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An examination of the uptake of lanthanum from aqueous solution by crab shell particles

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ABSTRACT

Removal of lanthanum (La) from aqueous solution by crab shell, *Portunus sanguinolentus*, was investigated. Based on the experimental results obtained at different pH conditions and La speciation, it was identified that the micro-precipitation of lanthanum carbonate ($La_2(CO_3)_3$) on the surface of crab shell is the main mechanism responsible for La removal by crab shell. The SEM images together with EDX analysis confirmed the presence of La on the surface of crab shell. Isotherm experiments at pH 5 revealed that the maximum biosorption potential of crab shell was 140.1 (mg La)/g, according to the Langmuir model. The La biosorption kinetics was very fast, and the kinetic data were successfully modeled using non-linear pseudo-first order model. Experiments at different ionic strength revealed that La biosorption capacity of crab shell was least affected even at high ionic strength of 0.214 M. Thus, crab shell was identified as a low-cost and potent biosorbent for the removal of La from liquid waste.

1. Introduction

Rare earth elements (REE) have gained considerable attention owing to their unique properties and a wide range of applications. These elements and their compounds have found a variety of applications especially in metallurgy, ceramic industry and nuclear fuel control [1,2]. Among REE, La is one of the most abundant and reactive elements. Lanthanum is used in many industries such as semi-conductor and ceramic industries [3,4] and the effluents emanating from these industries are often associated with high concentrations of La. Lanthanum can cause cancer with humans, and be a threat to the liver when it accumulates in the human body. Considering the accumulation property of La and its relative toxicity towards living organisms [5–7], there is a need to find a suitable and economical treatment method for La-bearing solutions.

Biosorption has been portrayed as potential technology for the treatment of heavy metal-bearing solutions [8,9]. Several biomaterials including bacteria, fungi, algae, industrial and agricultural wastes were identified as potential candidates for the removal of heavy metals [8,10]. Biosorption possesses inherent advantages such as low-cost, operation over a wide range of pH and temperature, biomass regeneration/reuse and toxicant recovery. In recent years, *Sargassum* has been examined extensively for La removal and the results showed that the seaweed possesses good binding capacity towards La [11,12]. Ion exchange has been proposed as major mechanism responsible for La removal in these studies with maximum biosorption observed around pH 5. Although many other natural biosorbents are abundant, they have not been studied for La removal.

In recent years, the adsorption capacity of crab shell towards various metal ions has been examined. For many heavy metal ions, crab shell showed excellent binding capacity [13,14] which is even higher than that of the commercial sorbents. For metal ions such as lead [13] and cobalt [15], crab shell showed very high binding capacity, even surpassing 0.5–1 g of metal ions per g of its dry weight. However, the biosorption potential of crab shell towards REE has not been investigated yet. In this article, the biosorption behavior and the mechanism associated with removal of La by crab are reported for the first time.

2. Materials and methods

2.1. Biosorbent and chemicals

Waste shells of *Portunus sanguinolentus* were collected from the Marina beach (Chennai, India) and were sun dried and crushed to a particle size in the range of 0.5–1 mm using ball mill. The shell particles were then treated with 0.1 M HCl for 4 h followed by washing several times with deionized water and then dried in an oven at 60 °C overnight. This pre-treatment process was carried out to ensure the removal of excess calcium carbonate on the shell surface [14]. The pre-treated crab shell particles will be designated

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Nomenclature

b	Langmuir equilibrium constant (L/mg)
b_T	Toth model constant (L/mg)
C_0	initial La concentrations in the solution (mg/L)
C_f	equilibrium La concentrations in the solution (mg/L)
k_1	pseudo-first order rate constant (1/min)
k_2	pseudo-second order rate constant (g/mg min)
K_F	Freundlich constant (mg/g) $(\mathrm{L/mg})^{1/n}$
M	mass of PCSP (g)
n	Freundlich constant
N	number of data points
n_T	Toth model exponent
PCSP	pre-treated crab shell particles
Q	La uptake (mg/g)
Q_{cal}	La uptake calculated from the model (mg/g)
Q_e	amount of La sorbed at equilibrium (mg/g)
$Q_{\max}$	maximum La uptake (mg/g)
Q_t	amount of La sorbed at time t (mg/g)
r^2	correlation coefficient
REE	rare earth elements
t	time (min)
V	solution volume (L)
ε	average percentage error (%)

as “PCSP” from now on in this paper. All chemicals including $La(NO_3)_3{\cdot}6H_2O$ (Sigma–Aldrich), NaCl (Merck), HCl (Merck) and NaOH (Merck) were of analytical grade.

2.2. Instrumentation

The concentrations of lanthanum in solutions were determined using inductively coupled plasma-atomic emission spectrometer (ICP-AES; Perkin-Elmer Optima 3000DV). To determine the major mechanism responsible for La removal, the La-loaded PCSP was dried, coated with thin layer of platinum and analyzed by scanning electron microscopy (SEM) equipped with energy dispersive X-ray analysis (JEOL, JSM-5600 LV).

2.3. Experimental procedure

Biosorption experiments were conducted by contacting 0.5 g of PCSP with 100 mL of La solution at desired pH in a 250 mL Erlenmeyer flasks kept on a rotary shaker at 160 rpm and 23 ± 2 °C. The pH of the solution was initially adjusted using 0.1 M HCl or NaOH and the pH of the reaction mixture was also controlled using the same chemical agents during experimental runs. After 8 h of contact time, the reaction mixture was filtered through a 0.45 μm PTFE membrane filter and analyzed for La concentration using ICP-AES. Isotherm experiments were conducted using different La concentrations ranging from 350 to 3500 mg/L at pH 5. Kinetic experiments were conducted using the same method as above, except that the samples were collected at different time intervals to determine the time point at which biosorption equilibrium was attained.

The amount of La sorbed by PCSP was calculated from the differences between the La quantity added to the PCSP and the La content of the supernatant using the following equation:

$$Q = \frac{V(C_0 - C_f)}{M} \tag{1}$$

where Q is the La uptake (mg/g); C_0 and C_f are the initial and equilibrium La concentrations in the solution (mg/L), respectively, V the solution volume (L) and M is the mass of PCSP (g). The removal efficiency can be calculated using:

$$\text{removal efficiency} = \frac{C_0 - C_f}{C_0} \times 100 \tag{2}$$

2.4. Mathematical modeling of experimental data

The biosorption isotherm was studied using the following three models, which can be expressed in their non-linear forms as

$$\text{Langmuir model}: \quad Q = \frac{Q_{\max} b C_f}{1 + bC_f} \tag{3}$$

$$\text{Freundlich model}: \quad Q = K_F {C_f}^{1/n} \tag{4}$$

$$\text{Toth model}: \quad Q = \frac{Q_{\max} b_T C_f}{[1 + (b_T C_f)^{1/n_T}]^{n_T}} \tag{5}$$

where $Q_{\max}$ is the maximum La uptake (mg/g), b the Langmuir equilibrium constant (L/mg), K_F the Freundlich constant (mg/g) $(\mathrm{L/mg})^{1/n}$, n the Freundlich constant, b_T the Toth model constant (L/mg) and n_T is the Toth model exponent.

The experimental biosorption kinetic data were modeled using pseudo-first and -second order kinetics, which can be expressed in their non-linear forms, as follows:

$$\text{Pseudo-first order model}: \quad Q_t = Q_e(1 - \exp(-k_1 t)) \tag{6}$$

$$\text{Pseudo-second order model}: \quad Q_t = \frac{Q_e^2 k_2 t}{1 + Q_e k_2 t} \tag{7}$$

where Q_e is the amount of La sorbed at equilibrium (mg/g), Q_t the amount of metal sorbed at time t (mg/g), k_1 the pseudo-first order rate constant (1/min) and k_2 is the pseudo-second order rate constant (g/mg min). All the model parameters were evaluated by non-linear regression using Sigma Plot (Version 4.0, SPSS, USA) software. The average percentage error between the experimental and predicted values is calculated using:

$$\varepsilon\ (\%) = \frac{\sum_{i=1}^{N}(Q_i - Q_{\mathrm{cal},i}/Q_i)}{N} \times 100 \tag{8}$$

where Q_{cal} represents La uptake values calculated from the model (mg/g) and N is the number of measurements. All experiments were done in triplicates and the data are the average values of three replicate experiments.

3. Results and discussion

3.1. Influence of pH and major removal mechanism

Initially, the effect of pH on La biosorption was studied in detail (Fig. 1). The results revealed that equilibrium pH values greater than 4 favored maximum La removals. The crab shell comprises mainly of calcium carbonate and chitin along with some proteins [14,16]. In the present study, the shells were washed extensively with 0.1 M HCl, which practically removed excess calcium carbonate. Repeated exposure to strong acidic conditions may disrupt the structure of crab shell as $CaCO_3$ plays a vital role in the rigidity of crab shell. Structurally, crab shell mainly consists of chitin, which is a straight chain polymer composed of β-1,4-*N*-acetylglucosamine [17]. In chitin, hydroxyl and acetamido groups are prevalent; in particular, acetamido group of chitin acts as a non-specific chelator and establishes weak hydrogen bonds with La in solution.

The remaining $CaCO_3$ in PCSP favors micro-precipitation of metal ions as $CaCO_3$ dissociates to Ca^{2+} and ${CO_3}^{2-}$. Also, there was a rapid raise in solution pH when PCSP was contacted with La solution. For instance, the initial pH 5 was increased to 9.6 within 15 min of contact. This effect was due to dissolution of ${CO_3}^{2-}$ species from

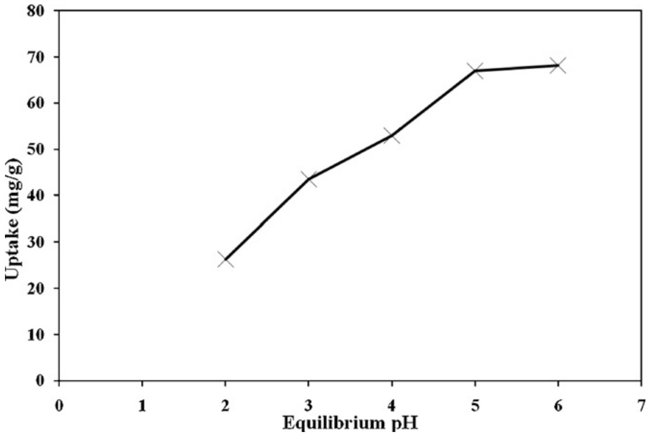

Fig. 1. Effect of solution pH on La uptake by PCSP (initial La concentration = 998 mg/L; temperature = 23 ± 2 °C, agitation speed = 160 rpm).

$CaCO_3$ in PCSP. The solubility of $CaCO_3$ may vary with the solution pH. The speciation of carbonate ions can be defined in three pH ranges, $pK_1 = 6.3$ and $pK_2 = 10.3$ [18]. Therefore, H_2CO_3, HCO_3^- and CO_3^{2-} species predominate for $pH < pK_1$, $pK_1 < pH < pK_2$, and $pH > pK_2$, respectively [15]. Among these carbonate species HCO_3^- and CO_3^{2-} could be responsible for the formation of insoluble lanthanum carbonate.

The hydrochemical behavior of REE is strongly influenced by their solution speciation [19]. At acidic pH values (pH < 5), La exists as La^{3+} [20]. Under these pH conditions, initial hydroxide concentration was negligible and hence the concentration of $LaOH^+$ was minimal. Considering this observation, the formation of $LaCO_3^+$ and $La(CO_3)_2^-$ is more likely to occur at these high carbonate concentrations from PCSP [21]:

$$La^{3+} + CO_3^{2-} \rightarrow LaCO_3^+ \tag{9}$$

$$La^{3+} + 2CO_3^{2-} \rightarrow La(CO_3)_2^- \tag{10}$$

$$La^{3+} + 2HCO_3^- \rightarrow La(CO_3)_2^- + 2H^+ \tag{11}$$

Pourret et al. [21] illustrated that the formation of $LaCO_3^+$ and $La(CO_3)_2^-$ strongly depends on the pH and carbonate content. $LaCO_3^+$ concentrations decrease with pH increase, whereas $La(CO_3)_2^-$ concentrations increase when pH increases. At weak acidic values and for light REEs, the formation of $LaCO_3^+$ is more favorable [21]. This species is likely to form strong $La_2(CO_3)_3$ precipitates, which are then adsorbed to the chitin on the surface of PCSP. At low pH values, the H_2CO_3 tends to dominate and theoretically La^{3+} cannot react with carbonate, which therefore resulted in decreased La biosorption.

3.2. SEM examination

The scanning electron microscopy equipped with EDX was used to determine the components of precipitates and analyze the morphology of PCSP before and after contact with La (Fig. 2). For PCSP, through EDX analysis, strong Ca peaks were observed, which implies that shell particles contain calcium carbonate. The peaks corresponding to carbon, nitrogen, oxygen, sulfur, and phosphorous were recorded in the EDX spectrum. These elements are present in the crab shell as the main constituents of chitin and protein. SEM images confirmed that the surface is not smooth and contains lumps of calcium salts. A significant change to the surface of PCSP was observed when contacted with La solution. Several La peaks were observed in the sample along with all other components identified in La-free PCSP. It is worth noting that strong Ca peaks were observed in La-loaded PCSP sample, indicating the fur-

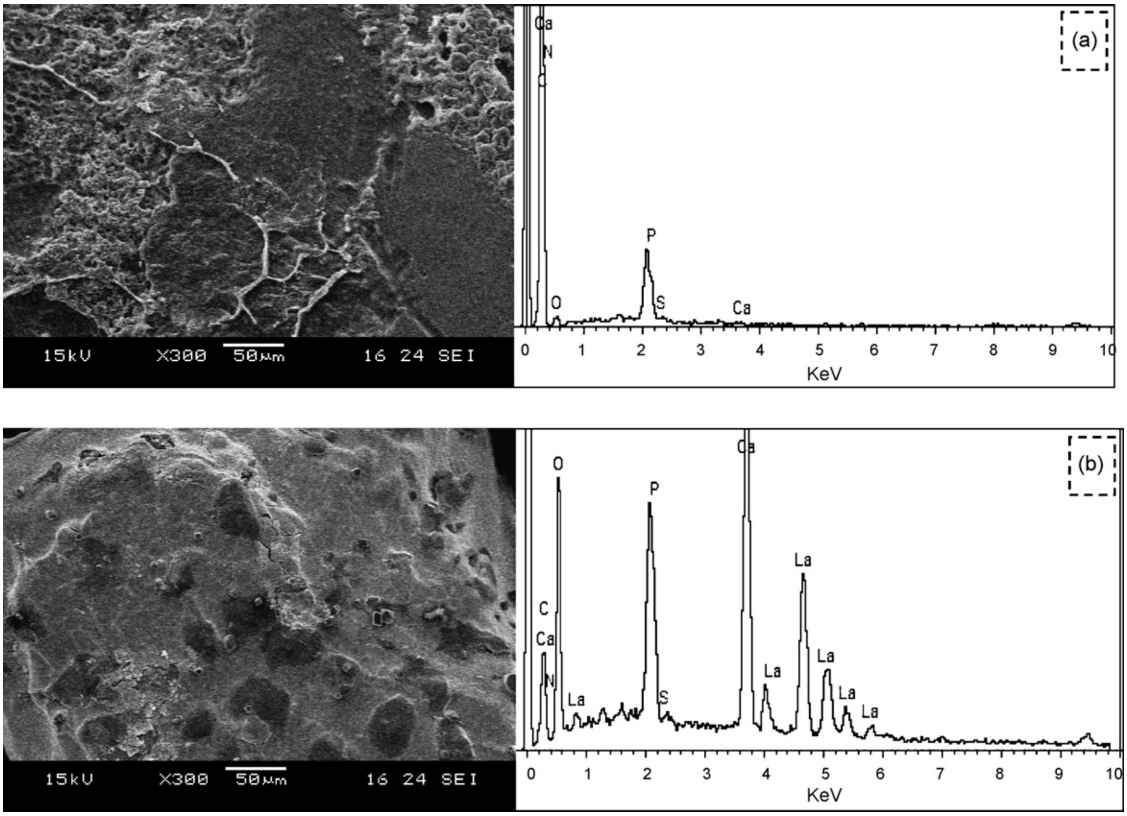

Fig. 2. SEM picture and EDX spectrum of PCSP (a) and La-loaded PCSP (b).

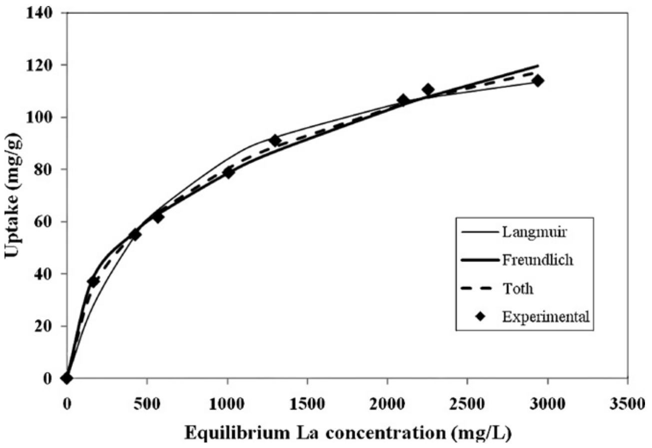

Fig. 3. Isotherms during La biosorption onto PCSP (pH 5; temperature = 23 ± 2 °C, agitation speed = 160 rpm).

Table 1
Isotherm model constants during La biosorption onto PCSP at pH 5.

Isotherm models	
Langmuir	
Q_{max} (mg/g)	140.1
b (L/mg)	0.0015
R^2	0.998
ε (%)	1.96
Freundlich	
K_F (mg/g)(L/mg)$^{1/n}$	5.25
n	2.56
R^2	0.999
ε (%)	0.59
Toth	
Q_{max} (mg/g)	382.9
b_T (L/mg)	0.0041
n_T	3.15
R^2	0.999
ε (%)	0.14

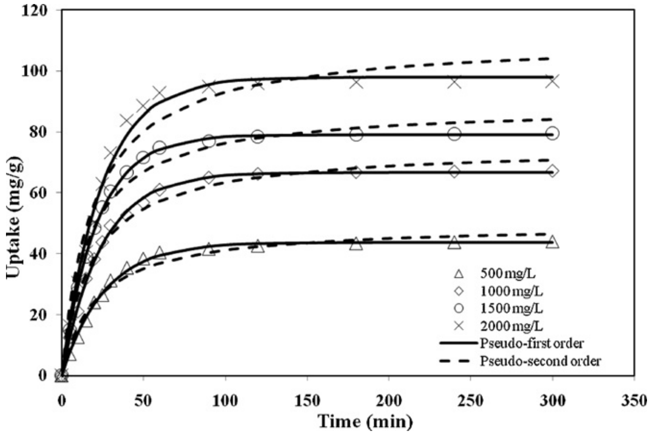

Fig. 4. Biosorption kinetics of La uptake onto PCSP (pH 5; temperature = 23 ± 2 °C, agitation speed = 160 rpm).

ther potential of PCSP in La biosorption. Thus, SEM/EDX analysis confirms the micro-precipitation of lanthanum carbonate onto the surface of PCSP.

3.3. Biosorption isotherms and modeling

PCSP exhibited steeper isotherm for La (Fig. 3), which implies the high degree of affinity of sorbate towards the sorbent. A close analysis of the shape of isotherm revealed that the isotherm was favorable and can be classified as “L-shaped” [22]. This means the ratio between the La concentration in the solution and that sorbed onto the biosorbent decreases with increase in the La concentration, providing a concave curve without a strict plateau.

Experimental isotherm related to the biosorption of La onto PCSP was tested using the Langmuir, Freundlich, and Toth models. Initially, the Langmuir model was applied to the present system and the model was able to describe the isotherm data with high r^2 and low % error values (Table 1). The Langmuir adsorption isotherm has traditionally been used to quantify and contrast the performance of different sorbents. The Langmuir model served to estimate the maximum metal uptake values (Q_{max}) where they could not be reached in the experiments. The constant b represents affinity between the sorbent and sorbate (Table 1). A comparison of the maximum adsorption capacity (Q_{max}) of PCSP for La obtained in the present study with those included in Table 2 indicated that PCSP shows higher sorption capacity as compared to other sorbents.

The Freundlich isotherm was originally empirical in nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. High K_F and n values indicate that the binding capacity reached its highest value, and the affinity between the biosorbent and La was also high. On comparing with the Langmuir model, the Freundlich model described the La biosorption isotherm with low % error and high r^2 values (Table 1).

Finally, the Toth model was examined for the La biosorption isotherm and this resulted in very good prediction of isotherm curves (Fig. 3) along with high r^2 and very low % error values (Table 1). The Toth isotherm [23], derived from potential theory, has proven to be useful in describing sorption in heterogeneous systems such as phenolic compounds on carbon. It assumes an asymmetrical quasi-Gaussian energy distribution with a widened left-hand side, i.e. most sites have sorption energy less than the maximum adsorption energy. The successful application of the Toth model to the present data supports the fact that the surfaces of the biosorbent are heterogeneous.

Table 2
Lanthanum removal by various adsorbents reported in the literature.

Sorbent	Pre-treatment	Optimum pH	Optimum temperature (°C)	Concentration range (mg/L)	Model used to calculate adsorption capacity	Uptake (mg/g)	References
PCSP	0.1 M HCl	5.0	23 ± 2		Langmuir	140.1	This work
Sargassum polycystum	$CaNO_3$	5.0	–	56–1000	–	138.9	[11]
Myxococcus xanthus	–	4.5	28	56	–	137.5	[25]
Sargassum fluitans	HCl and H_2SO_4	5.0	30	–	Langmuir	73.6	[12]
Pseudomonas aeruginosa	NaCl	5.0	20 ± 5	139–972	Brunauer–Emmett–Teller	40.3	[26]
Platanus orientalis	–	4.0	30	25–300	Langmuir	26.7	[27]
Bentonite	–	6.0	20	–	Langmuir	37.0	[28]

Table 3
Biosorption kinetic model parameters at different initial La concentrations.

Initial La concentration (mg/L)	$(Q_e)_{\text{exp}}$ (mg/g)	Pseudo-first order				Pseudo-second order			
		k_1 (1/min)	Q_e (mg/g)	r^2	ε (%)	k_1 (g/mg min)	Q_e (mg/g)	r^2	ε (%)
500	44.0	0.039	43.8	0.999	1.7	0.0010	49.8	0.994	4.7
1000	67.2	0.042	66.7	0.999	0.3	0.0007	75.3	0.997	3.2
1500	79.6	0.047	79.2	0.999	0.8	0.0006	88.7	0.996	3.5
2000	96.8	0.051	98.0	0.998	2.1	0.0005	110.8	0.993	5.0

3.4. Biosorption kinetics

For any practical application, the process design, operation control and sorption kinetics are very important. The sorption kinetics in a wastewater treatment is significant, as it provides valuable insights into the reaction pathways and the mechanism of a sorption reaction. Also, the kinetics describes the solute uptake, which, in turn, controls the residence time of a sorbate at the solid–solution interface. Since biosorption is a metabolism-independent process, it would be expected to be a very fast reaction [10]. Experimental kinetic data at different initial La concentrations revealed that more than 90% of La ions were removed in the first 60 min (Fig. 4). This initial quick phase was followed by slow attainment of equilibrium as high amount of carbonate were initially available for micro-precipitation of La, but thereafter, the formation of lanthanum carbonate would be difficult due to decrease in carbonate release from the PCSP. On changing the initial La concentration from 500 to 2000 mg/L, the uptake increased from 44 to 96.8 mg/g whereas the removal efficiency decreased from 44.8 to 24.6%. This difference in removal efficiencies can be attributed to the fact that at relatively low initial metal concentrations, the ratio of the initial moles of metal ions to the available surface area was low and subsequently the fractional sorption became independent of initial concentration of La. However, at higher concentrations the available surface area became less compared to the moles of metal ions present, which led to decreased fractional sorption. Hence, the percentage metal removal was dependent upon the initial metal ion concentration [14].

To evaluate the differences in the biosorption kinetic rates and the metal recoveries, the kinetics of metal uptake was described by a pseudo-first and -second order models. The model rate constants, equilibrium metal uptakes along with r^2, and % error are presented in Table 3. Regardless of the kinetic equation used, the description of the biosorption kinetics was very good. The correlation coefficients were always greater than 0.993 at all concentrations ranges examined. However, % error values revealed that the pseudo-first order model described the La biosorption kinetic data better than what the pseudo-second order model did. In addition, the calculated equilibrium uptake values were very close to the experimental Q_e values. The rate constant (k_1) increased with an increase in initial La concentration. The pseudo-second order model is based on the sorption capacity of the solid phase, and predicts the sorption behavior over the entire study range [24]. However, for the present La kinetic data, the model showed a tendency to overestimate the quantity of metal removed. Also, the model was unable to predict the experimental kinetic curves. The pseudo-second order model rate constant (k_2) decreased with an increase in initial La concentration (Table 3). The curves predicted by pseudo-first and -second order models are shown in Fig. 4.

3.5. Ionic strength

An important experimental parameter to be investigated in biosorption experiments is the ionic strength, which influences the binding of solutes to the biomass surface. The effect of ionic strength on the La biosorption onto PCSP was studied by adding NaCl in the concentration ranges of 0.043–0.214 M (Fig. 5). As the ionic strength increased, La uptake capacity of PCSP was affected. This decrease may be ascribed to the competition between ions, changes in metal activity, or in the properties of the electrical double layer. The cation, Na^+, may compete with La^{3+} ion for the carbonate ions from the PCSP. The presence of anions can lead to the following: (1) formation of complexes with higher affinity than the original form (i.e. an enhancement of sorption) or (2) formation of complexes with lower affinity for the sorbent [10]. To confirm this, ion chromatography was used to analyze both Na^+ and Cl^- concentrations. From Fig. 5, it is clear that as the ionic strength increased, both Na^+ and Cl^- uptake by PCSP also increased. However, compared to the initial concentrations of Na^+ and Cl^- ions used, the uptake of these ions by PCSP was not significant. Also, the decrease in La uptake by PCSP was only 9% even at high NaCl concentration of 0.214 M. This observation clearly shows that the La removal by PCSP is highly favorable even at high NaCl concentrations. It is known that precipitation is relatively insensitive to changes in ionic strength [13,15]. Ions such as phosphate, hydroxide and carbonate have a strong tendency to form complexes with metals while perchlorate, chloride and nitrate show very little tendency to do so [18].

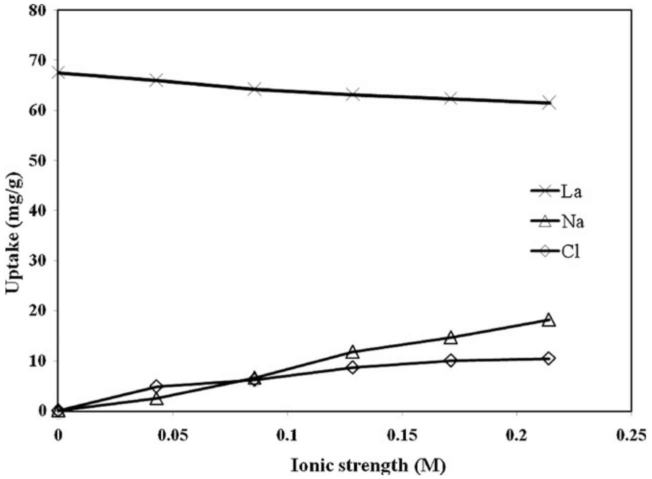

Fig. 5. Effect of ionic strength on the uptake of La by PCSP (initial La concentration = 1000 mg/L; pH 5; temperature = 23 ± 2 °C, agitation speed = 160 rpm).

4. Conclusions

The present study demonstrated the high La binding capacity of pre-treated crab shell particles. The important findings include:

- Due to the presence of calcium carbonate and chitin, PCSP performed well in La biosorption. Micro-precipitation of lanthanum carbonate followed by sorption onto the surface of PCSP surface was found to be the major mechanism responsible for La removal by PCSP. SEM along with EDX analysis confirmed the presence of La on the surface of PCSP.
- The performance of crab shell during La removal was affected by solution pH with pH 5 found be practical and efficient condi-

tion for La biosorption. Isotherm experiments revealed that PCSP could bind as much as 140.1 mg of La per gram of biosorbent, according to the Langmuir model. However, based on the correlation coefficients and %error values, the Toth model described the La-biosorption isotherm better compared to the Langmuir and Freundlich models.

- The presence of high NaCl concentrations had very little impact on the La biosorption capacity of PCSP.
- Thus, crab shell being low-cost and easily available biomaterial can be considered for decontamination of wastewater containing La. Due to its high mechanical strength, crab shell is also well suited for column applications involving wastewater treatment.

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