Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Der Pharmacia Lettre, 2015, 7 (6):166-179
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-5071
USA CODEN: DPLEB4

Recovery of cerium (III) from electronic industry effluent using novel biohydrogel: Batch and column studies

Jaya Sre Varshini C., Devlina Das and Nilanjana Das*

Environmental Biotechnology Division, School of Bio Sciences and Technology, VIT University, Vellore, India

---

ABSTRACT

The present investigation attempts to recover the cerium(III) ions from aqueous environment using a novel biohydrogel modified by sporopollenin (SP) and xylan (XY). Optimization of various parameters viz., pH (2.0-10.0), contact time (20-160 min), biohydrogel dosage (1.0-5.0 g/L) and initial Ce(III) concentration (50-450 mg/L) was done. Maximum Ce(III) uptake was noted to be 278.2 mg/g in case of SP- biohydrogel and 180.4 mg/g in case of XY- biohydrogel under optimized conditions. The process was found to follow homogeneous chemical mode of adsorption in case of SP- biohydrogel, whereas heterogeneity and chemical mode of adsorption was noted in case of XY- biohydrogel. This was further confirmed by SEM analysis. Intra-particle diffusion and Boyd plot suggested two phase diffusion in case of both the biohydrogels. Thermodynamic studies showed that the process was endothermic and spontaneous in nature. FT-IR analysis showed the involvement of functional groups viz., aldehydes, esters and hydroxyl groups in case of SP- biohydrogel and amides, alkenes and xylan spectrum for XY- biohydrogel during Ce(III) biosorption. The effects of co- ions in binary and ternary system was studied during Ce(III) biosorption. Maximum adsorption efficiency and recovery of Ce(III) from electronic industrial effluent using SP- biohydrogel were noted as 88.4% and 86.8% which were obtained in column mode at a flow rate of 1 ml/min, bed height of 12 cm and 0% dilution. Regeneration studies suggested that SP- biohydrogel could be reused upto 5 cycles and could serve as a cost effective alternative for the recovery of cerium from waste water.

Key words: Biohydrogel, cerium (III), corn style, sporopollenin, xylan

---

INTRODUCTION

Global demand for rare earth metals (REMs) is increasing dramatically in recent years and prices of rare earth metals are also increasing rapidly [1]. The increasing prices of REMs and the increased worldwide demand for REMs have necessitated the need to search for the recovery technology with sufficient economic potential. Among the REMs, Cerium is the most abundant and reactive element which has drawn special attention. Cerium has many potential uses in different areas such as chemical engineering, luminescence, agriculture, catalysis, nuclear energy, therapeutic applications and magnetism [2, 3]. Radioisotopes of cerium (III) are marked products of nuclear fission and common constituent of liquid radioactive wastes arising from nuclear power productions [4].

Conventional technologies viz. precipitation, filtration, liquid-liquid extraction, solid-liquid extraction, ion exchange, super critical extraction, electrowinning, electrorefining, electro slag refining etc. which have been developed for the recovery of REMs are not attractive due to the problems involving cost and energy consumption. In recent years, research attention has been focused on biosorption which is a proven technology and the research over the past few years provided a better understanding of the recovery of rare earth metals through biosorption using certain potential biosorbents [5]. The group of cheap biomaterials constitutes the basis for a new cost effective technology that can find its application in the recovery of REMs. In spite of published research works on biosorption of cerium (III) [3], no report is available on the recovery of cerium using biomaterials in an industrial context under real wastewater conditions.

Hydrogels have received increasing attention now a days due to their significance in applications in various fields such as personal health products, civil construction, industrial, agricultural production, medical materials, baby diapers, soil for agriculture and horticulture, absorbent pads etc. They are also being used in environmental applications for the removal of undesired heavy metal ions and dyes. The properties of hydrogel depend strongly on the degree of polymer crosslinking, chemical composition of the polymer chains, and interactions of the network. Hydrogels, particularly those based on natural polymers, can absorb and retain large amounts of water, saline solutions or physiological solutions as high as hundreds to thousands of times of their own weight due to considerable hydrophilic groups with three-dimensional network structures [6]. The hydrophilicity of hydrogels can be enhanced by the presence of hydrophilic groups, such as hydroxide radical, carboxyl, and amide [7, 8]. The main advantages of hydrogel-based adsorbents are easy loading, capturing of cations with simple chemicals in most cases, reusability and the possibility of semi-continuous operation [9].

The aim of the present work was to develop a novel biohydrogel and examine its adsorption potentiality for the recovery of cerium from industrial effluent. Biohydrogel was prepared using corn style, a biowaste material along with chitosan and cross linking agent gluteraldehyde. Corn style (CS) has already been reported as potent adsorbent for Ce(III) biosorption in our previous study [3]. Sporopollenin, a complex biopolymer, occurs naturally as a component of spore / pollen walls of land plants [10] and having a good physical strength and chemical stability [11]. The ability of sporopollenin to serve as adsorbent has been reported in case of heavy metals [12, 13, 14]. Xylan is the main hemicelluloses component of secondary cell walls constituting about 20-30 % of the biomass of hardwoods and herbaceous plants. Over the past few years, efforts have been given to obtain adsorbent and hydrogels from xylan rich hemicelluloses due to its lower cost and easy availability. Recently, the high sorption capacity of chitosan- xylan hybrid on heavy metals has been reported [15].

To improve the performance of biohydrogel and increase the surface area for cerium adsorption, biohydrogel was modified by sporopollenin (SP) and xylan (XY) in the present study. The sorption kinetics and biosorption equilibrium employing different isotherm models and thermodynamic parameters in batch mode was studied along with recovery of cerium from wastewater in column mode. This is the first report on the application of biohydrogel modified by sporopollenin and xylan for the effective recovery of Ce(III) from wastewater.

MATERIALS AND METHODS

Chemicals and reagents

All the chemicals including chitosan, Cerium chloride, glacial acetic acid, gluteraldehyde, sporopollenin (SP) and xylan (XY) were of analytical grade and purchased from Sigma Aldrich, India.

Metal solution preparation

Cerium stock solution (1000 mg/L) was prepared separately from $CeCl_3$. $7H_2O$ in deionized water. The working solutions were prepared by diluting the stock solutions to appropriate volumes.

Preparation and characterization of biohydrogel

For preparation of biohydrogel, Corn style (CS), biowaste materials of plant origin was collected, washed thoroughly with deionised water and dried in an oven at 60°C for 24 h. The dried samples were pulverized in a grinder and sieved to obtain particles in the size range of 425-600 µm. An amount of 0.04 g CS was dispensed in 50 ml of 2% (v/v) glacial acetic acid and stirred for 1 h at room temperature. The suspension was divided into two parts A and B. Sporopollenin (6.0 g) was added in solution A and xylan (6.0 g) was added in solution B. Chitosan (1.5 g) was added to the above solutions and stirred for 8 h. To the slurry, 1 ml of gluteraldehyde was added to obtain a thick gel with a smooth consistency. The gel was refrigerated at 4°C and thawed at 60°C. The process of refrigerating and thawing was continued for three to four times. Finally, the hydrogel was dried, powdered and stored for future use.

The BET surface area of biohydrogel was calculated following the standard procedure [16]. Thermogravimetric analysis of biohydrogel was carried out under high purity helium supplied at a purge gas flow rate of 0-1000 ml/min (Diamond TG/DTA, Perkin Elmer, USA). All samples were subjected to a 10°C/min heating rate and characterized between 25°C -800°C.

The swelling ratios of SP- biohydrogel and XY-biohydrogel were calculated by immersing the biohydrogels in de-ionized water for 1 hour and comparing the wet weight to the dry weight following the equation:

Swelling ratio = $\dfrac{W_W - W_d}{W_d} \times 100$ (1)

where W_w is the wet weight (g) of the biohydrogel ,W_d is the dry weight (g) of the biohydrogel

Batch biosorption studies

The experiments were conducted in 250 ml Erlenmeyer flasks at 28±1°C on a rotary shaker at 120 rpm varying pH ranging from 2.0 to 10.0, initial cerium concentration ranging from 50 mg/L to 450 mg/L and biohydrogel dosage 1.0 to 5.0 g/L, contact time 20 to 160 min. The samples were filtered using Whatman No. 1 filter paper after 2 h of mixing. The concentration of Cerium present in the filtrate was estimated using UV spectrophotometer at 252.4 nm. The cerium uptake capacities were calculated using the mass balance equation as shown below:

$$q = \frac{C_0 - C_f}{M} \times V \tag{2}$$

Where q is the sorption capacity i.e. the amount of Ce(III) adsorbed onto a unit amount of biomass (mg /g); C_0 and C_f are the concentrations (mg/ L) of Cerium in the initial solution and after adsorption respectively; V is the volume of the aqueous phase (L); and M is the amount of the biomass (g/L).

Equilibrium and Kinetic studies

The equilibrium data were analyzed using two parameter isotherms- Langmuir, Freundlich and Dubinin-Radushkevich (D-R). Kinetic experiments were conducted under optimized conditions and samples were withdrawn at regular intervals for analysis. The pH of the solution was monitored using 0.1 N HCl or 0.1 N NaOH solutions. Pseudo-first order, pseudo-second order and intra-particle diffusion model have been used for modeling the kinetic data for adsorption of Ce(III) on biohydrogels.

Thermodynamic parameters

The Gibbs free energy, enthalpy and entropy (ΔG, ΔH, ΔS) for the adsorption process were obtained from the experiments carried out at different temperatures using the following equations:

$$\log \frac{q_e}{C_e} = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \tag{3}$$

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

where q_e/C_e is called the adsorption affinity, which is the ratio of amount of cerium adsorbed per unit mass to the solute concentration in unit volume of the solution at equilibrium. The values of ΔH and ΔS were determined from the slope and the intercept of the linear plot of log (q_e/C_e) vs 1/T. These values were used to calculate ΔG which is the fundamental criterion of spontaneity. Reaction occurs spontaneously at given temperature if the value of ΔG is negative.

Instrumental analysis

The surface morphology of the biohydrogels before and after cerium adsorption was analyzed using scanning electron microscopy (SEM) (Stereo Scan LEO, Model-400). EDX analysis were conducted using Noran System Six model Energy Dispersive X-ray Microanalysis System (Thermo Electron Corporation, Japan) attached to SEM. Accelerating voltage was kept constant at 15 kV, to facilitate the emission of secondary X-rays.

Fourier transformed infrared spectra were recorded on an Avatar 330 model (Thermo Nicolet Co., USA) FT-IR spectrophotometer. For FT-IR studies, 5 mg of biohydrogel before and after adsorption was encapsulated in 400 mg of KBr translucent discs which were obtained by pressing the ground material with the aid of a bench press. Each experiment was repeated at least twice, both producing good results.

Column studies

Industrial effluent was collected from electronic industry located in the outskirts of Chennai, Tamil Nadu, India. The concentration of cerium in the effluent was analyzed using UV-Visible spectrophotometer and pH was adjusted to 6.0. Recovery experiments were conducted in a glass column (15 cm in length) having an internal diameter of 3 cm.

The column was packed with SP- biohydrogel. To study the column efficiency, the experiments were conducted at various bed depths (4, 8 and 12 cm), flow rates (1, 3, 5 ml/min) and at various dilutions (0%, 25% and 50%).

The total quantity of cerium biosorbed in the column (M_{ad}) was calculated from the area above the breakthrough curve (outlet cerium concentration versus time) multiplied by the flow rate. Dividing the metal mass (M_{ad}) by the adsorbent mass (M) leads to the uptake capacity (Q) of the biomass. The total amount of cerium ions sent to the column was calculated from the following equation:

$$M_{total} = \frac{C_o . F \cdot t_e}{1000} \qquad (5)$$

where C_0 is the inlet metal concentration (mg /L), F the volumetric flow rate (mL/h) and t_e is the exhaustion time (h). Total metal recovery (%) 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:

$$Total metal re cov ery(\%) = \frac{M_{ad}}{M_{total}} \times 100 \qquad (6)$$

Modeling of Column data

To analyze the adsorption data of Ce(III) in column mode, breakthrough curves (C_t/C_0 vs. time) were drawn and the data were evaluated with the help of models viz. BDST model [17] and Thomas model [18] following the equations :

BDST model :
$$t = \frac{N_0 Z}{C_0} + \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_b} - 1\right) \qquad (7)$$

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 and C_b are the initial and breakthrough concentrations respectively.

Thomas model :
$$\frac{C}{C_o} = 1 + \exp\left(\frac{kTH}{F}(Q_0 M - C_0 V_{eff})\right) \qquad (8)$$

Where C and C_0 are the final and initial concentrations, k_{TH} is the Thomas rate constant, F is the flow rate (ml/min), V_{eff} is the volume of effluent treated (ml), Q_0 is the maximum biosorption capacity (mg/g), M is the mass of the biohydrogel (g).

Column desorption and recovery

Regeneration experiments were performed using 0.1 M HCl as a desorbing agent for the recovery of Ce(III) ions. After every cycle of adsorption/desorption, the column was washed with de-ionized water till a pH of 7.0 was reached. The experiments were performed till the efficiency of the column showed a drastic decrease.

RESULTS AND DISCUSSION

Characterization of biohydrogel

The biohydrogel was characterized for its adsorption potential. The BET surface area was found to be 0.45 and 0.28 m^2/g in case of SP- biohydrogel and XY- biohydrogel. Thermogravimetric analysis suggested a lower weight loss percentage in case of SP- biohydrogel (34.5%) as compared to XY- biohydrogel (56.9%) which suggested an enhanced crosslinking in case of SP- biohydrogel than XY- biohydrogel.

The swelling ratios were calculated to be 87.0 % and 76.2 % in case of SP- biohydrogel and XY- biohydrogel respectively which accounted the enhanced hydrophilic nature of the SP-biohydrogel owing to more hydrophilicity property. The enhanced hydrophilic nature is an important criterion in pollutant remediation via adsorption [19].

Effect of parameters

It is well known that pH plays an important role in biosorption process. It affects the activity of the functional groups present in the biosorbent that are responsible for metal adsorption and also affects the composition of metallic ions to get adsorbed to the active sites [20]. The effect of pH on biosorption of Ce(III) onto SP- biohydrogel and XY- biohydrogel were noted. Figure 1 (a) showed that maximum Ce(III) uptake occurred at pH 6.0 in case of both forms of biohydrogels . At low pH 2.0, minimum uptake of Ce(III) was noted which may be due to the increased mobility of H^+ ions, and thus the hydrogen ions were adsorbed preferentially rather than the metal ions [21]. At higher pH values, number of H^+ ions is lower and greater number of ligands with negative charges resulted in greater cerium biosorption [22].

The contact time is one of the important parameter for rapid sorption process [23, 24]. The uptake of cerium by the biohydrogels increased with the increase in contact time and reached the equilibrium state at the end of 60 min for SP- biohydrogel and 80 min for XY- biohydrogel as shown in Figure 1 (b). The metal uptake was found to be higher in the initial stage followed by the equilibrium state. This is because the biohydrogels contains a higher number of binding sites for the binding of cerium in the early stage [5, 20, 25]. As the time increased, the binding sites available on the biohydrogel surfaces are filled up and thus the cerium uptake capacity decreased which could be possibly due to the equilibrium established in sorbate-sorbent interactions [26].

Biomass dosage is one of the parameter that affects the sorption capacity [22]. The effects of biomass dosage on cerium uptake using biohydrogels were studied by varying the dosage range from 1.0 to 5.0 g/L. The uptake of Ce(III) increased with an increase in biosorbent dosage due to the availability of more number of binding sites for the Ce(III) ions to the binding sites [20,27]. Maximum sorption was found at 3 g/L for SP- biohydrogel and 4 g/L for XY- biohydrogel shown in Figure 1(c). Further increase in the biohydrogel dosage did not show any improvement in the biosorption capacity due to the binding of almost all the ions to the sorbent and the establishment of equilibrium between the ions bound to the biosorbent and those remaining unsorbed in the solution.

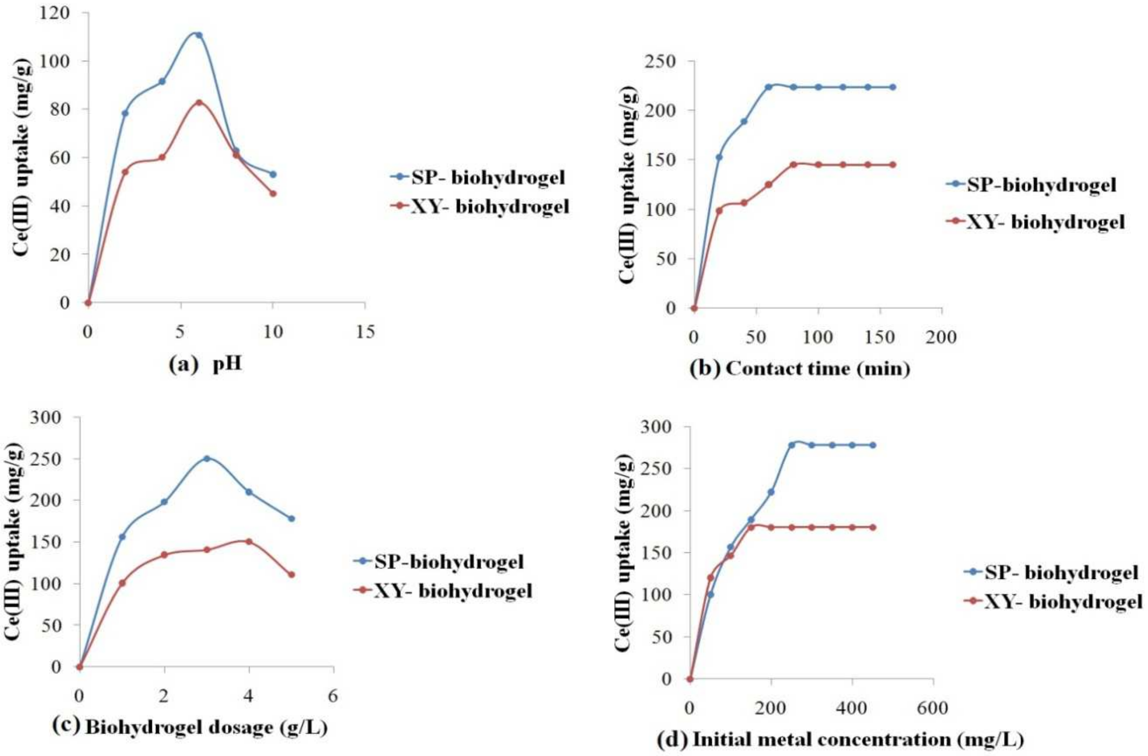

Figure 1: (a) Effect of pH (b) Effect of contact time (c) Effect of biohydrogel dosage (d) Effect of initial metal concentration on cerium (III) biosorption using SP- biohydrogel and XY- biohydrogel

The effect of initial Ce(III) concentration onto SP- biohydrogel and XY- biohydrogel was studied by varying the cerium concentration ranging from 50 mg/L to 450 mg/L. The amount of metal uptake by biohydrogels increased with an increase in cerium ion concentration and remained constant after equilibrium time. Maximum Ce(III) uptake was noted at 280 mg/L by SP- biohydrogel and 150 mg/L for XY- biohydrogel as shown in Figure 1(d). The sorption process was rapid at the earlier stages and gradually decreased with the adsorption process. The initial concentration provides an important driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases, hence a higher initial concentration of metal ion may increase the adsorption capacity [28].

Equilibrium studies

Equilibrium studies were conducted to get a deeper insight on the equilibrium obtained between the metal biosorbed and the residual metal content. Among the various two parameter isotherms, Langmuir isotherm was found to exhibit the best fit for SP- biohydrogel owing to the low error values (11.4%) high R^2 Value (0.991) suggesting homogenous monolayer mode of adsorption (Figure 2(a)). Whereas Freundlich isotherm fitted well for XY- biohydrogel having high correlation coefficient values (0.968) as shown in Table1 which suggested a heterogenous mode of adsorption in the present case (Figure 2(b)). Moreover, D-R isotherm exhibited a poor fit owing to the high error values and low correlation coefficient values for both the biohydrogels.

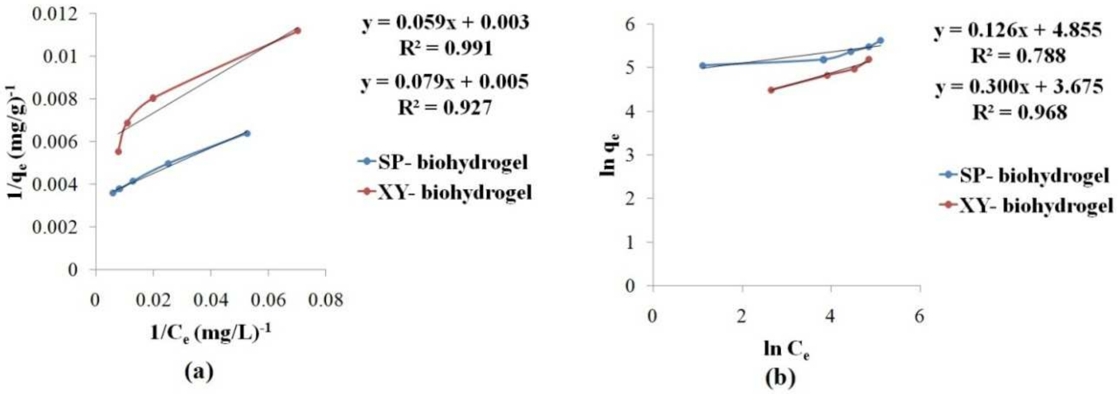

Figure 2: (a) Langmuir isotherm and (b) Freundlich isotherm for the sorption of cerium (III) on SP- biohydrogel and XY- biohydrogel

Table 1 Equilibrium isotherm model and kinetic model parameters for Ce(III) adsorption on SP- biohydrogel and XY- biohydrogel

Isotherm models	Model parameters	SP-biohydrogel	XY-biohydrogel
Langmuir	q_m (mg/g)	333.3	200
	K_L (L/mg)	0.05	0.06
	APE (%)	11.42	26.45
	R^2	0.991	0.927
Freundlich	K_F (mg/g)	128.3	39.4
	n	7.93	3.33
	APE (%)	56.27	7.23
	R^2	0.788	0.968
D-R isotherm	q_m (mg/g)	260.0	176.4
	β	$8*10^{-5}$	$9*10^{-5}$
	E (KJ/mol)	0.079	0.074
	APE (%)	70.48	21.56
	R^2	0.926	0.908
Kinetic models			
Pseudo first order	K_1 (g/mg/min)	0.059	0.029
	q_e (mg/g)	246.0	199.9
	APE (%)	19.43	35.21
	R^2	1.000	0.946
Pseudo second order	K_2 (g/mg/min)	2.3*10-4	1.2*10-4
	q_e (mg/g)	333.3	250.0
	APE (%)	10.68	13.47
	R^2	1.000	0.986
Intra-particle diffusion	v	22.5	17.5
	C	107.6	6.164
	APE (%)	11.54	10.56
	R^2	0.975	0.973

Kinetic studies

Information on the kinetics of pollutant uptake is required for selecting optimum operating conditions for full scale batch process. Table 1 represents the kinetic constants for pseudo-first order, pseudo-second order and intra-particle diffusion. Results suggested that Pseudo second order fractional power exhibited the best fit among all the models owing to the low error values (10.6 % and 13.4%) and high correlation coefficient values (1.0 and 0.986) for SP- biohydrogel and XY- biohydrogel. The suitability of pseudo second order model suggested the involvement of chemical mode of adsorption via valence forces through sharing or exchange of electrons (Figure 3a).

In the present study, both intra-particle diffusion and film diffusion played a significant role. As shown in Figure 3(b) and Figure 3(c), both intra-particle diffusion and Boyd plot showed a good linearity. Moreover, in case of intra-particle diffusion, the adsorption process was found to occur in 2 phases for SP- biohydrogel and XY- biohydrogel both. The Boyd curves were found to be quite linear but they did not pass through the origin which suggested the involvement of both film diffusion and intra-particle diffusion (Figure 3c). Moreover, a higher linearity was noted in case of SP- biohydrogel as compared to XY- biohydrogel owing to the faster interaction of the cerium ions with sporopollenin (SP) which could be due to the involvement of more number of functional groups compared to Xylan (XY).

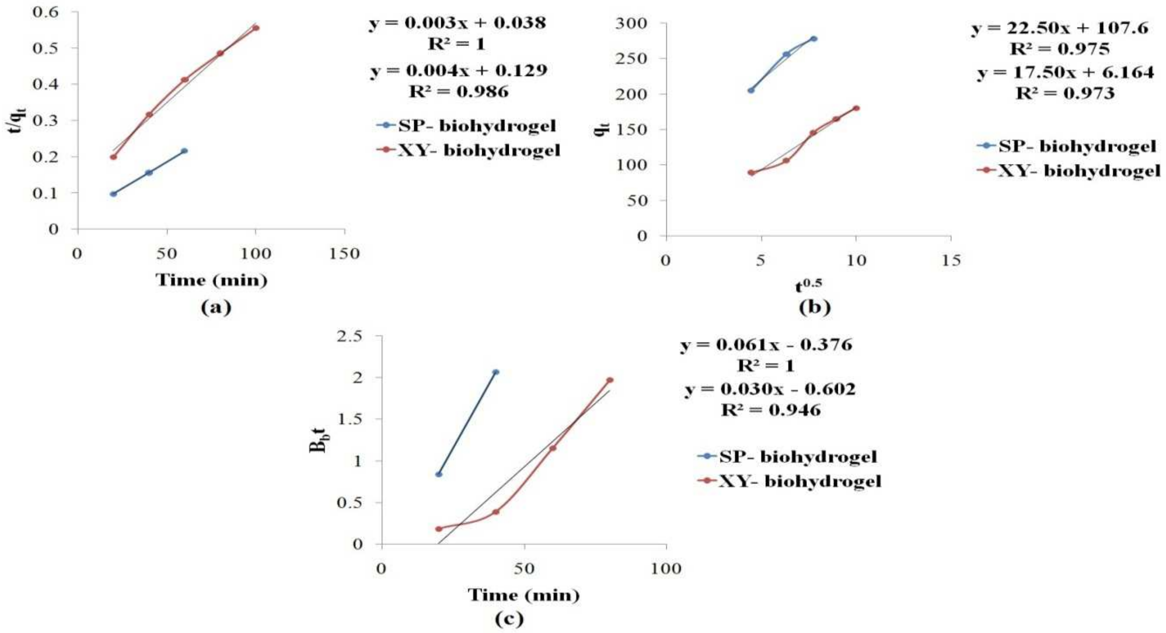

Figure 3: (a) Pseudo- second order kinetic model (b) Intra-particle diffusion model (c) Boyd plot for the sorption of cerium(III) on SP- biohydrogel and XY- biohydrogel

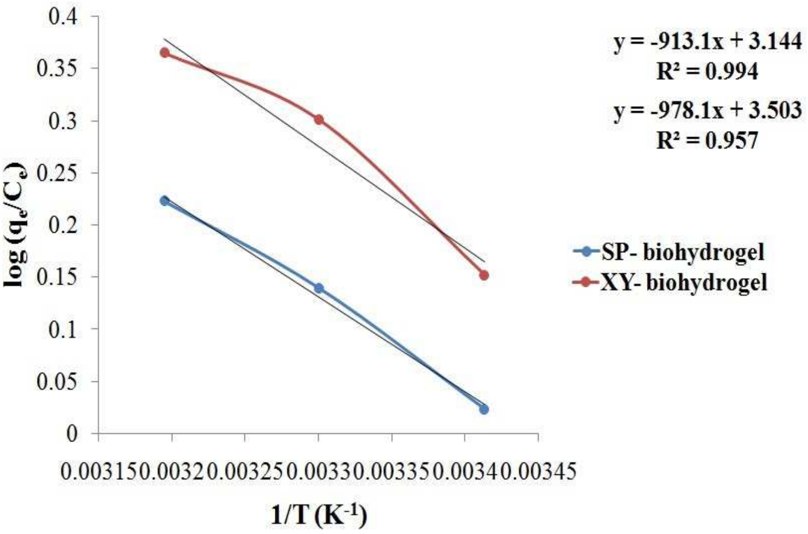

Figure 4: Thermodynamic parameters of SP- biohydrogel and XY-biohydrogel

Thermodynamic studies

As shown in Table 2, the process was found to be spontaneous for SP- biohydrogel and XY- biohydrogel. As indicated by a negative ΔG values and maximum spontaneity was noted at 40 °C for the biohydrogels. The values of ΔH and ΔS were calculated from the slope and intercept of the plot of log (q_e/C_e) vs 1/T as shown in Figure (4). The results indicated that the process was endothermic or heat absorbing in nature as indicated by the positive values of ΔH (17.48 KJ/mol for SP-biohydrogel and 18.72 KJ/mol for XY- biohydrogel. An increase in randomness at the solid/solution interface was suggested by the positive value of ΔS.

Table 2: Thermodynamic parameters

Biosorbents	Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/(mol.K))
SP- biohydrogel	293	-0.1	+17.48	+0.060
	303	-0.7		
	313	-1.3		
XY- biohydrogel	293	-0.931	+18.72	+0.067
	303	-1.581		
	313	-2.251		

Spectroscopic studies

In the present study, the mechanism of biosorption was elucidated using various spectroscopic techniques viz., FT-IR (Figure 5), SEM (Figure 6) and EDX analysis (Figure 7). Infrared spectra can yield valuable information regarding the chemical groups involved in the biosorption process. As shown in Figure (5), major peak stretches at 3346.50 cm^{-1}, 2918.30 cm^{-1}, 1654.26 cm^{-1} and 1000.82 cm^{-1} confirmed the involvement of primary amines, alkenes, amides and xylan spectrum in case of XY- biohydrogel [15]. Moreover, a higher number of functional groups were found to be involved in case SP- biohydrogel. Major stretches were noted at 3400, 3342.64 cm^{-1}, 2924.56 cm^{-1}, 1726.29 cm^{-1}, 1425.40 cm^{-1}, 1327.03 cm^{-1}, 1157.29 cm^{-1}, 1105.21 cm^{-1}, 1029.99 which confirmed the involvement of hydroxyl groups, primary amines, alkanes, aldehydes, alcohols and esters [29]. Higher change in transmittance was noted in case of SP- biohydrogel which suggested a higher involvement of functional groups (C=O stretch in aldehyde, C-OH bend in alcohol, C-Cl stretch) resulted in a higher uptake of Cerium than in XY- biohydrogel in the biosorption process.

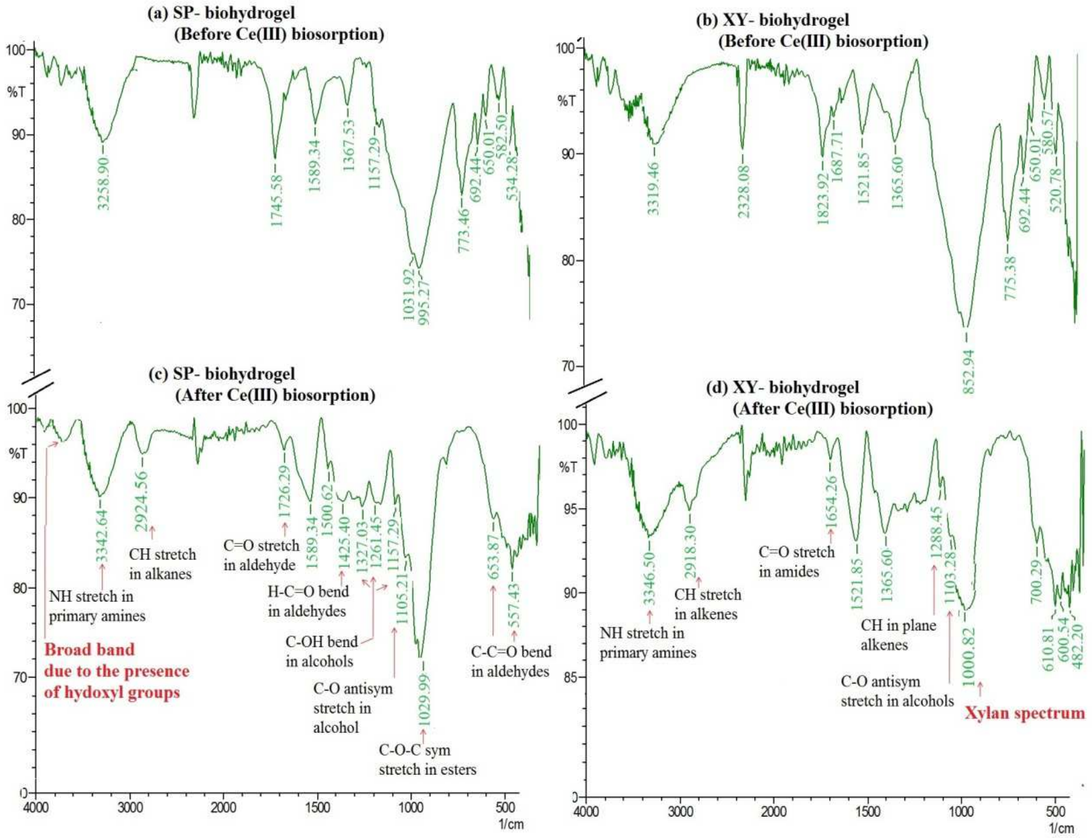

Figure 5: FTIR spectrum of (a) SP- biohydrogel before and (c) after Ce(III) biosorption (b) XY- biohydrogel before and (d) after Ce(III) biosorption

Scanning electron microscopy analysis revealed the surface topology of SP- biohydrogel and XY- biohydrogel before and after biosorption of Ce(III) ions. As shown in Figure 6(a) and Figure 6(b), a homogenous surface roughness was noted in case of SP- biohydrogel which was attributed to the homogenous distribution of sporopollenein. The overall particle size of SP-biohydrogel was smaller than XY- biohydrogel due to which the overall surface area of SP-biohydrogel was higher as compared to that of XY- biohydrogel. The surface coverage of cerium was found to be homogenous in case of SP- biohydrogel whereas a heterogenous distribution of metal solution was noted in case of XY- biohydrogel (Figure 6c and d). The elemental compositions of biohydrogels surface were analyzed using EDX (Figure 7a, b). Ce(III) peak of higher intensity was noted in case of SP- biohydrogel after Ce(III) adsorption (Figure 7c) compared to XY- biohydrogel (Figure 7d) .

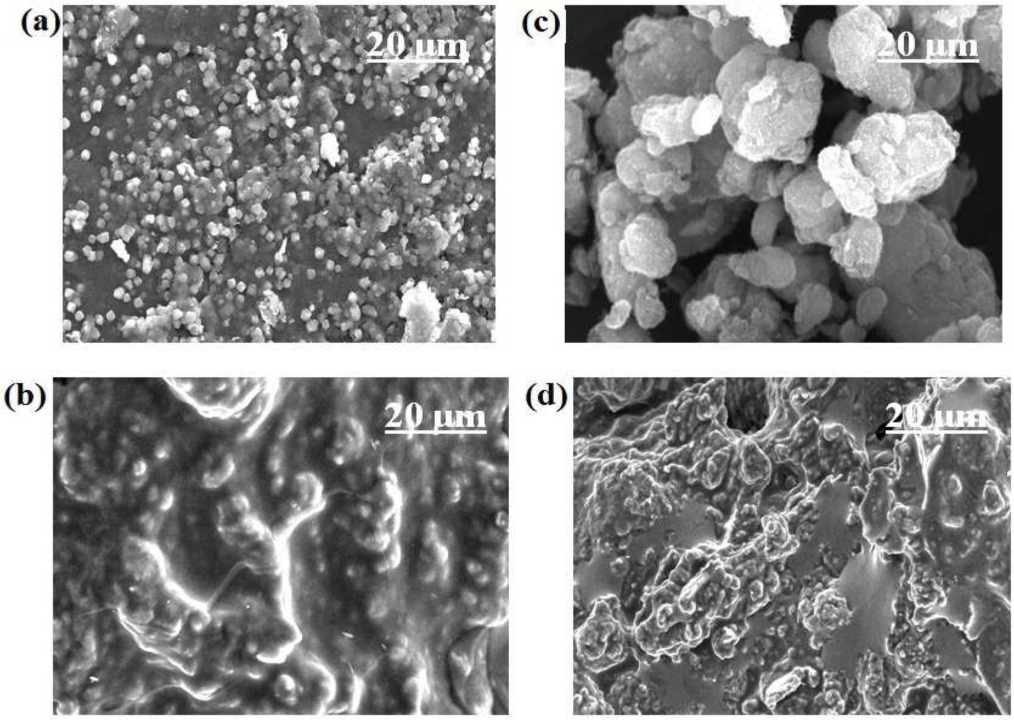

Figure 6: SEM analysis of SP- biohydrogel (a) before and (c) after Ce(III) biosorption SEM analysis of XY- biohydrogel (b) before and (d) after Ce(III) biosorption

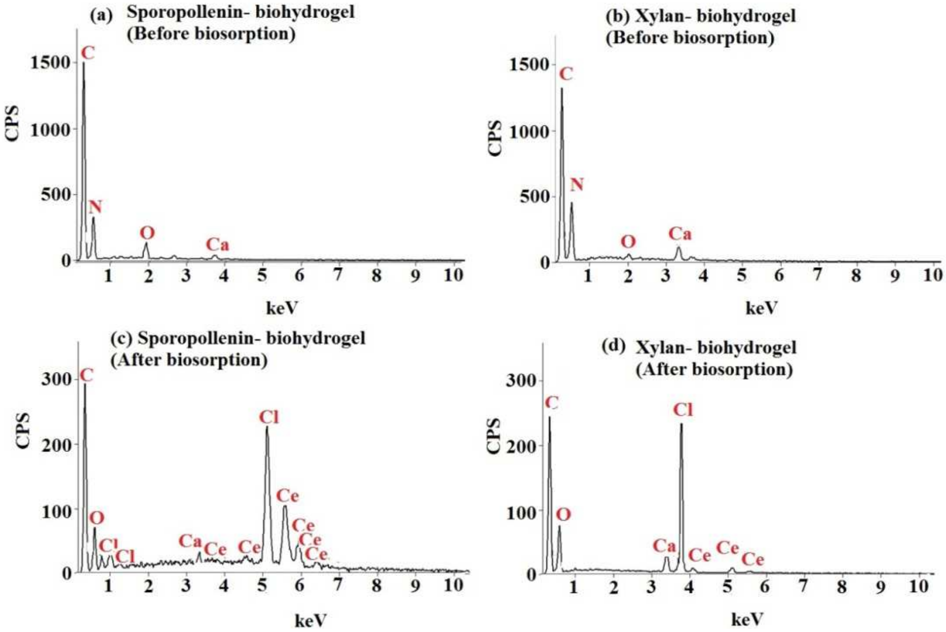

Figure 7: EDX analysis of SP- biohydrogel (a) before and (c) after Ce(III) biosorption EDX analysis of XY- biohydrogel (b) before and (d) after Ce(III) biosorption

---

Effect of co-ions

A simulated condition was developed where Ce(III) uptake was monitored in presence of other co-metal ions. Among the three co- metal ions viz., Cd(II), Pb(II) and La(III), Cd(II) was found to show a predominant effect on Ce(III) biosorption thereby reducing its uptake level to a considerable extent (135.9 mg/g; 100.5 mg/g) followed by Pb(II) (176.2 mg/g; 117.3 mg/g) and La(III) (200.7 mg/g; 166.9 mg/g) as shown in Figure (8). The selectivity factor (β) was calculated in the case of both SP- biohydrogel and XY- biohydrogel. The order of the selectivity factor is given as: Ce-Cd (1.22)> Ce-Pb (1.3) > Ce-La (1.5). In all the cases, the selectivity factor was more than 1 which signified that the preference of cerium(III) was highest among the other co-ions. 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 3, based on the extended Langmuir equation, the interaction factor (η_2) was found to be highest in the case of both SP- biohydrogel (2.9) and XY- biohydrogel (3.4) which signified that cadmium had the most predominant effect on cerium (III) biosorption. In case of SP- biohydrogel, the interaction of cerium was found to increase in the case of ternary system (0.39) as compared to that of binary system whereas a constant interaction was noted in the case of XY- biohydrogel (0.31) for both binary and ternary systems. The interaction effect of Pb in the case of ternary system was found to be higher in SP- biohydrogel (1.5) with respect to XY- biohydrogel (2.9).

In order to improve the fitness, SRS equation 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 exhibit a good fit in the case of both SP- biohydrogel and XY- biohydrogel in binary and ternary system owing to the high correlation coefficient values and low APE values.

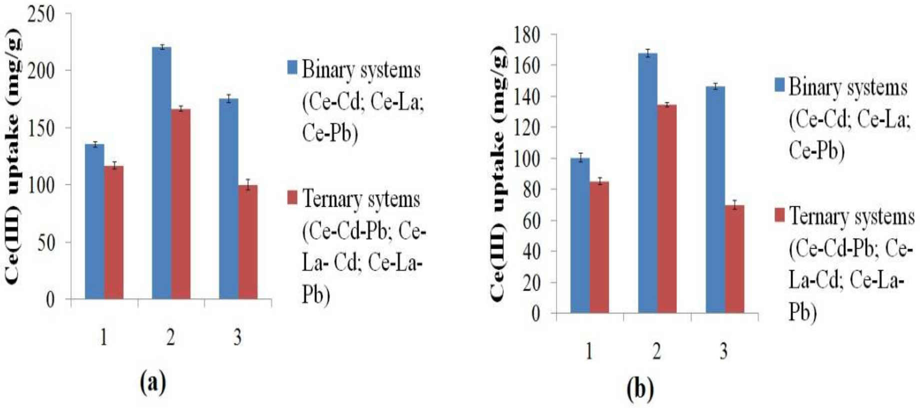

Figure 8: Effect of co-ions on biosorption of cerium (III) on (a) SP- biohydrogel and (b) XY- biohydrogel

Table 3: Extended Langmuir and SRS equation parameters for binary and ternary systems

Extended Langmuir				**SRS**			
SP- biohydrogel							
Ce-Cd		Ce-Cd-Pb		Ce-Cd		Ce-Cd-Pb	
η_1	0.21	η_1	0.39	K_{Fi}	36.54	K_{Fi}	36.54
η_2	2.9	η_2	2.9	n_i	3.1	n_i	3.1
b_1	0.06	η_3	1.5	θ_{ij}	2.6	θ_{ij}	3.9
b_2	0.34	b_1	0.06	R^2	0.967	R^2	0.984
R^2	0.874	b_2	0.34	APE(%)	5.23	APE(%)	2.85
APE(%)	21.55	b_3	0.19				
		R^2	0.778				
		APE(%)	65.14				
XY- biohydrogel							
Ce-Cd		Ce-Cd-Pb		Ce-Cd		Ce-Cd-Pb	
η_1	0.29	η_1	0.31	K_{Fi}	40.89	K_{Fi}	40.89
η_2	3.4	η_2	3.4	n_i	4.2	n_i	4.2
b_1	0.04	η_3	2.9	θ_{ij}	1.5	θ_{ij}	2.8
b_2	0.41	b_1	0.04	R^2	0.959	R^2	0.993
R^2	0.829	b_2	0.41	APE(%)	9.12	APE(%)	10.84
APE(%)	50.14	b_3	0.21				
		R^2	0.790				
		APE(%)	20.45				

Packed bed column studies

As the adsorption efficiency was found to be higher in case of SP- biohydrogel compared to XY- biohydrogel, column studies were conducted using SP- biohydrogel for the recovery of cerium.

Effect of column parameters

The recovery of cerium (III) using SP- biohydrogel was studied as a function of various parameters viz., bed height (4 cm- 12 cm), flow rate (1 ml/min -5 ml/min) and effluent dilutions (0%, 25% and 50%) Figure (9). As shown in Table 4, bed height of 12 cm resulted in the maximum adsorption efficiency of 88.4% at a flow rate of 1 ml/min and 0% dilution. The results were supported by the maximum value of treated volume (240 ml), breakthrough time (240 min) and exhaustion time (280 min) which was attributed to the maximum interaction between Ce(III) ions and functional groups present on the biohydrogel. The effect of flow rate on the recovery of Ce (III) ions was studied at the maximum bed height (12 cm) and 0% dilution. In contrast to the results obtained above, the adsorption efficiency was found to be inversely related to the flow rate. The maximum adsorption efficiency was noted at the minimum flow rate of 1 ml/min which could be possibly due to the maximum time allotted for the sorbate-sorbent interaction. Various dilutions were performed at maximum bed height (12 cm) and minimum flow rate (1 ml/min) in order to study the cerium (III) biosorption. The breakthrough time and adsorbed metal values were found to increase till a dilution of 50% after which stabilization was noted (Table 4).The increase in the adsorption could be possibly attributed to the decrease in amount of the total metal passed through the column thereby resulting in a decrease in the residual metal content.

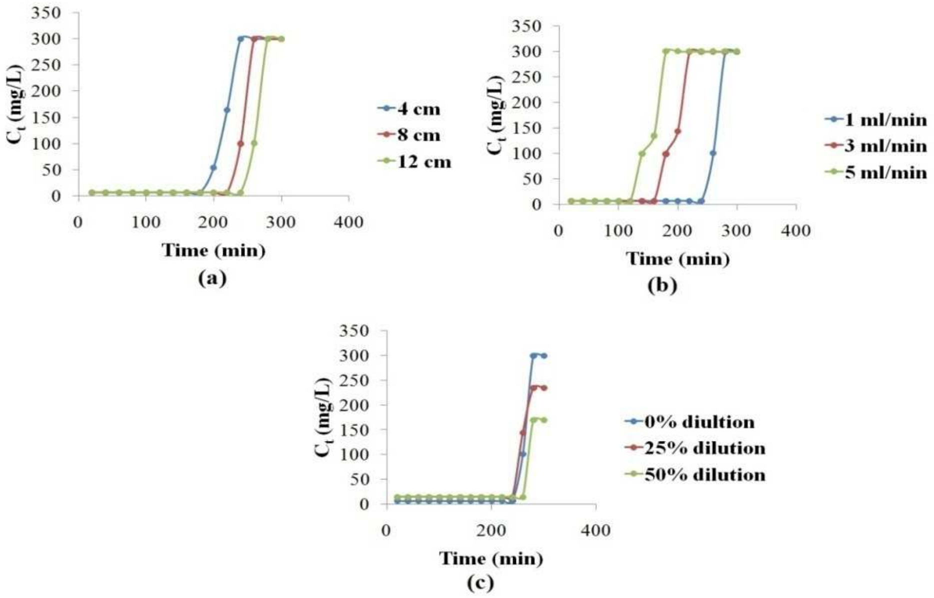

Figure 9: Breakthrough curves for biosorption of cerium (III) onto SP- biohydrogel (a) at different bed heights (flow rate – 1 ml/min, dilution 0%) (b) at different flow rates (bed height- 12 cm, 0%) and (c) at different dilutions (bed height 12 cm, flow rate 1 ml/min)

Column data modeling

Several mathematical models have been developed for lab scale column data analysis. One of the most commonly used adsorption model is the bed depth service time model (BDST), which states the relation between the bed height (cm) and service time (min). Figure 10 (a) shows the plot of service time vs bed height at various dilutions. The flow rate was maintained at 1 ml/min. The model exhibited an excellent fit owing to an R^2 value of 1.0. As shown in Table 5, an increase in dilution resulted in a decrease in sorption capacity owing to the reduction in the concentration of metal sent through the column. The rate constant values showed a decrease in trend (the least being in the case of 50% dilution) which suggested that a progressively longer bed was required to avoid breakthrough [30].

In the present study the Thomas model was used to evaluate the column breakthrough data as shown in Figure 10 (b). Based on the plot of $\ln(C_o/C_t)-1$) vs volume of effluent treated (V_{eff}), the Thomas model parameters were calculated and tabulated (Table 5). The model exhibited a good fit based on the correlation coefficient value (R^2: 0.986). The rate constant (K_{TH}) which characterizes the rate of solute transfer from liquid to solid phase was found to increase with an increase in dilution which signified a higher sorption rate at a low metal concentration due to the availability of more number of surface functional groups. The results were supported by an increase in the maximum uptake (Q_o) values. Electronic wastewater analysis was performed using packed bed column under optimum conditions (flow rate: 1ml/min, bed height: 12 cm and dilution: 0%). Apart from cerium(III) recovery (86.8%), a decrease in the overall COD, BOD, TDS, TSS and heavy metals was noted which justified the biosorption potential of SP- biohydrogel (Table 6).

Table 4: Column data and parameters obtained at different bed heights, flow rates and dilutions for Ce(III) biosorption using SP-biohydrogel

	4 cm	8 cm	12 cm
Bed height (flow rate- 1 ml/min; dilution-0%)			
t_b(min)	180	220	240
t_e(min)	240	260	280
M_{total}	72	78	84
M_{ad}	60.3	68.4	74.2
Efficiency (%)	83.8	87.7	88.4
Volume treated (ml)	180	220	240
	1 ml/min	3 ml/min	5 ml/min
Flow rate (bed height- 12 cm; dilution-0%)			
t_b(min)	240	160	120
t_e(min)	280	220	180
M_{total}	84	66	54
M_{ad}	74.2	54.0	42.4
Efficiency (%)	88.4	81.8	78.6
Volume treated (ml)	240	160	120
	0%	25%	50%
Dilutions (flow rate- 1 ml/min; bed height-12 cm)			
t_b(min)	240	260	280
t_e(min)	280	280	300
M_{total}	84.0	67.2	54.1
M_{ad}	74.2	57.3	43.1
Efficiency (%)	88.4	85.2	79.5
Volume treated (ml)	240	260	280

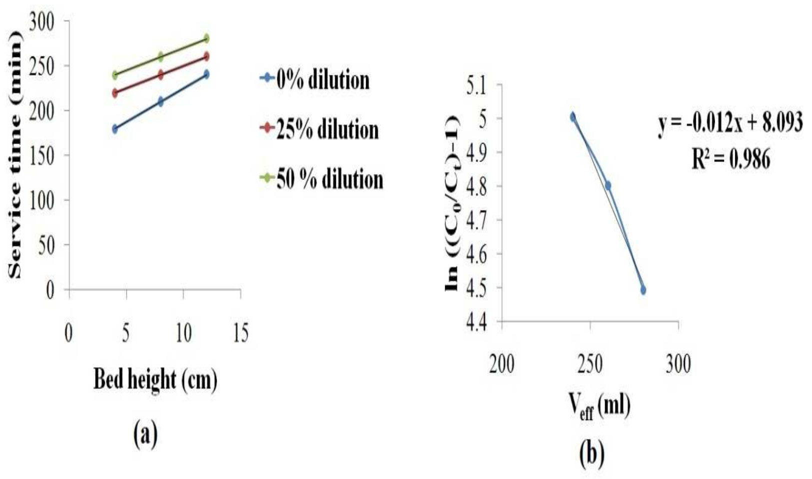

Figure 10: (a) BDST model and (b) Thomas model

Table 5: Bed depth service time model and Thomas model parameters for biosorption of cerium(III) on SP- biohydrogel at different effluent dilutions

Model	0%	25%	50%
BDST model			
Slope	7.5	5.0	5.0
Intercept	150	200	220
N_o(mg/L)	0	17.62	35.25
K_a(L/min)	-	$4.9*10^{-4}$	$2.0*10^{-4}$
R^2	1	1	1
Thomas model			
V_{eff} (ml)	240	260	280
C_o	300.0	245.2	180.6
K_{TH}(min^{-1})	$2.0*10^{-5}$	$2.4*10^{-5}$	$3.3*10^{-5}$
Q_o(mg/g)	640.2	533.5	388.0

Table 6 Analysis of electronic waste industrial effluent

Parameters	Before SP- biohydrogel treatment (mg/L)	After SP- biohydrogel treatment (mg/L)
pH	6.8	6.4
Dissolved Oxygen	7.1±0.02	5.8±0.09
Chemical Oxygen Demand	3200.7±0.04	45.6±0.07
Biological Oxygen Demand	615.2±0.08	22.7±0.04
Total Dissolved Solids	1683.8±0.21	120.5±0.02
Total Suspended Solids	116.4±0.09	20.8±0.06
Zinc	83.7±0.01	5.4±0.02
Lead	98.1±0.03	6.3±0.09
Cerium	**390.2±0.04**	**6.8±0.02**
Cadmium	101.1±0.06	16.2±0.04
Lanthanum	190.7±0.30	20.9±0.01

Regeneration and recovery studies

The regeneration of a biohydrogel is crucial for a process from the point of view of cost effectiveness. Therefore, attempts were made to regenerate the SP- biohydrogel for simultaneous recovery of cerium (III) ions (Figure 11). As shown in Table 7, the maximum recovery was noted to be 86.8%. The biohydrogel was found to recover upto 75.1 % cerium (III) at the end of fifth cycle. After the fifth cycle, a drastic fall in the recovery was noted which could be attributed to the damages on the surface of the biohydrogel due to the continuous contact with the desorbing agent (0.1 M HCl).

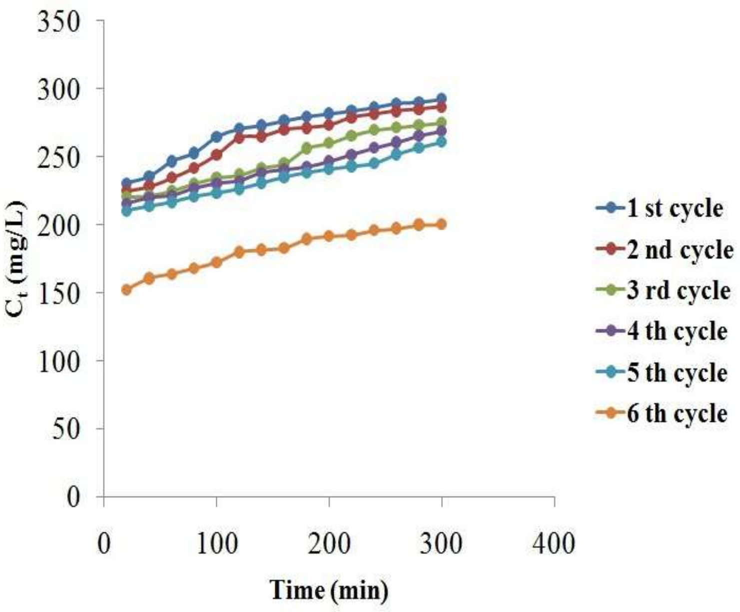

Figure 11: Reuse of SP- biohydrogel during six regeneration cycles

Table 7: Regeneration parameters for recovery of cerium(III)

Cycles	M_d	M_{total}	Recovery (%)
1	78.1	90	86.8
2	75.9	90	84.4
3	71.8	90	79.7
4	69.6	90	77.4
5	67.6	90	75.1
6	52.5	90	58.4

CONCLUSION

The present study is the first report on application of SP- biohydrogel for the recovery of cerium from aqueous environment. Maximum cerium (III) biosorption of 278.2 mg/g for SP- biohydrogel and 180.4 mg/g for XY- biohydrogel was noted under optimized condition. Equilibrium studies suggested a homogeneous mode for SP- biohydrogel and heterogeneous mode for XY- biohydrogel of biosorption to be the underlying phenomena. Kinetic and thermodynamic studies defined the chemical and endothermic mode of adsorption process. Maximum recovery of 86.8 % cerium from electronic wastewater was noted under optimum column conditions (flow rate: 1ml/min, bed height: 12 cm and dilution: 0%). Though the recovery of cerium is reported using a solvent extraction method, it is not preferred due to some disadvantages such as high consumption of reagent and energy, low selectivity, high operational cost and generation of secondary metabolites. In addition, solvent extraction procedures are usually time-consuming and labor-intensive. Therefore, the application of SP- biohydrogel may be considered as a cost effective adsorbnet which could be successfully reused upto 5 cycles and could serve as potential agent for the recovery of cerium from electronic industrial effluent.

Acknowledgements
The authors are grateful to VIT University for providing necessary laboratory facilities.

REFERENCES

[1] N. Das, D. Das, *J. Rare Earth.*, **2013**, 31,933.
[2] R. Md. Awual, T. Yaita, H. Shiwaku, *Chem. Eng. J*., **2013**, 327.
[3] C.J.S. Varsihini, D. Das, N. Das, *J. Rare earths.*, **2014**, 32,745.
[4] S.S. Dubey, B.S. Rao, *J. Hazard. Mater*., **2011**, 186, 1028.
[5] C. Qing, *J. Rare Earths.*, **2010**, 28, 125.
[6] M. Diao, Q. Li, H. Xiao, N. Duan, J. Xu, *J. Environ. Chem. Eng.*, **2014**, 2, 1558.
[7] T.S. Anirudhan, A.R. Tharun, *Chem. Eng. J.*, **2012**, 181–182, 761.
[8] J. Liu, Y. Su, Q. Li, Q. Yu, B. Gao, *Bioresour. Technol.*, **2013**, 143, 32.
[9] H.Kasgoz, S. Ozgumus, M. Orbay, *Polymer*, **2003**, 44, 1785.
[10] W. T. Fraser, A. C. Scott, A. E. S. Forbes, I. J. Glasspool, R. E. Plotnick, F. Kenig, B. H. Lomax, *New Phytol.*, **2012**, 196, 397.
[11] Y.Wang, Y. C. Lin, J. So, Y. Du, C. Lo, *Physiol. Plant.*, **2013**,149, 13.
[12] F. Gode, E. Pehlivan, *Bioresour. Technol.*, **2007**, 98, 904.
[13] I. Gubbuk, L. Gürfidan, S. Erdemir, M. Yilmaz, *Water Air Soil Pollut.*, **2012**, 223, 2623.
[14] I.H. Gubbuk, *J. Hazard. Mater.*, **2011**, 186, 416.
[15] S. Wu, J. Hu, Y. Du, X. Shi, H. Deng, L. Zhang, *J. Environ. Chem.Eng.*, **2014**, 2, 1568.
[16] Z.E. Khalid, O. El. Gamam, S.D. Ramy, *Int.J. Min. Proc.*, **2013**, 120, 26.
[17] J.B. Zambrano, A. Szygula, M. Ruiz, A.M. Sastre, E. Guibal, *J. Environ. Manage.*, **2010**, 91,2669.
[18] C.H. Thomas, *Ann. NY. Acad Sci.*, **1948**, 49, 161.
[19] R. Kumar, M. I. Arun, A.F. Ismail, T. Matsuura, *Desalination*, **2013**, 318, 1.
[20] M.T. Mostaedi, M. Asadollahzadeh, A. Hemmati, A. Khosravi, *Res. Chem. Intermed*., **2013**, 42, 1.
[21] M.C. Palmieri, B. Volesky, O. Garcia, *Hydrometallurgy*, **2002**, 67, 31.
[22] S.I. Zafar, M. Bismam, A. Saeed, M. Iqbal, *Fresen. Environ. Bull.*, **2008**, 17, 2109.
[23] C. Kutahyali, S. Sert, B. Cetinkaya, S. Inan, M. Eral, *Sep. Sci. Technol*., **2010**, 45, 1456.
[24] K. Vijayaraghavan, M. Sathishkumar, R. Balasubramanian, *Ind. Eng. Chem. Res*., **2010**, 49, 4405.
[25] N.S. Awwad, H.M.H. Gad, M.I. Ahmad, H.F. Aly, *Colloids Surf B: Biointerface*., **2010**, 81, 593.
[26] A. Verma, S. Chakraborty, J.K. Basu, *Sep. Purif. Technol.*, **2006**, 50, 336.
[27] M.T. Mostaedi, *Chem. Ind. Chem. Eng. Q*., **2013**, 19, 79.
[28] H. Lalhruaitluanga, K. Jayaram, M.N.V. Prasad, K.K. Kumar, *J. Hazard. Mater.*, **2010**, 175, 311.
[29] M. Sener, H.K.D. Reddy, B. Kayan, *Ecol. Eng.*, **2014**, 68, 200.
[30] D. Charumathi, N. Das, *Desalination.*, **2012**, 285, 22.