exhaustion times are observed on progressive reuse of the biomass. The uptake based on the initial biomass weight is found to be marginally decreased. The breakthrough time t_b, exhaustion time t_e, column capacity q and mass transfer data are presented in Table 5. It indicates that decreased breakthrough time has no impact on the biosorption capacity as it remains reasonably constant over five cycles of operations.

Fig. 5 shows the elution curve for five consecutive desorption cycle. The flow rate of the elution varied between 1.2 and 1.6 ml/min as indicated. In all cycles the elution curves shows a similar trend. Table 6 summarizes the time of elution, elution efficiency column peak time and the peak concentration and the maximum concentration factor CF for the elution curve. It indicates that the desorption efficiency is flow rate independent. Furthermore, the maximum concentration and the corresponding concentration factor is consistent over five cycles of operations irrespective of desorption performance and flow rate.

4. Conclusions

We have demonstrated effective removal of copper from wastewater by a column of pretreated *A. niger* biomass. The sorbed Cu(II) can be effectively eluted with hydrochloric acid. After acid elution the biomass can be regenerated and reused effectively. Thomas and BDST models have been used successfully for the evaluation of the column performance. At the same initial metal ion concentration, a packed column reactor shows a higher uptake of Cu(II) in comparison to a batch reactor.

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