Packed bed column studies on recovery of Cerium(III) from electronic wastewater using biosorbents of animal and plant origin

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The recovery of Cerium(III) has been investigated in packed bed column using biowaste materials of animal (prawn carapace) and plant origin (corn style). Experiments have been conducted to study the effect of important parameters such as bed depth (4-12 cm) and flow rate (1-5 mL/min) and initial Ce(III) concentration (50-500 mg/L). Recovery of Ce(III) is found to be higher in case of prawn carapace (PC) as compared to corn style (CS) at initial metal concentration values of 400 mg/L (92.1%) and 350 mg/L (81.5%) respectively. The bed depth service time (BDST) model and Thomas model are used to analyze the column data in terms of Ce(III) uptake rate and column capacities. BDST model exhibit a good fit for both PC and CS and the adsorption capacity (N₀) estimated from this model is 282.0 mg/L for PC and 246.7 mg/L for CS respectively. The effect of co-ions on adsorption of Ce(III) is analyzed in binary and ternary systems using extended Langmuir and SRS equations. Regeneration studies suggest maximum reusability of biosorbents upto six cycles. Based on the Ce(III) uptake efficiency, PC and CS has been employed for the recovery of Ce(III) ions from electroplating wastewater. A maximum recovery of 80.1% Ce(III) is successfully achieved.

Keywords: Biosorbent, BDST model, Cerium (III), Packed bed column, Recovery, Thomas model

Cerium (III), as the most plentiful element in the family of rare earth metals (REMs) or lanthanide elements find several applications in areas such as chemical engineering, luminescence, agriculture, catalysis, nuclear energy, metallurgy microelectronics, which are quite different from other lanthanide elements. Ce(III) is accompanied by other rare earth elements in its minerals, as well as in spent nuclear fuel¹. High purity is usually required for its utilization in industry where it is used, for example, for sulfur control in steels, ceramic, catalyst support, pyrophoric alloys, publishing powders, etc². The toxicity of Ce(III) is considered to be in low or moderate range³. Due to the technological importance of Ce(III), separation, sorption and recovery of Ce(III) from industrial waste streams has become important both environmentally and economically.

In general, the methods which have been proposed for the recovery of REMs includes co-precipitation, solvent extraction, ion-exchange, solid-phase extraction, etc.⁴⁻⁷. However, these common methods have been found to be quite expensive and ineffective due to high consumption of reagent and energy, low selectivity, high operational cost and generation of secondary metabolites⁸. Alternatively, biosorption has been introduced as a low cost alternative technology for the recovery of REMs⁹. There are reports on Ce(III) biosorption using leaf powder¹⁰, crab shell¹¹, bacterial biomass¹² and *Citrus reticulate*² etc. from aqueous solution in batch system.

Most of the research using biosorbents for metal ion removal is based on batch kinetic and batch equilibrium studies. The sorption capacity of biosorbent, obtained from batch equilibrium experiments is useful in providing fundamental information about the effectiveness of metal biosorbent systems. However, the data of batch studies may not be applicable to most treatment system (such as continuous operations) where contact time is not sufficient for the attainment of the equilibrium¹³. In the practical operation of full scale biosorption processes, column experiments are preferred for continuous wastewater treatment, as it makes the best use of the concentration difference known to be a driving force for heavy metal biosorption and allows more efficient utilization of biosorbent capacity and results in a better quality of the effluent¹⁴⁻¹⁶. Hence, there is a need to perform biosorption studies in column mode.

From the perspectives of process modeling, the dynamic behaviour of a fixed bed column is described in terms of breakthrough curve¹⁷. A plot of effluent solute concentration versus time is referred as breakthrough

curve which is an S-shaped curve. Breakthrough is the point on the S-shaped curve at which the eluent solute concentration increases beyond the allowable value. The point where the eluent solute concentration reaches 95% of the influent concentration is usually called the point of column exhaustion¹⁸.

The shape of breakthrough curves depends on the nature of wastewater being treated. If there is only adsorbable component in wastewater, the adsorption will be short and the breakthrough curve will be steep. If there is a mixture of components having different adsorption capabilities, the sorption zone will be deep and the breakthrough will be flatter. Residence time is the major design parameter for the adsorption systems. The optimum residence time determines the size of the adsorbing column and amount of adsorbent.

The aim of the present work was to study the potential of biowaste materials viz. prawn carapace and corn style as biosorbents for the recovery of cerium (III) ions from electronic wastewater in column mode. This is the first attempt for the recovery of Ce(III) in a continuous mode using biowaste materials.

Experimental Section

Preparation of biosorbents

Biosorbents of animal origin, prawn carapace (PC) and plant origin, corn style (CS) were procured from a local fish market and vegetable shop at Vellore, Tamil Nadu, India, washed thoroughly with deionised water and dried in an oven at 60°C for 24 h. The dried biosorbents were pulverized in a grinder and sieved to obtain particles in the size range of 425-600 µm.

Preparation of Ce(III) solutions

Stock solution of Ce(III) was prepared by dissolving required quantity of CeCl₃.7H₂O in deionised water. This solution was further diluted to prepare different working concentrations. The *p*H of the solution was adjusted with 0.1 N HNO₃ and 0.1 N NaOH solutions.

Packed bed column experiments

Column studies were conducted in glass column with an internal diameter of 3 cm and 15 cm in length packed with prawn carapace and corn style separately. Initially Ce(III) concentration of 300 mg/L for prawn carapace and 250 mg/L for corn style was used in column experiments. Ce(III) solution was pumped through the column in a downflow mode at a desired flow rate by a peristaltic pump (RivotekTM). To study the recovery of Ce(III) in a continuous mode, experiments were conducted at various bed heights (4-12 cm), flow rates (1-5 mL/min) and initial Ce(III)

concentrations (50-500 mg/L). The biosorbent dosages were increased for different bed heights. Samples were collected at the exit at different time intervals and analyzed for Ce(III) concentration. The columns were run till exhaustion of the biosorbent capacity.

The total amount of metal ions sent to the column can be calculated from the following equation:

$$M \text{ total} = \frac{C_0 \cdot F \cdot t_e}{1000} \qquad \dots (1)$$

where $C_{\rm o}$ is the inlet $C_{\rm e}$ (III) concentration (mg/L), F is the volumetric flow rate (mL/h) and $t_{\rm e}$ is the exhaustion time (h).

The metal recovery (%) with respect to flow volume was calculated from the ratio of metal mass adsorbed (M_{ad}) to the total amount of metal ions sent to the column (M_{total}) as follows:

Total metal removal (%) =
$$\frac{M_{ad}}{M_{total}} \times 100$$
 ... (2)

All continuous experiments were performed in duplicates. The data were the mean values of the two replicate experiments.

Effect of co-ions

The biosorption of Ce(III) was studied in the presence of co-ions viz., Cu(II), Fe(II) and Zn(II) in a 2-metal system (binary) and 3-metal system (ternary). The uptake values of Ce(III) were calculated and the experiments were repeated in duplicates in case of both animal and plant sources. Among the various interactions, the most favorable ones were chosen so that the Ce(III) uptake was affected to the highest extent. The interaction factors were calculated using extended Langmuir and Sheindorf-Rebhun-Sheintuch (SRS) equations and tabulated. The selectivity factor was calculated following the standard Equations¹¹.

Modeling of column data

To analyze the dynamic biosorption of Ce(III) in column mode, breakthrough curves (C_t/C_0 vs. time) were plotted and the data were evaluated with the help of models viz. BDST model¹⁹ and Thomas model²⁰ following the Equations :

BDST model :
$$t = \frac{N_0 Z}{C_0} + \frac{1}{K_a C_0} \ln \left(\frac{C_0}{C_b} - 1 \right) \qquad \dots (3)$$

where N_0 is the column capacity (mg/L), K_a is the rate constant (min⁻¹), Z is the bed height (cm), C_0 (mg/L)

and C_b (mg/L) are the initial and breakthrough Ce(III) concentrations respectively.

Thomas model :

$$\frac{C}{C_o} = 1 + \exp\left(\frac{kTH}{F}(Q_0M - C_0V_{eff})\right) \qquad \dots (4)$$

where C (mg/L) and C_o (mg/L) are the final and initial concentrations, kTH (L/mg/min) is the Thomas rate constant, F is the flow rate (mL/min), V_{eff} is the volume of effluent treated (mL), Q_o is the maximum biosorption capacity (mg/g), M is the mass of the biosorbent (g).

Column desorption and regeneration studies

Column desorption studies were conducted using prawn carapace and corn style which were saturated with Ce(III). After the column reached exhaustion, the Ce(III) loaded biosorbents were regenerated using 0.1M HCl. The flow rate was adjusted to 1 mL/min. After elution, deionized water was used to wash the bed until the pH in the wash water stabilized near to 7.0. Sorption studies were carried out by filling the column again with Ce(III). After the biosorbent exhausted in the column, regeneration studies were done by feeding the elutant into the column. The experiments were performed in eight cycles desorption coupled with adsorption. The surface morphology of PC was analyzed after 1st, 4th and 7th cycle using a Scanning electron microscope (Hitachi-S-3400) at a magnification of 20µm.

Analysis of electronic wastewater in column mode

The electronic wastewater was collected from an electroplating industry located in Chennai, India. The physico-chemical characteristics of effluent sample were analyzed promptly after collection using standard analytical methods²¹. The studies were conducted in the column packed with the prawn carapace (PC) which showed a higher sorption capacity of Ce(III) as compared to corn style (CS). Before performing recovery experiments, the *p*H of the wastewater was adjusted to 6.0. The concentration of Ce(III) after adsorption was analyzed using UV Spectrophotometer at a wavelength of 252.4 nm. The treated samples collected from the exit were analyzed for Ce(III) concentrations.

Results and Discussion

Packed bed column studies

Effect of bed height

In order to study the effect of bed height on the breakthrough time, Ce(III) solution (concentration

300 mg/L for PC and 250 mg/L for CS, pH 6.0) was passed through the adsorption column at a flow rate 1 mL/ min by varying the bed height. Figure 1 represents the breakthrough curves at varying bed heights at a constant flow rate of 1mL/min. Various column parameters such as breakthrough time $(t_{\rm h})$, exhaustion time (t_e) and recovery percentage were determined (Table 1). Based on the results obtained, a linear relation was noted between the recovery (%) and the bed height owing to the availability of more number of functional groups for efficient biosorption. Maximum Ce(III) recovery was characterized by a longer breakthrough period and a delayed exhaustion time. Among the two biosorbents, PC was found to be more efficient owing to its higher biosorption potential (breakthrough time: 140 min) as compared to CS (breakthrough time: 120 min) for the recovery of Ce(III).



Fig. 1 — Breakthrough curves for Ce(III) biosorption onto (a) PC and (b) CS at various bed heights (Flow rate- 1 mL/min; Initial metal concentration- 300 mg/L for PC (a) and 250 mg/L for CS (b)

	Table 1 — C	olumn data and param	eters obtained at differe	nt bed heights	
Bed height	t _b (mins)	t _e (mins)	$M_{ad}(mg/L)$	$M_{total}(mg/L)$	Recovery%
		Animal s	source (PC)		
4	100	190	42.87	57.0	75.22
8	120	210	51.55	63.0	81.83
12	140	280	66.59	75.0	88.79
		Plant so	ource(CS)		
4	70	140	25.43	35.0	72.67
8	100	180	33.74	45.0	74.98
12	120	210	40.11	52.5	76.41
	Table 2 — C	Column data and paran	neters obtained at differ	ent flow rates	
Flow rate	t _b (mins)	t _e (mins)	$M_{ad}(mg/L)$	$M_{total}(mg/L)$	Recovery%
		Animal	source(PC)		
1	100	190	42.8	57.0	88.7
3	50	110	60.8	99.0	61.4
5	30	90	69.6	135.0	51.6
		Plant so	ource(CS)		
1	70	140	25.4	35.0	72.6
3	50	110	18.7	27.5	68.9
5	30	80	12.6	20.0	63.2

Effect of flow rate

Flow rate is one of the important factor for evaluating the sorbents for continuous treatment of metal containing wastewater on an industrial scale²². The effect of flow rate on the recovery of Ce(III) was studied varying the flow rate from 1 to 5 mL/min at a constant bed height (4 cm) and initial Ce(III) concentrations (300 mg/L for PC and 250 mg/L for CS respectively) as shown in Fig. 2. The results could be possibly attributed to the inverse relation between residence time and flow rate. This could be explained by the fact that at lower flow rate, Ce(III) ions could effectively interact with the functional groups for a higher time duration²³. In other words if the residence time of the solute in the column is not large enough for the adsorption equilibrium to be reached at the given flow rate, the Ce(III) solution leaves the column before the equilibrium occurs. It was observed that the adsorbent got saturated easily at higher flow rates. A sharp decrease in Ce(III) recovery was noted in case of both plant and animal sources. As shown in Table 2, maximum recovery was noted at a flow rate of 1 mL/min (PC: 88.7%; CS: 72.6%).

Effect of initial metal concentration

Initial metal concentration is also an important parameter for determining the biosorption efficiency in a column mode since wastewaters from various sources have a wide range of Ce(III) ion concentration. The effect of initial Ce(III) concentration was studied at various concentrations ranging from 100-500 mg/L for



Fig. 2 — Breakthrough curves for Ce(III) biosorption onto (a) PC and (b) CS at different flow rate (Bed height- 12 cm, initial metal concentration- 300 mg/L for PC (a) and 250 mg/L for CS (b)

PC and 50-450 mg/L for CS respectively at a fixed bed height 12 cm and flow rate- 1 mL/min. The breakthrough curves for Ce(III) biosorption onto PC and CS at different initial metal concentrations. A were plotted As shown in Table 3, an increase in adsorption (M_{ad}) was noted with an increase in Ce(III) due to an increased availability of Ce(III) ions which resulted in an enhanced recovery. Maximum recovery of 92.1% at 400 mg/L for PC and 81.5% at 350 mg/L for CS was noted (Table 3).

Modeling of column data

BDST model

One of the most applied models for adsorption of metals in column mode is the bed depth Service time (BDST) model. The model parameters were calculated from the slope and intercept of BDST plot which characterizes the rate of solute transfer to the solid phase from the fluid phase²⁴. Table 4 shows the values for various parameters of BDST model. The model was found to exhibit a good fit based on the correlation coefficient values (Fig. 3). An increase in

the column capacity and the rate of adsorption was noted with an increase in Ce(III) concentration. Moreover, the column capacity was found to be higher in case PC (264.3 mg/L) as compared to that of CS (158.6 mg/L). A decrease in rate was noted with an increase in Ce(III) concentration due to the decrease in randomness at the sorbent-sorbate interface. Although the biosorption of Ce(III) onto PC was characterized by a high sorption capacity, the rate of biosorption was found to be lower as compared to CS. The inverse relation between rate and sorption capacity indicated that the biosorption process preferred a decrease in randomness at the sorbatesorbent interactions. However, the magnitude of the K_a values was found to be quite small in the present case which indicated that a longer bed depth was needed to overcome breakthrough 25 .

Thomas model

Thomas model is one of the most widely used model for describing the column breakthrough data in sorption studies. Table 5 shows the values for various

Table 3 — Column data and parameters obtained at different Ce(III) concentration						
Initial Ce(III)	t _b (mins)	t _e (mins)	$M_{ad}(mg/L)$	$M_{total}(mg/L)$	Recovery%	
Animal source (PC)						
100	160	300	21.1	30.0	70.6	
200	150	290	41.9	58.0	72.3	
300	140	280	66.5	75.0	88.7	
400	90	190	66.3	72.0	92.1	
500	70	160	69.4	85.0	81.7	
Plant source (CS)						
50	170	250	8.85	12.5	70.8	
150	150	220	24.3	33.0	73.6	
250	120	210	40.1	52.5	76.4	
350	100	160	45.6	56.0	81.5	
450	40	110	31.2	49.5	63.2	
		Table 4 — BDS	ST parameters			
C _o (mg/L)	N _o (mg/L)	K _a (L/mg/min)	Slope	Intercept	\mathbf{R}^2	
		Animal so	urce (PC)			
100	70.5	$1.06*10^{-4}$	5.00	100.0	1.000	
200	141.0	3.78*10 ⁻⁵	5.00	90.0	1.000	
300	211.5	5.73*10 ⁻⁵	5.00	80.0	1.000	
400	282.0	8.41*10 ⁻⁵	5.00	30.0	1.000	
500	264.3	7.59*10 ⁻⁵	3.75	26.6	0.964	
Plant source (CS)						
50	26.4	1.85*10-4	3.75	123.3	0.964	
150	79.3	$1.18*10^{-4}$	3.75	103.3	0.964	
250	220.3	1.14*10 ⁻³	6.25	46.6	0.986	
350	246.7	$1.00*10^{-3}$	5.00	40.0	1.000	
450	158.6	1.56*10 ⁻³	2.50	10.0	1.000	



Fig. 3 - Bed depth service time model (BDST) for (a) PC and (b) CS

Table 5 — Thomas parameters					
C _o (mg/L)	V _{eff} (ml)	$K_{Th}(min^{-1})$	Q _o (mg/g)		
Animal source (PC)					
100 ppm	160	1.6*10 ⁻⁴	213.03		
200 ppm	150	8.0*10 ⁻⁵	426.10		
300 ppm	140	$5.3*10^{-5}$	643.17		
400 ppm	90	$4.0*10^{-5}$	852.21		
Plant source (CS)					
50 ppm	170	5.4*10-4	119.72		
150 ppm	150	$1.8*10^{-4}$	359.17		
250 ppm	120	$1.1*10^{-4}$	598.61		
350 ppm	100	$7.7*10^{-5}$	839.61		

parameters of Thomas model. The Thomas model parameters were calculated from linearized plot of ln (C_o/C_t) -1) versus volume of effluent treated (V_{eff}) (Fig. 4). The rate constant (K_{Th}) which characterizes the rate of solute transfer from the liquid to solid phase was found to increase with increase in concentration. The rate of Ce(III) uptake was found to



Fig. 4 — Thomas model for (a) (PC) and (b) (CS)

be higher in case of plant source (CS) as compared to animal source (PC) which suggested an increased randomness at the sorbate-sorbent interface in former case (CS). Moreover, the uptake values were found to be higher in case PC owing to the decreased randomness at the sorbate-sorbent interface²⁶. These results were found to lie in accordance with thode inferred from BDST model. The maximum uptake values were noted to be 852.2 mg/g and 839.6 mg/g for PC and CS respectively. However, the model was found to exhibit a poor fit owing to the low correlation coefficient values.

Effects of Co-ions

Among the three co-ions viz., Cd(II), La(III) and Pb(II), Cd was found to have a predominant effect on Ce(III) biosorption thereby reducing its uptake level to a considerable extent (100.2 mg/g; 98.7 mg/g) followed by Pb (156.2 mg/g; 118.3 mg/g) and La (180.4 mg/g; 149.4 mg/g). In order to study the metal - metal interactions with the sorbent, an interaction factor (η) was specifically noted for binary and ternary systems. As shown in Table 6, based on the extended Langmuir equation, the interaction factor (η_2) was found to be the maximum in case of both PC (3.2) and CS (1.9) which validated the effect of Cd(II) on Ce(III) biosorption.

In order to improve the fitness, SRS model was employed to describe the binary and ternary data. The model comprised of a competitive coefficient (θ) which assumes an exponential distribution of adsorption energies available for each metal ion. The model was found to be a good fit in case of both PC and CS (ternary system) owing to high R² values and low APE values. The competitive coefficient values



detailed analysis of the effluent was performed and

Fig. 5 — Effect of co-ions on Ce(III) biosorption in binary and ternary system onto (a) PC and (b) CS



Fig. 6 — Regeneration cycles for Ce(III) biosorption onto (a) PC and (b) CS from wastewater (Bed height- 12 cm; flow rate-1 mL/min; metal concentration - 400 ppm for PC and 350 ppm for CS)

Table 8 — Analysis of electronic wastewater					
Parameters	Before cerium(III) adsorption (mg/L)	After cerium(III) adsorption (mg/L)			
		(PC)	(CS)		
pН	6.8	6.1	6.4		
Dissolved Oxygen	7.1 ± 0.02	5.3±0.01	$6.0{\pm}0.04$		
Chemical Oxygen Demand	3200.7±0.04	51.4±0.02	57.2±0.01		
Biological Oxygen Demand	$615.2{\pm}0.08$	29.1±0.09	35.7±0.01		
Total Dissolved Solids	1683.8 ± 0.21	146.2 ± 0.07	153.9±0.03		
Total Suspended Solids	116.4±0.09	29.6±0.04	32.8±0.01		
Zinc	83.7±0.01	5.6±0.03	6.1 ± 0.08		
Lead	98.1±0.03	$8.1{\pm}0.11$	8.7±0.05		
Cerium	390.2±0.04	7.3±0.10	10.1 ± 0.04		
Cadmium	101.1 ± 0.06	15.79±0.06	21.1±0.01		
Lanthanum	190.7±0.30	22.5±0.09	28.7 ± 0.02		

the results were tabulated. Table 7 shows that the maximum recovery of Ce(III) was 80.1% in case of PC and 76.7% for CS. In case of PC, the recovery of cerium was found to be 69.1% at the end of 7th cycle after which a drastic decrease in metal uptake capacity was noted because of the surface damages caused by the continuous process of metal uptake. The surface topologies of PC were observed at the end of 1^{st} , 4^{th} and 7^{th} cycles respectively. As shown in Fig. 7, a distortion in the cell was observed with the increase in number of cycles. The damage in the cell surface resulted in merging of cells which further caused an increase in overall smoothness of the surface.

Figure 8 represents the schematic presentation of the whole biosorption process in column mode.

Analysis of electronic wastewater

Electronic wastewater was analysed in packed bed column under optimum conditions (flow rate: 1 mL/min, bed height: 12 cm). Table 8 shows the



Fig. 7 — Scanning electron microscopy images of PC (a) 1^{st} cycle (b) 4^{th} cycle (c) 7^{th} cycle



Fig. 8 - Schematic representation of Ce(III) biosorption in column mode using PC and CS

adsorption of Ce(III) by PC and CS which justified the biosorption potential of prawn carapace (Table 8). Apart from Ce(III) recovery, an overall decrease in COD, BOD, TDS, TSS and other heavy metals was also noted.

Conclusion

Column studies on adsorption of Ce(III) have been conducted using biosobents of animal source (prawn carapace) and plant source (corn style). The experiments were performed at various bed depths (4-12 cm), flow rates (1-5mL/min) and initial Ce(III) concentration (50-500 mg/L). The column data has been analyzed using BDST and Thomas models. Results showed a higher column capacity in case of PC as compared to CS. An inverse relation is noted between the uptake and the rate of uptake owing to the decrease in randomness at the sorbate-sorbent

interface. The effect of co-ions (Cd(II), La(III) and Pb(II)) on the Ce(III) uptake was studied in binary and ternary systems. Among the three metals, Cd(II) is found to show the most predominant effect on Ce(III) biosorption followed by Pb(II) and La(III). The data was analyzed using extended Langmuir and SRS equations. In case of binary systems, the extended Langmuir model is found to exhibit a good fit in case of both PC and CS. In the case of ternary systems, the SRS equation is found to be more appropriate in case of PC as compared to CS. In order to regenerate the adsorbent, an elution step is carried out with 0.1 M HCl and seven adsorption-desorption cycles are carried out in a continuous manner. Results suggested that both PC and CS could effectively retain the biosorption potential upto six cycles. SEM analysis suggest a cell wall distortion with an increase in number of cycles. Application oriented studies for the recovery of Ce(III) are carried out in column mode. The results suggest that PC could easily recover upto 80.1% of the Ce(III) from electroplating wastewater. Based on the results of the column studies conducted with electronic wastewater, it may be concluded that PC can serve as potential biosorbent for the recovery of cerium from wastewater.

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