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## Relevant Approach to Assess the Performance of Biowaste Materials for the Recovery of Lanthanum (III) from Aqueous Medium.

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### ABSTRACT

The aim of the present study was to assess the performance of the biowaste materials to recover lanthanum (III) from aqueous solution. The biosorbents from animal origin viz., crab shell ( $C_R$ S), prawn carapace (PC), fish scales (FS), egg shell (ES) and plant origin viz. Neem sawdust (NS), corn style (CS), pineapple crown ( $P_A$ C), orange peel (OP) were chosen and the influence of various factors viz. pH, contact time, biomass dosage and initial metal concentration on lanthanum (III) sorption were investigated under batch mode. The experimental isotherm data were analyzed using Langmuir and Freundlich model to characterize the adsorption process. The adsorption capacities of  $C_R$ S, PC, FS, ES were found to be 90.9, 200.0, 250.0 and 100.0 mg/g whereas 166.6, 76.9, 100.0 and 125.0 mg/g for NS, CS,  $P_A$ C and OP respectively. Langmuir model found to be the best fit for FS and Freundlich model for NS respectively. FS and NS can be used as potential biosorbents for La(III) recovery from aqueous environment.

**Keywords:** Biowaste materials; Lanthanum(III); Langmuir model; Freundlich model ; recovery

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## INTRODUCTION

Lanthanum(III) is one of the most abundant and reactive elements among the rare earth elements (REEs) and has drawn special attention. Current applications of lanthanum as a pure element or in association with other compounds are in super alloys, catalysts, special ceramics and in organic synthesis [1]. It is used in many industries such as semi-conductor and ceramic industries [2,3] and the effluents emanating from these industries are often associated with high concentrations of lanthanum. Therefore, there is a scope to recover lanthanum from La-bearing effluents.

Different conventional methods have been proposed for the recovery of REEs, such as co-precipitation, solvent extraction, ion-exchange, solid-phase extraction, etc. [4 -6]. But all these methods have some disadvantages, such as high consumption of reagent and energy, low selectivity, high operational cost and generation of secondary metabolites [7]. Solvent extraction and ion-exchange are the two most common methodologies for the recovery of REEs from various matrices. Though there is report on recovery of lanthanum (III) using solvent extraction method [8] it is not preferred due to the requirement of large volume of solvent, which may create health problems [9]. In addition, solvent extraction procedures are usually time consuming and labor-intensive [10]. Therefore, many researchers have started developing a cost effective and eco-friendly method to recover rare earth metals from aqueous environment.

Biosorption can be defined as the removal / recovery of metal or metalloid species, compounds and particulates from solution by non- living biological matter [11]. The process is rapid, low cost, eco-friendly, effective and non- generation of secondary metabolites in comparison with conventional chemical methods [12]. Biosorbent materials execute a high metal loading capacity and in some cases are highly specific for elements of particular interest [13]. The utilization of inexpensive biosorbents is currently receiving wide attention because of their abundant availability [14]. There are reports on lanthanum(III) biosorption using *Citrus reticulata*, *Agrobacterium sp.*, bamboo charcoal, *Plantanus orientalis*, rice husk etc.

In the present study, biowaste materials of animal and plant origin which are available abundantly were used and screened as biosorbents for the recovery of La(III) from aqueous solution. The effects of solution pH, initial metal concentration, biosorbent dosage, and contact time on lanthanum adsorption have been investigated in batch mode. Isotherm studies related to the process were performed.

## MATERIALS AND METHODS

### Preparation of biosorbents

The biowaste materials of animal origin viz. crab shell ( $C_R S$ ), prawn carapace (PC), fish scales (FS), egg shell (ES) and plant origin viz. neem sawdust (NS), corn style (CS), pineapple crown ( $P_A C$ ), orange peel (OP) were used as biosorbents. All the materials were obtained from the local market, washed thoroughly with deionized water and dried at 60°C for 24 h. The materials were kept in air tight plastic bottles after drying. The particle size was maintained in the range 425-600  $\mu m$ .

### Preparation of Lanthanum (III) solution

Stock solution (1000 mg/L) of lanthanum(III) was prepared by dissolving required quantity of lanthanum(III) chloride dissolved in deionised water. For experiments, 100 mg/L of La(III) solutions was prepared and used. The pH of the solution was adjusted with 0.1 N  $HNO_3$  and NaOH solutions.

### Screening of biosorbents

The experiments were conducted in 250 ml Erlenmeyer flasks at  $28 \pm 1^\circ C$  on a rotary shaker at 120 rpm varying pH ranging from 3.0 to 9.0, initial La(III) concentration 50 mg/L to 350 mg/L and biomass dosage 0.05 to 0.35 g/L. The samples were filtered using Whatman No. 1 filter paper after 4 h of mixing. The concentration of La(III) present in the filtrate was estimated using UV spectrophotometer at 250 nm wavelength.

The La(III) uptake capacities were calculated using the mass balance equation as shown below:

$$q = \frac{C_0 - C_f}{M} \times V \tag{1}$$

Where  $q$  is the sorption capacity i.e. the amount of La(III) ion biosorbed onto a unit amount of biomass (mg /g) ;  $C_0$  and  $C_f$  are the concentrations (mg/ L ) of La(III) ion in the initial solution and after biosorption respectively;  $V$  is the volume of the aqueous phase (L) ; and  $M$  is the amount of the biomass (g/L). The biowaste materials were screened based on their adsorption capacities.

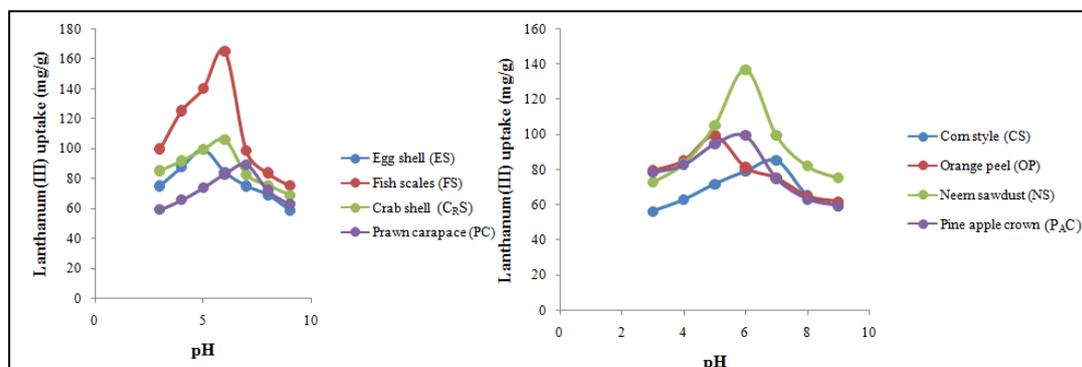
**Batch sorption isotherm studies**

From the experimental data, the applicability of Langmuir and Freundlich isotherm models were judged.  $R^2$  values and isotherm constants values were determined from the models.

**RESULTS AND DISCUSSION**

**Effect of pH**

pH is an important parameter that affects the functional groups present in the biosorbent and the composition of the metal ions that get adsorbed to the active sites. In order to study the effect of pH on lanthanum(III) biosorption onto different biosorbents viz., FS, PC, ES, C<sub>R</sub>S, NS, OP, P<sub>A</sub>C and CS the batch sorption studies were carried out at different pH values ranging from 3.0 to 9.0. Maximum lanthanum(III) uptake was noted at pH 6.0 ( Figure 1). At low pH 3.0, minimum uptake 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 [15]. 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 [16]. Thus the order of La(III) uptake by animal sources was FS>C<sub>R</sub>S>ES>PC; and plant sources was NS>OP>P<sub>A</sub>C>CS.

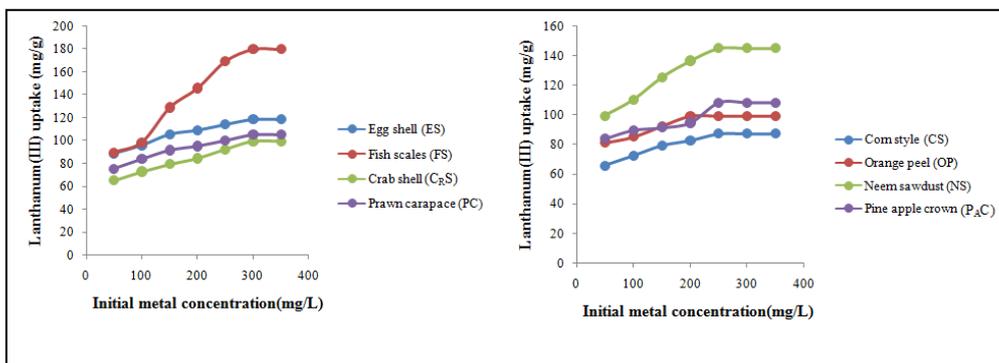


**Figure 1: Effect of pH on biosorption of lanthanum (III).**  
Initial metal concentration- 200 mg/L; biosorbent dosage- 0.2 g/100 ml, contact time-2 h.

**Effect of initial metal concentration**

The effect of initial metal ion concentration on the lanthanum(III) biosorption was studied by varying the concentration from 50 mg/L to 350 mg/L as shown in Figure 2. In case of low lanthanum(III) concentration, the ratio of initial number of metal ions to the available surface area is smaller and thus the adsorption process becomes independent of initial concentrations. However, at higher concentrations, the available sites of adsorption become fewer, and hence the sorption of metal ions depends upon the initial concentration. The amount of lanthanum (III) uptake by various biosorbents increased with increase in lanthanum(III) concentration and remained constant after equilibrium time. 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,

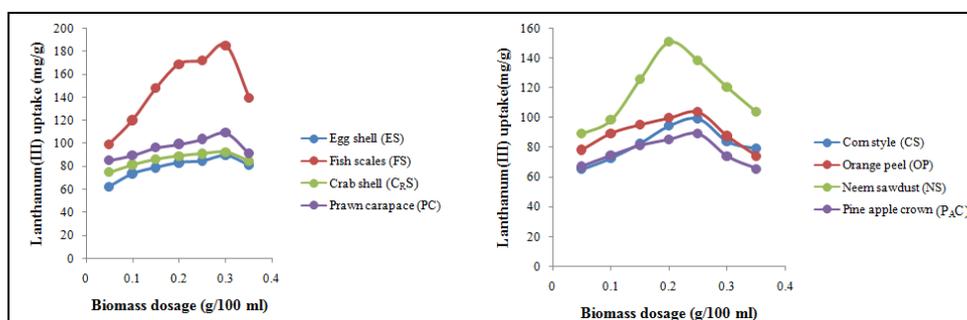
hence a higher initial concentration of metal ion may increase the adsorption capacity [17]. La(III) uptake by animal and plant source was as follows: FS>ES>PC>C<sub>R</sub>S; NS>P<sub>A</sub>C>OP>CS.



**Figure 2: Effect of initial metal concentration on lanthanum (III) biosorption.**  
pH-6.0; biomass dosage- 0.2 g/100 ml; contact time- 2 h.

### Effect of biosorbent dosage

Biomass dosage is one of the parameter that affects the sorption capacity [16]. The effect of biosorbent dosage on lanthanum(III) biosorption by animal and plant sources are given in Figure 3. The dosage was varied from 0.05 to 0.35 g/100 mL. The uptake of 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 [14,18]. Maximum sorption was found at 0.3 g/100 ml for FS and 0.2 g/100 ml for NS. 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 unadsorbed in the solution. The order of La(III) uptake by animal and plant source was as follows: FS>PC>C<sub>R</sub>S>ES and NS>OP>CS>P<sub>A</sub>C.



**Figure 3: Effect of biomass dosage on biosorption of lanthanum (III).**  
pH-6.00; initial metal concentration- 300 mg/L for animal source and 250 mg/L for plant source; contact time- 2 h.

### Effect of contact time

The contact time is one of the important parameter for rapid sorption process [19, 20]. The effect of contact time on lanthanum(III) biosorption is given in Figure 4. The uptake of metal ions by the biosorbents increases with the increase in contact time and reached the equilibrium state at the end of 4h for animal sources and 3h for plant sources. 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 [1,14, 21]. 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 [22]. Thus, the order of La(III) sorption by various animal and plant sources are as follows: FS>C<sub>R</sub>S>ES>PC; NS>OP>P<sub>A</sub>C>CS.

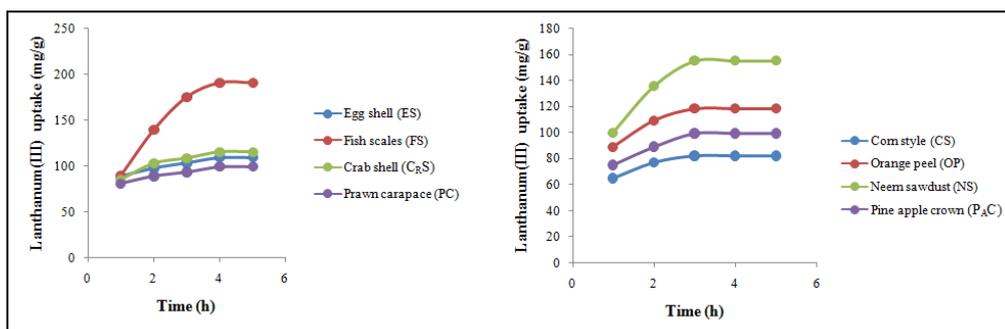


Figure 4: Effect of contact time on biosorption of lanthanum (III)

pH- 6.00; initial metal concentration- 300 mg/L and 250 mg/L for animal and plant source; biomass dosage- 0.2 g/100 ml for plant source and 0.3 g/100 ml for animal source.

### Adsorption isotherms

Adsorption isotherm provides the relationship between the concentration of adsorbate present in the solution and the amount of adsorbate adsorbed onto the biosorbent at equilibrium condition. The equilibrium of lanthanum(III) biosorption is modeled using adsorption-type isotherms. The Langmuir and Freundlich isotherm model were used to describe the biosorption equilibrium of biomass. The Langmuir adsorption isotherm suggests monolayer sorption on a homogeneous surface with identical sites in terms of energy without interaction between adsorbed molecules [23]. The equation can be written as follows:

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \quad (2)$$

where  $q_{eq}$  (mg/g) and  $C_{eq}$  (mg/L) are amount of absorbed lanthanum per unit weight of biomass and unadsorbed lanthanum concentration in solution at equilibrium respectively.  $q_{max}$  (mg/g) is the maximum amount of lanthanum per unit weight of biomass required to form a complete monolayer on the surface bound at high  $C_{eq}$  and  $b$  is a constant.  $q_{max}$  and  $b$  are evaluated from the linear plot of the logarithmic equation Eq. 3

$$\frac{1}{q_{eq}} = \frac{1}{q_{max}} + \frac{1}{b q_{max} C_{eq}} \quad (3)$$

The Freundlich equation based on sorption on a heterogeneous surface [24] is given below as Eq. (4):

$$q_e = K_F C_e^{1/n} \quad (4)$$

Where  $K_F$  and  $n$  are Freundlich constants, whereas  $K_F$  and  $n$  are indicators of adsorption capacity and adsorption intensity of the sorbents respectively.

Eq. 4 can be linearized in logarithmic form as Eq. 5

$$\log q_{eq} = \log K_{F+} + \frac{1}{n} \log C_{eq} \quad (5)$$

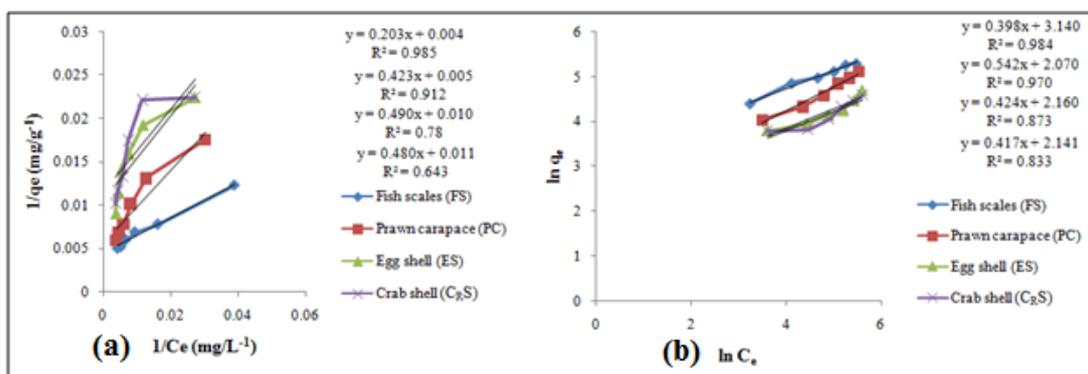
The adsorption data obtained for lanthanum(III) adsorption onto biowaste materials used as a biosorbents in the present investigation were modeled. The values of Langmuir and Freundlich constants for the biosorption of lanthanum(III) by various animal and plant sources are presented in Table-1. Among the biosorbents from animal sources, FS showed the maximum La(III) uptake capacity of 250.0 mg/g and a high  $R^2$  value (0.985) as compared to other biosorbents. Thus, Langmuir model was found to be the best fit for FS suggesting monolayer coverage on the biosorbent (FS) surface. In case of biosorbents of plant origin,

Freundlich model was found to be the best fit for NS showing higher correlation coefficient value ( $R^2=0.992$ ) with slope (1/n) and intercept  $\log K_f$  compared to other biosorbents.

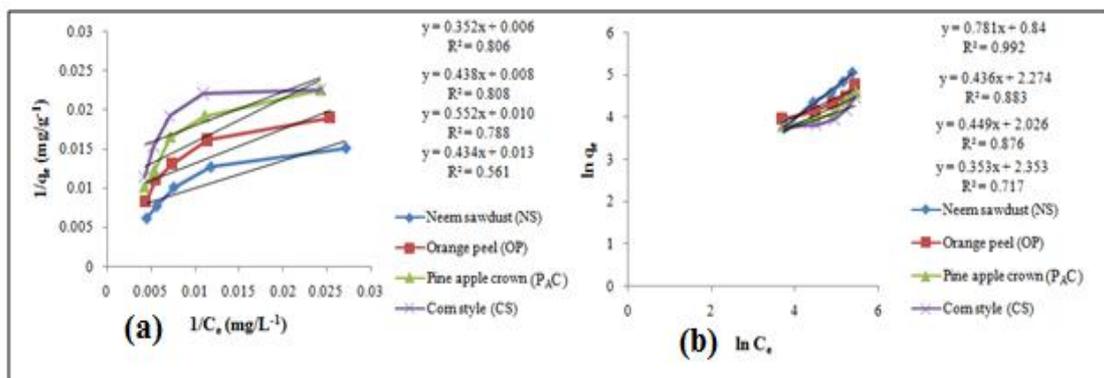
**Table 1: Linear regression data for Langmuir and Freundlich isotherms for Lanthanum (III) biosorption.**

Model	Parameters	FS	PC	ES	C <sub>R</sub> S	NS	OP	P <sub>A</sub> C	P <sub>A</sub> C
Langmuir	q <sub>m</sub> (mg/g)	250.0	200.0	100.0	90.9	166.6	125.0	100.0	76.9
	K <sub>L</sub>	0.02	0.01	0.02	0.02	0.02	0.01	0.02	0.02
	R <sup>2</sup>	0.985	0.912	0.780	0.643	0.806	0.808	0.788	0.561
Freundlich	K <sub>f</sub> (mg/g)	23.1	7.9	8.6	8.5	2.3	9.7	7.5	10.5
	n	2.5	1.8	2.3	2.4	1.3	2.3	2.2	2.8
	R <sup>2</sup>	0.984	0.970	0.873	0.833	0.992	0.883	0.876	0.717

\* FS- Fish scales; PC- Prawn carapace; ES- Egg shell; C<sub>R</sub>S- Crab shell; NS- Neem sawdust; OP- Orange peel; P<sub>A</sub>C- Pineapple crown; CS- Corn style.



**Figure 5: (a) Langmuir and (b) Freundlich isotherm models for lanthanum(III) adsorption by animal sources.**



**Figure 6: (a) Langmuir and (b) Freundlich isotherm models for lanthanum(III) adsorption by plant sources.**

### CONCLUSION

In the present study, the sorption characteristics of biowaste materials for the recovery of lanthanum(III) was assessed. The maximum biosorption capacity was obtained for FS and NS. Langmuir and Freundlich models were used for the mathematical modeling of the biosorption equilibrium of lanthanum(III) ions onto biosorbents. The biosorption equilibrium data fitted well to the Langmuir model for FS and Freundlich model for NS. As the biowaste materials viz. FS and NS are cost free easily available materials and showed maximum adsorption capacity for lanthanum (III), they can be used as potential biosorbents for the recovery of La(III) from aqueous environment.



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