



## **Enhanced uptake of rare earth metals using surface molecular imprinted biosorbents of animal origin: Equilibrium, Kinetic and Thermodynamic studies**

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**Abstract:** The surface molecular imprinted (SMI) biowaste materials of animal origin viz. prawn carapace (PC), and fish scales (FS) were used as adsorbents for the enhanced recovery of the rare earth metals viz. cerium(III) and lanthanum (III) from aqueous solution. The adsorption capacities were notably increased from 218.3 mg/g to 363.5 mg/g for Ce(III) imprinted PC, and 200.0 mg/g to 312.3 mg/g for La (III) imprinted FS respectively. The Langmuir model showed the best fit for Ce(III) adsorption whereas Freundlich model was found to be more favourable for adsorption of La(III) ions. The process followed a homogeneous mode in the case of SMI PC whereas heterogeneity in cases of SMI FS was further confirmed by scanning electron microscopy (SEM). Kinetic studies indicated that adsorption followed pseudo first order model for Ce(III) ions and pseudo second order model for La(III) ions. FTIR analysis confirmed the involvement of more functional groups in case of SMI biosorbents. Maximum Recovery of 89% Ce(III) and 87 % La(III) was noted using SMI PC and SMI FS respectively. Regeneration studies suggested that the biosorbent SMI PC and SMI FS could be consistently reused upto 6 cycles.

**Keywords:** Biowaste materials, cerium (III), lanthanum (III), recovery, surface molecular imprinting.

### **Introduction**

In recent years, the rare earth metals (REMs) have received considerable attention with their increasing demands in high tech industries due to their unique properties and new applications being associated with other metals<sup>1</sup>. Traditional techniques used to separate REMs include precipitation, ion exchange; filtration, solvent extraction etc<sup>2</sup>. Among these methods, solvent extraction method has been widely used because of the effective extraction capacity and separation selectivity. But this method is not preferred due to the requirement of large volume of solvent, which may create health problems<sup>3</sup>. In addition, solvent extraction procedures are usually time consuming and labor-intensive<sup>4</sup>.

Biosorption has increasingly received attention for the recovery of REMs from aqueous media because it is simple, relatively low cost, and effective process<sup>5</sup>. In our previous study, use of abundantly available biowaste materials of plant and animal origin as biosorbents have been reported for the recovery of cerium (III) and lanthanum (III) from aqueous solution<sup>6,7</sup>.

The surface molecular imprinting is a method for the preparation powerful adsorbents having the ability for high selective adsorption of target chemical species by using a molecular template<sup>8,9</sup>. Functional and cross linking monomers are co-polymerized in presence of target imprint molecule which acts as a molecular template<sup>8</sup>. The functional monomers form a complex with the imprint molecule initially, and then their

functional groups become highly cross-linked polymeric structure. Subsequently, the removal of the imprint molecule reveals binding sites which are complementary in size and shape to the analyte. Then the molecular memory is introduced into the polymer, which is capable of rebinding the analyte with a very high specificity. For metal ions, molecular imprinting can be interpreted as ionic imprinting<sup>10,11</sup>. In recent years, ion-imprinted polymers have been prepared and used for selective removal, separation, preconcentration and extraction of metal ions.<sup>12-15</sup>. Haijia et al.<sup>16</sup> reported that surface molecular imprinted biosorbents prepared from fungal mycelium could selectively adsorb nickel(II) ions showing 30-50 % higher metal uptake compared with the non- imprinted biosorbent.

So far, no report is available on the use of molecular imprinted biosorbents for the recovery of REMs. Therefore, in the present study, the surface imprinted adsorbents prepared from the biowaste materials of animal origin have been used for the recovery of two rare earth metals viz. cerium(III) and lanthanum(III) from aqueous environment.

## Materials and Methods

### Metal solution preparation

Cerium and Lanthanum stock solutions (1000 mg/L) were prepared separately from  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  and  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  in deionized water. The working solutions were prepared by diluting the stock solutions to appropriate volumes.

### Preparation of biosorbents

Biowaste materials viz. Prawn carapace (PC) and Fish scales (FS) were purchased from a local fish market at Vellore, and used Tamil Nadu, India and used as biosorbents. They were washed thoroughly with deionised water to remove dirt and impurities and later 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  $\mu\text{m}$ .

### Preparation of surface imprinted biosorbents

The surface imprinting of the dried biosorbents was done following the method of Haijia et al<sup>16</sup> with minor modifications.

### Batch biosorption studies

The experiments were conducted using surface imprinted biosorbents in 250 ml Erlenmeyer flasks at  $28 \pm 1^\circ\text{C}$  on a rotary shaker at 120 rpm varying parameters viz. pH ranging from 3.0 to 9.0, initial metal concentration 200 mg/L to 500 mg/L, biomass dosage 2.0 to 12.0 g/L and contact time 20 to 160 min. The samples were filtered using Whatman No. 1 filter paper after 2 h of mixing. The concentration of Ce(III) present in the filtrate was estimated using UV spectrophotometer at 252.4 nm wavelength and for La(III) at 250.0 nm. Similar experimental conditions were followed for non imprinted biosorbents used as control.

The metal uptake capacities were calculated using the mass balance equation using standard formulae<sup>6</sup>.

### Equilibrium, Kinetic and Thermodynamic studies

The equilibrium data were analyzed using two parameter isotherms- Langmuir, Freundlich and Dubinin- Radushkevich (D-R). Kinetic and thermodynamic studies was conducted following the method reported earlier<sup>6,7</sup>.

### Instrumental analysis

FT-IR, SEM and EDAX analysis were done following the standard procedures<sup>6,7</sup>.

### Regeneration studies

In the recycling experiments, the imprinted biosorbents were exposed to 0.1M HCl. The regenerated biosorbents were used in the next sorption cycle.

## Results and discussion

### Effect of parameters

The effect of pH on uptake of Ce(III) and La(III) on imprinted biosorbents viz. PC and FS were noted. Maximum Ce(III) and La(III) uptake was noted at pH 6.0. At low pH 3.0, minimum uptake of Ce(III) and La(III) was seen which may be due to the increased mobility of H<sup>+</sup> ions, and thus the hydrogen ions are adsorbed preferentially rather than the metal ions<sup>17</sup>. At higher pH values, number of H<sup>+</sup> ions is lower and greater number of ligands with negative charges results in greater metal ions biosorption<sup>18</sup>.

The amount of metal uptake by imprinted biosorbents increased with increase in metal ion concentration and remained constant after reaching equilibrium time. Thus, the maximum Ce(III) uptake was noted at 400 mg/L by imprinted PC and 350 mg/L for La(III) by imprinted FS. 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<sup>19</sup>.

Biomass dosage is one of the parameter that affects the sorption capacity<sup>18</sup>. The effects of biomass dosage on imprinted were studied by varying the dosage range from 2.0 to 12.0 g/L. The uptake of Ce(III) and La(III) increased with an increase in biosorbent dosage due to the availability of more number of binding sites for the metal ions to the binding sites<sup>20, 21</sup>. Maximum sorption was found at 4 g/L for Ce(III) by imprinted PC and 6g/L for La(III) by imprinted FS. Further increase in the biosorbent 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 unsorted in the solution.

The contact time is one of the important parameter for rapid sorption process<sup>22,23</sup>. The uptake of metal ions by the imprinted biosorbents increases with the increase in contact time and reached the equilibrium state at the end of 60 min for Ce(III) and 80 min for La(III). The metal uptake was found to be higher in the initial stage followed by the equilibrium state. This is because the biosorbent contains a higher number of binding sites for the binding of metals in the early stage<sup>20,24,25</sup>. As the time increases, the binding sites available on the biosorbent surface are get filled and thus the metal uptake capacity decreases which could be possibly due to the equilibrium established in sorbate-sorbent interactions<sup>26</sup>. Figure 1 shows the uptake of Ce(III) and La(III) on non imprinted and imprinted biosorbents. The data of non imprinted biosorbents PC and FS presented here is based on our earlier reported work<sup>6,7</sup>.

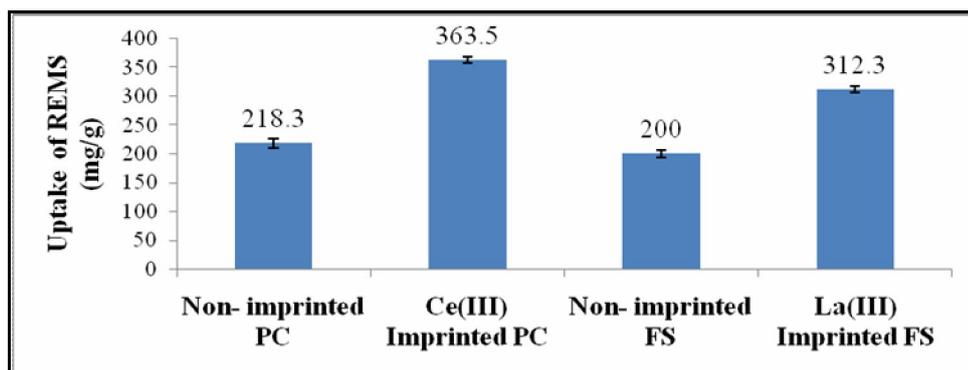


Figure 1 Uptake of REMs using imprinted and non imprinted biosorbents

### Adsorption isotherms

To examine the relationship between sorbate and sorbent at equilibrium, various two parameter isotherm models were employed for fitting the equilibrium data. The isotherm constants, R<sup>2</sup> values and APE (%) values are presented in Table 1.

Among the two parameter isotherms (Langmuir, Freundlich and D-R) tested, Langmuir model exhibited the best fit for Ce(III) imprinted PC thereby suggesting a homogeneous monolayer mode of biosorption (R<sup>2</sup>: 0.986, APE value: 2.52%). In case of La(III) imprinted FS, Freundlich isotherm showed a good fit and therefore suggesting heterogeneous mode of biosorption (R<sup>2</sup>:0.971, APE value: 0.68%). D-R isotherm exhibited a poor fit owing to the high APE and low R<sup>2</sup> value.

### Kinetic studies

For Ce(III) imprinted PC, pseudo-first order model exhibited a best fit owing to the low APE values and high  $R^2$  value of 1.000 (Table 1) thereby indicating physisorption. Whereas for La(III) imprinted FS, pseudo-second order model showed the best fit owing to the high  $R^2$  value 1.000 and low APE value indicating chemisorption.

**Table 1: Equilibrium and kinetic model for biosorption of Ce(III) and La(III)**

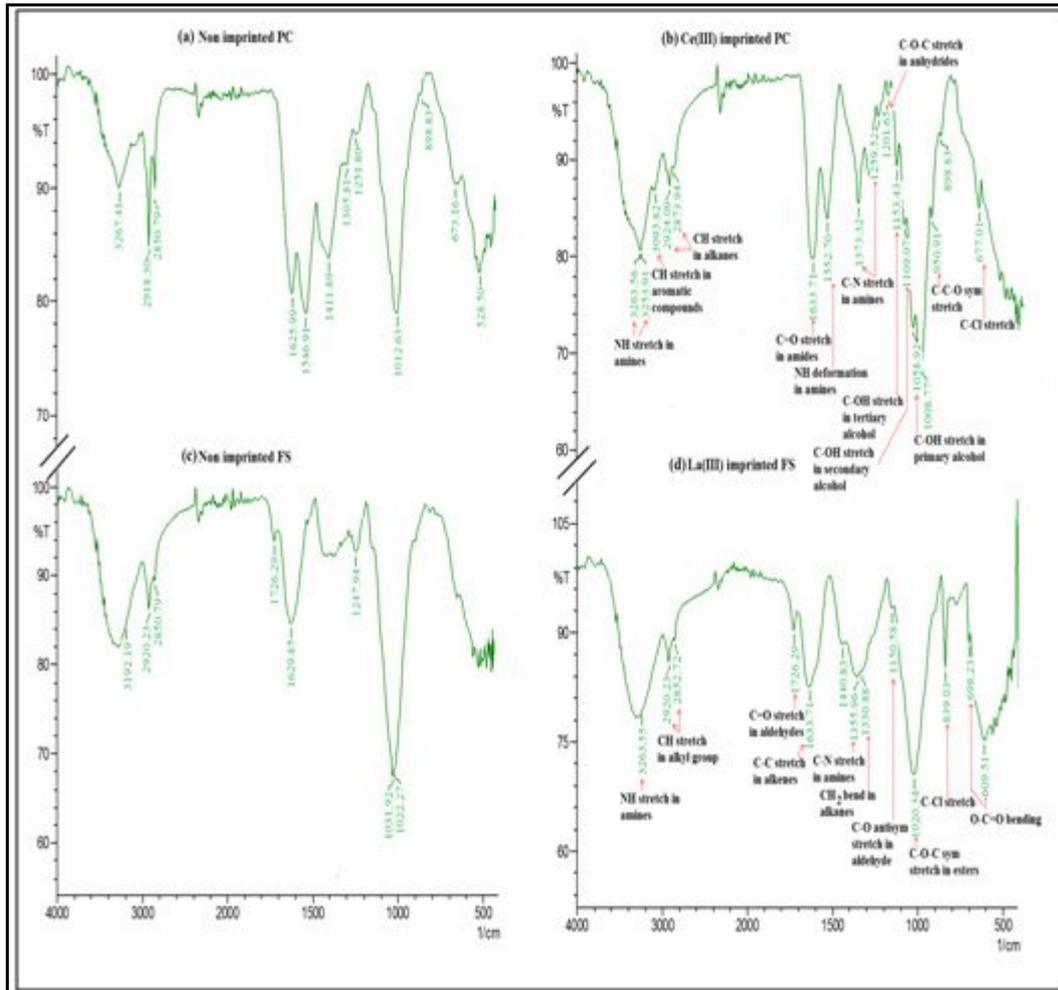
Model	Parameters	Ce(III) imprinted PC	Non imprinted PC	La(III) imprinted FS	Non imprinted FS
Isotherm model Langmuir	$q_m$ (mg/g)	1000.0	1000.0	500.0	250.0
	$K_L$	$2.34 \times 10^{-3}$	0.001	0.032	0.030
	APE (%)	2.52	6.83	27.79	10.70
	$R^2$	0.986	0.979	0.963	0.982
Freundlich	$K_F$ (mg/g)	4.60	25.7	220.3	40.65
	N	1.25	2.90	13.80	3.41
	APE (%)	4.93	3.16	0.68	43.22
	$R^2$	0.945	0.983	0.971	0.971
D-R isotherm	$q_m$ (mg/g)	425.8	152.3	319.2	181.4
	B	0.001	0.014	$9 \times 10^{-5}$	$6 \times 10^{-5}$
	E (KJ/mol)	0.022	0.074	0.074	0.091
	APE (%)	3.20	2.89	0.38	0.08
	$R^2$	0.986	0.657	0.913	0.854
Kinetic studies Pseudo first order	$K_1$ (g/mg/min)	0.032	0.324	0.043	0.895
	$q_e$ (mg/g)	147.2	217.77	258.2	175.7
	APE (%)	19.80	0.731	22.22	0.317
	$R^2$	1.000	0.993	0.998	0.954
Pseudo second order	$K_2$ (g/mg/min)	$1.7 \times 10^{-4}$	$2.8 \times 10^{-4}$	$8.9 \times 10^{-5}$	$5.3 \times 10^{-3}$
	$q_e$ (mg/g)	500.0	500.0	500.0	250.0
	APE (%)	62.40	33.69	21.30	0.860
	$R^2$	0.994	0.903	1.000	0.996
Intra-particle diffusion	v	23.04	27.61	23.47	66.30
	C	49.55	44.23	101.8	70.18
	APE (%)	31.26	12.80	31.75	1.15
	$R^2$	0.974	0.980	0.971	0.989

### Thermodynamic studies

Maximum spontaneity was noted at 50°C for both the imprinted biosorbents and the process was found to be spontaneous indicated by a negative  $\Delta G$  values. The values of  $\Delta H$  and  $\Delta S$  were calculated from the slope and intercept of the plot of  $\log(q_e/C_e)$  vs  $1/T$ . The results indicated that the process was endothermic or heat absorbing in nature as indicated by the positive values of  $\Delta H$  (+18.25 KJ/mol for Ce(III) imprinted PC and +9.11 KJ/mol for La(III) imprinted FS). An increase in randomness was suggested by the positive values of  $\Delta S$  (0.0594 KJ/mol K for Ce(III) imprinted PC and 0.0337 KJ/mol K for La(III) imprinted FS).

### FT-IR analysis

Figure 2a and 2c depicts the FT-IR spectral analysis of non imprinted biosorbents PC and FS. The strong and broad band at  $3267.41 \text{ cm}^{-1}$  corresponds to NH stretch in amines. The bands at  $2920.23 \text{ cm}^{-1}$  indicated CH stretching vibrations in alkyl groups. The peaks at  $1726.29 \text{ cm}^{-1}$  was assigned to C=O stretching in aldehydes.



**Figure 2- FT-IR analysis of (a) Non imprinted PC; (b) Ce(III) imprinted PC (c) Non imprinted FS; (d) La(III) imprinted FS**

In case of imprinted PC (Figure 2b) and imprinted FS (Figure 2d), the peaks at 2918.30, 2850.79, 1625.99, 1546.91, 1012.63 and 673.16  $\text{cm}^{-1}$  had shifted to 2924.09, 2873.94, 1633.71, 1552.70, 1058.92 and 677.01  $\text{cm}^{-1}$  after biosorption which corresponds to CH stretch in alkanes, C=O stretch in amides, NH deformation in amines, C-OH stretch in primary alcohol, C-Cl stretch. Presence of additional peaks (C-O-C stretch in anhydrides, C-C-O sym stretch, C-OH stretch in secondary and tertiary alcohol) in case of Ce(III) imprinted PC resulted in the higher uptake than FS. Higher change in transmittance was noted in case of imprinted PC indicating a higher involvement of functional groups in the biosorption process.

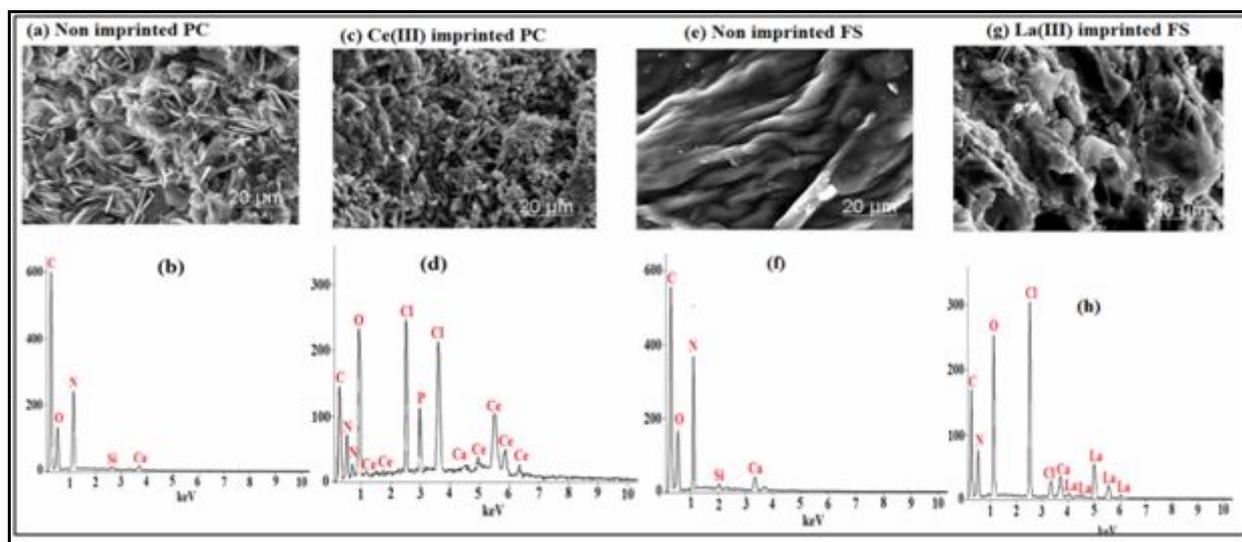
**Scanning electron microscope (SEM) analysis**

Figure 3a and 3e shows a smooth surface on the non imprinted PC and FS. Ce(III) biosorption onto imprinted PC(Figure 3c), showed homogeneity in the surface adsorption by covering a few areas on the surface of the biosorbent. In case of La(III) imprinted FS (Figure 3g), heterogeneous mode of biosorption was noted after biosorption. The results of SEM analysis confirmed that Ce(III) biosorption onto imprinted PC followed a homogeneous mode of biosorption and heterogeneous mode of sorption in case of La(III) imprinted FS.

**EDAX analysis**

X-ray dispersion analysis of the raw as well as imprinted biosorbents viz. Ce(III) imprinted PC and La(III) imprinted FS was performed to study the surface changes of the elements. The EDAX spectrum of non imprinted biosorbents (Figure 3b and 3f) indicated the presence of C (51.8%, 49.5%), O (36.6%, 32.8%) and Si (15.5%, 17.7%) N and Ca as natural species on the biosorbents. These signals are due to X-ray emissions from the polysaccharides and proteins present on the cell wall of the biosorbent. After biosorption, a decrease in C, O, N peaks were noted signifying their involvement in the biosorption process. Disappearance of Si signal

indicated its involvement in biosorption. Cerium (Ce) signal was found to be present in higher amount than lanthanum signal in FS (Figure 3h) which confirmed higher uptake of Ce(III) onto imprinted PC(Figure 3d).



**Figure 3 (a) SEM and (b) EDAX analysis of Non imprinted PC (c) SEM and (d) EDAX analysis of Ce(III) imprinted PC (e) SEM and (f) EDAX analysis of Non imprinted FS (g) SEM and (h) EDAX analysis of La(III) imprinted FS**

### Reuse and Regeneration studies

The reusable nature of Ce(III) imprinted PC and La(III) imprinted FS was tested for several cycles by alternating adsorption and desorption cycles. Results suggested that the imprinted biosorbents could be effectively reused upto 6 cycles.

### Conclusion

In the present study, surface imprinted biosorbent PC showed increase in Ce(III) uptake from 218.3 mg/g to 363.5 mg/g whereas La (III) imprinted FS showed increase in uptake from 200.0 mg/g to 312.3 mg/g respectively. The equilibrium data fitted well to the Langmuir model for Ce(III) imprinted PC and Freundlich model for La(III) imprinted FS. FT-IR analysis suggested the involvement of amines, anhydrides and alcohol groups for the imprinted biosorbents. It can be concluded that surface imprinted biosorbents can be used for the enhanced uptake of other metal ions from aqueous environment.

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