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Screening of Biowaste Materials for the Sorption of Cerium (III) from Aqueous Environment.

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ABSTRACT

The adsorption of cerium (III) from aqueous solution has been investigated on various biosorbents of plant and animal origin. The biosorbents of animal origin viz. crab shell (C_RS), prawn carapace (PC), fish scales (FS), egg shell (ES) and plant origin viz. neem sawdust (NS), corn style(CS), pineapple crown (P_AC), orange peel (OP) were used for the study. The influence of various factors viz. pH, contact time, biomass dosage and initial metal concentration on cerium sorption were investigated under batch mode. Maximum removal of cerium was noted by the sorbents of animal origin (PC) and plant origin (CS) respectively. The cerium adsorption capacities of PC, ES, C_RS, FS were found to be 1000.0, 166.6, 90.9, 200.0 mg/g whereas 250.0, 142.8, 71.4 and 200.0 mg/g were noted for CS, P_AC, OP , NS respectively. Langmuir and Freundlich models were applied to characterize the adsorption process. The adsorption data for prawn carapace (PC) fitted well with the Freundlich isotherm model whereas Langmuir model exhibited best fit in case of corn style (CS).

Key words: Biowaste material, Biosorption, Cerium (III) , Isotherm model.

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INTRODUCTION

Cerium, as the most abundant and one of the important members of the rare earth metals (REMs), has some well-established uses which are quite different from others [1]. It has many potential uses such as chemical engineering, luminescence, agriculture, catalysis, nuclear energy, metallurgy microelectronics, therapeutic application, magnetism. High purity is usually required for its utilization in industry where it is used, for example, for sulfur control in steels, ceramic, catalyst support, pyrophoric alloys, publishing powders, etc. Cerium(III) is accompanied by other rare earth elements in its minerals, as well as in spent nuclear fuel [2]. Radioisotopes of Cerium(III) are marked products of nuclear fission and common constituent of liquid radioactive wastes arising from nuclear power productions [3]. The toxicity of Ce(III) is considered to be in low or moderate range [4]. Removal of Ce(III), because of its importance as a radiotoxic fission product in radioactive waste, has been the subject of several investigations [3,5]. Therefore, separation, sorption and recovery of cerium from nuclear and industrial waste streams are important both environmentally and economically.

Several conventional methods viz., pyrometallurgy, hydrometallurgy, solvent extraction, ion exchange and chemical precipitation were employed for the separation of REMs from its associated minerals[6]. Disadvantages associated with conventional methods are highly expensive, generation of secondary metabolites, special operation condition and restriction on separable REMs [7]. An efficient and eco-friendly method is needed to separate and recover the rare earth elements. Thus biosorption is an alternative method for the recovery of REMs [8,9].

Biosorption can be defined as the removal of metal or metalloid species, compounds and particulates from solution by non- living biological matter [10]. The process is rapid, low cost, eco-friendly, effective and non- generation of secondary metabolites in comparison with conventional chemical methods [11]. Biosorbent materials execute a high metal loading capacity and in some cases are highly specific for elements of particular interest [12]. The utilization of inexpensive biosorbents is currently receiving wide attention because of their abundant availability [1]. There are few reports on cerium(III) biosorption using leaf powder [13], crab shell [14], bacterial biomass [15] and *Citrus reticulate*[1] etc. In the present study, various biowaste materials of animal and plant origin which are available abundantly were used and screened as biosorbents for the removal of Ce(III) from aqueous solution. The effects of solution pH, initial metal concentration, biosorbent dosage, and contact time on cerium 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_RS), prawn carapace (PC), fish scales (FS), egg shell (ES) and plant origin viz. neem sawdust (NS), corn style(CS), pineapple crown (P_AC), orange peel (OP) were used as biosorbents. All the materials were obtained from local market, washed thoroughly with deionized water and dried at 60^{o}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 µm.

Preparation of Cerium (III) solution

Stock solution (1000 mg/L) of cerium (III) was prepared by dissolving required quantity of cerium(III) chloride dissolved in deionised water. For experiments, 100 mg/L of Ce (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±1^{o}C on a rotary shaker at 120 rpm varying pH ranging from 3.0 to 9.0, initial Ce (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 Ce (III) present in the filtrate was estimated using UV spectrophotometer at 252.4 nm wavelength.

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

$$q_e = \frac{C_0 - C_f}{M} \times V \qquad (1)$$

Where q is the sorption capacity i.e. the amount of Ce(III) ion biosorbed onto a unit amount of biomass (mg/g) ; C_0 and C_f are the concentrations (mg/ L) of Ce(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 biosorbents 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 on Ce (III) sorption

The effect of pH on cerium (III) biosorption is shown in Figure 1. Maximum Ce(III) uptake was noted at pH 6.0 for prawn carapace and corn style. Decrease in cerium uptake was noted below the optimum pH value because of the precipitation and competition faced by hydronium ions [16]. Thus, the order of Ce(III) uptake in case of plant source and animal source was as follows: Corn style>Pine apple crown>Orange peel and Neem saw dust ; Prawn carapace> Egg shell> Fish scales> Crab shell.

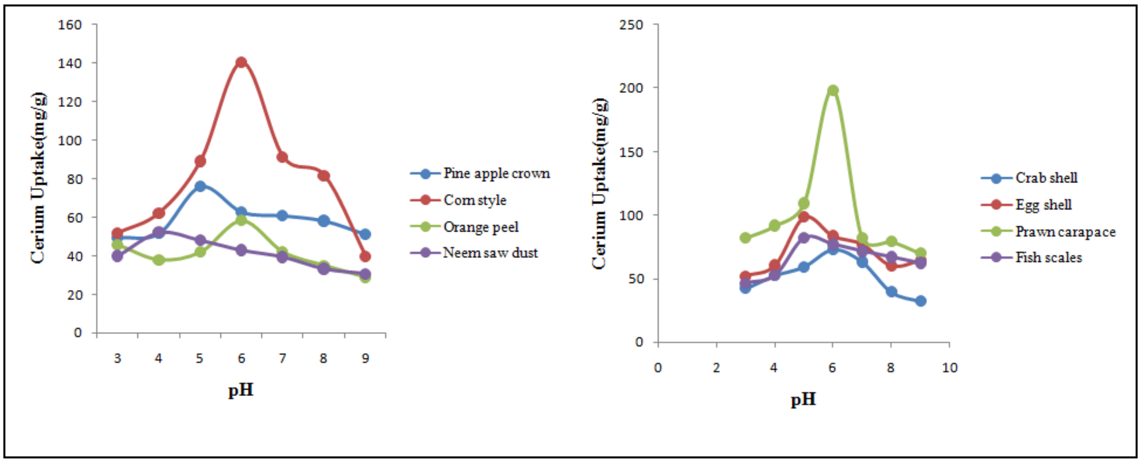

Figure 1: Effect of pH on Ce(III) biosorption using biowaste materials

Effect of initial metal ion concentration on Ce (III) sorption

The initial metal 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]. The effect of initial metal ion concentration on the Ce(III) uptake was studied by varying cerium concentration from 50 mg/L to 350 mg/L (Figure 2). In case of low Ce (III) concentration, the proportion of the initial number of moles of metal ions to the available surface area is lesser and later the fractional adsorption process becomes independent of initial concentration. But at higher concentration, the uptake of metal ions depends on the initial concentration due to the availability of the fewer adsorption sites. As the concentration of Ce (III) increased, the uptake was also found to increase and remained constant after equilibrium time. Maximum cerium uptake was noted at 300 mg/L for PC and 250 mg/L for CS. Thus, the order of Ce(III) uptake in case of plant source and animal source was as follows: Corn style>Orange peel>Neem saw dust and Pine apple crown ; Prawn carapace> Egg shell> Fish scales> Crab shell.

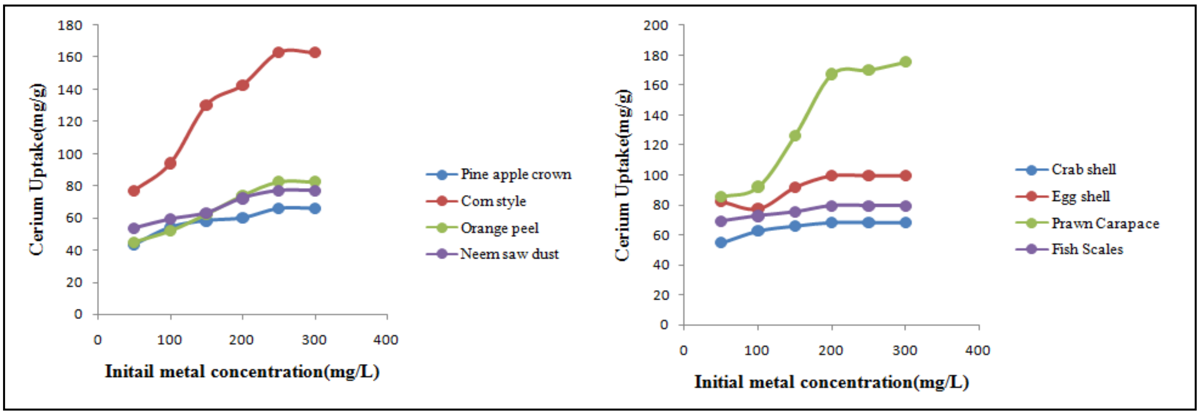

Figure 2: Effect of initial metal concentration on Ce(III) biosorption using biowaste materials

Effect of biomass dosage on Ce(III) sorption

The effect of biomass dosage on Ce (III) uptake is shown in Figure 3. The dosage was varied from 0.05 to 0.35 g/L. Cerium uptake capacity was found to increase with an increase in the biosorbent dosage. The highest Ce(III) uptake by CS and PC was 0.25 g/L under optimized condition. Decrease in cerium uptake was noted beyond the optimum value due to the insufficient number of adsorption sites and clumping of the biosorbents [18]. The order of Ce (III) uptake in case of plant source and animal source was as follows: Corn style>Orange peel> Neem saw dust and Pine apple crown; Prawn carapace>Fish scales>Egg shell> Crab shell.

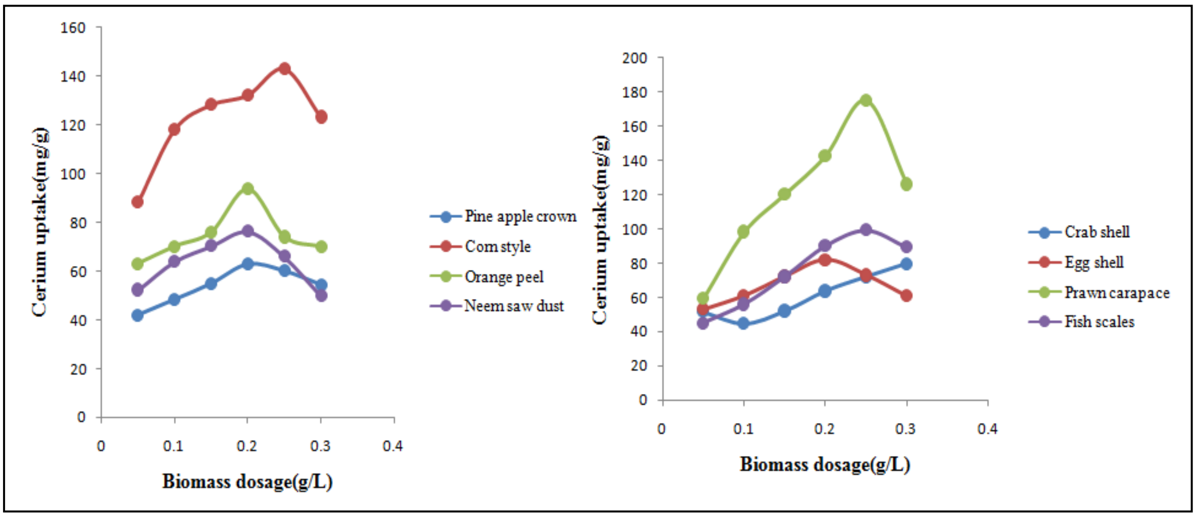

Figure 3: Effect of biomass dosage on Ce(III) biosorption using biowaste materials

Effect of contact time on Ce(III) sorption

Figure 4 showed that the cerium uptake efficiencies of the biosorbents sharply increased with the increase in time and attained equilibrium after a certain period of time. An increase in uptake was noted till a period of 6h in case of animal sources and 4h in case of plant sources respectively. Beyond the optimum time period, the uptake values were found to reach a steady state with further increase which could be possibly due to the equilibrium established in sorbate-sorbent interactions [19]. Among the various animal and plant sources used, maximum cerium uptake of 218.3 mg/g and 180.2 mg/g by PC and CS was noted under optimized condition. The order of Ce (III) uptake in case of plant source and animal source was as follows: Corn style>Pine apple crown> Neem saw dust > Orange peel ; Prawn carapace>Fish scales>Egg shell> Crab shell.

Adsorption isotherms

Analysis of equilibrium data is important for developing a model that can be used for designing the adsorption system. The Langmiur and Freundlich isotherm model were used to study the nature of sorption process.

Langmuir equation is valid for monolayer sorption on to a surface with a finite number of identical sites [20] and its expression is given by (Eq. 2)

$$q_{eq} = \frac{q_{\max} bC_{eq}}{1 + bC_{eq}} \tag{2}$$

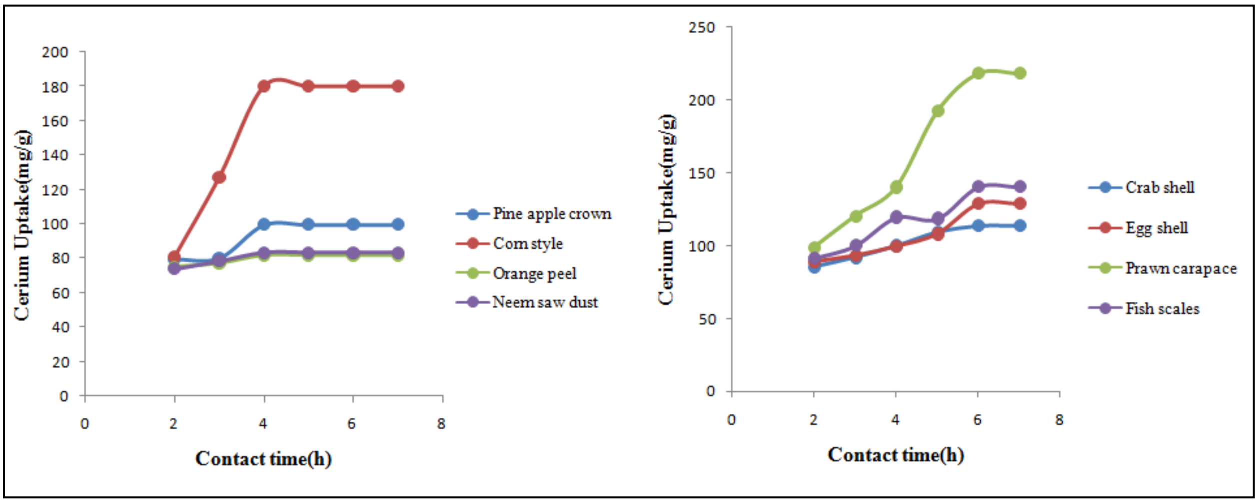

Figure 4: Effect of contact time on Ce(III) biosorption using biowaste materials

where q_{eq} (mg/g) and C_{eq} (mg/L) are amount of absorbed cerium per unit weight of biomass and unadsorbed cerium concentration in solution at equilibrium respectively. q_{max} (mg/g) is the maximum amount of cerium 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

$$\frac{1}{q_{eq}} = \frac{1}{q_{\max}} + \frac{1}{bq_{\max} C_{eq}} \tag{3}$$

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

$$q_e = K_F C_e^{1/n} \tag{4}$$

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 [21].

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

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

The data obtained for cerium(III) adsorption onto biowaste materials were fitted in the models. The values of Langmuir and Freundlich constants for the biosorption of cerium(III) by various animal and plant sources are presented in Table-1. Corn style (CS) showed the maximum cerium uptake capacity of 250.0 mg/g and a high R^2 value (0.994) compared to other biosorbents of plant origin (Figure 5a,b). Thus, Langmuir model was found to be the best fit for CS which suggested that the cerium ions are adsorbed in the form of monolayer coverage on the biosorbent CS. In case of biosorbents of animal origin, Freundlich model was found to be the best fit for prawn carapace (PC) and higher correlation coefficient value ($R^{2=}$0.983) with slope (1/n) and intercept log K_f was noted compared to other biosorbents(Figure 6a,b) suggesting the heterogeneous mode of adsorption.

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

Model	Parameters	PC	ES	C_RS	FS	CS	P_AC	OP	NS
Langmuir	q_m(mg/g)	1000.0	166.6	90.9	200.0	250.0	142.8	71.4	200.0
	K_L	0.02	0.02	0.04	0.01	0.01	0.02	0.07	0.04
	R^2	0.979	0.960	0.892	0.756	0.994	0.920	0.927	0.955
Freundlich	K_F(mg/g)	25.4	24.9	4.9	18.2	25.7	16.6	5.3	13.6
	n	2.6	3.5	2.8	2.7	2.9	3.3	3.0	3.0
	R^2	0.983	0.610	0.772	0.592	0.980	0.607	0.416	0.327

*PC- Prawn carapace; ES- Egg shell; C_RS- Crab shell; FS- Fish scales; CS- Corn style; P_AC- Pineapple crown; OP- Orange peel; NS- Neem sawdust.

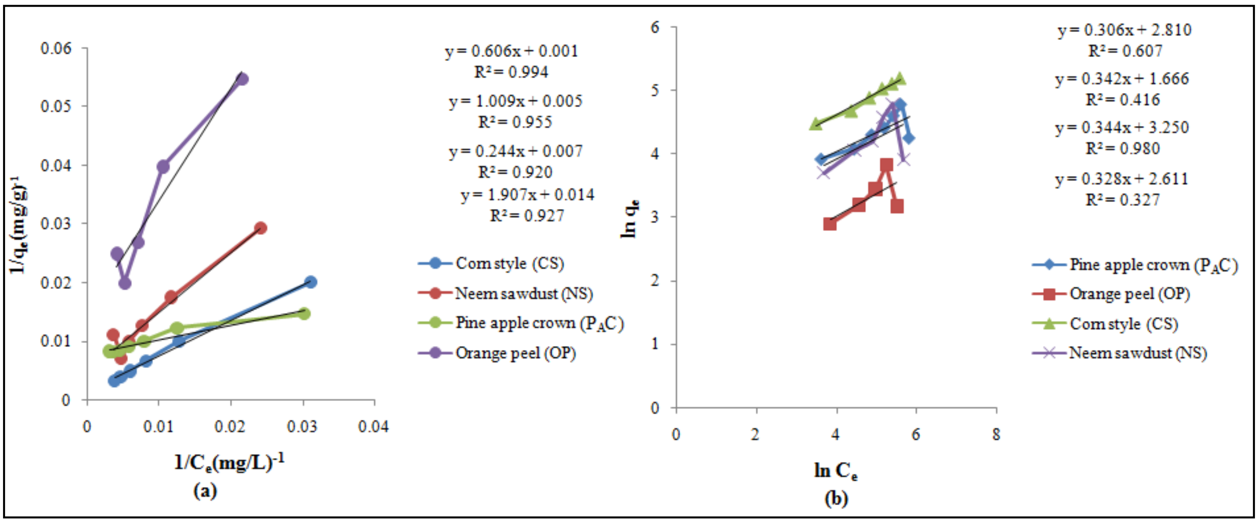

Figure 5: (a) Langmuir and (b) Freundlich isotherm models for Ce(III) adsorption using plant sources

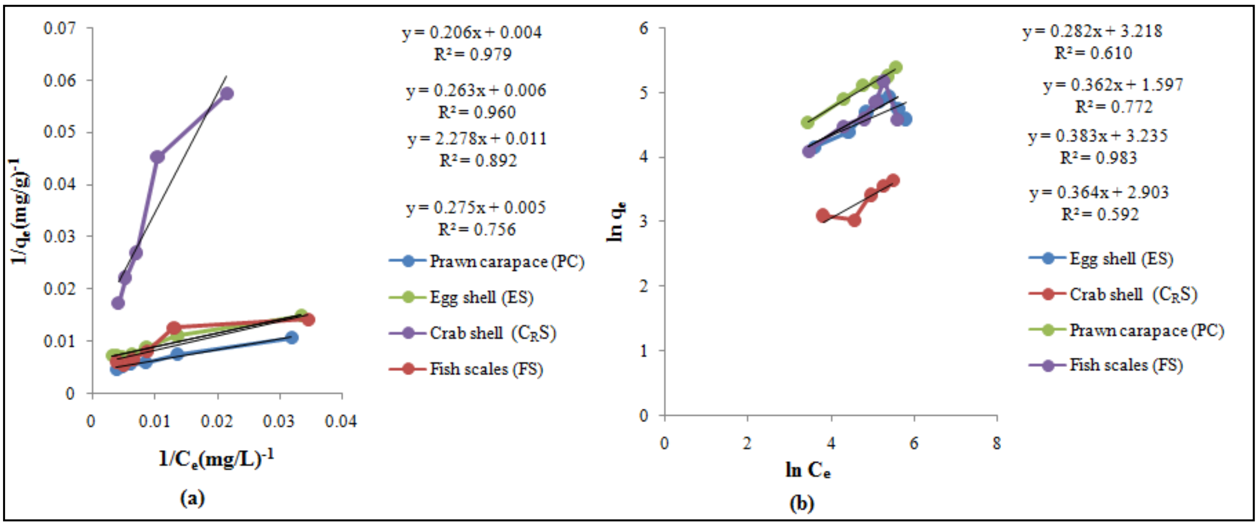

Figure 6: (a) Langmuir and (b) Freundlich isotherm models for Ce(III) adsorption using animal sources

CONCLUSION

The aim of this work was to find out the potentiality of biowaste materials to adsorb cerium (III) from aqueous solution. The biowaste materials of plant and animal origin were screened based on their cerium(III)uptake capacities. Among the biosorbents, the maximum cerium biosorption capacities were shown by prawn carapace (PC) of animal origin and corn style (CS) of plant origin respectively. Equilibrium data were fitted to Langmuir and Freundlich models. The Langmuir model exhibited a best fit to the sorption of Ce(III) on CS confirming the homogeneous monolayer mode of adsorption and Freundlich models showed a best fit to the sorption of Ce(III) on PC confirming the heterogeneous mode of adsorption. Based on the results of the present study, it can be concluded that prawn carapace and corn style could serve as a potential biosorbent for the efficient sorption of cerium from aqueous environment.

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REFERENCES

[1] Mostaedi MT. Chem Ind Chem En Q 2013; 19 (1) : 79-88.
[2] Awual R Md, Yaita T, Shiwaku H. Chem Eng J 2013; 327-335.
[3] Dubey S S, Rao B S. J Hazard Mater 2011; 186 : 1028-1032.
[4] Filipi R, Nesmerak K, Rucki M, Roth Z, Hanzlikova I, Tichy, M. Chem Listy 2007; 101 : 793-798.
[5] Yantasee W, Fryxell GE, Addleman RS, Wiacek RJ, Koonsiripaiboon V , Pattamakomsan K, Sukwarotwat V, Xu J, Raymond KN. J Hazard Mater 2009;168 : 1233-1238.
[6] Fu F, Wang Q. J Environ Manage 2011; 92: 407-418.
[7] Wase DA.(Ed). CRC Press 1997; pp.11-88.
[8] Babel S, Kurniawan TA. J Hazard Mater 2003;97:219-243.
[9] Dias JM, Alvim-Ferraz MCM, Almeida MF. J Environ Manage 2007; 85:262-274.
[10] Davis TA, Volesky B, Mucci A. Water Res 2003; 37: 4311-4330.
[11] Ahuja P, Gupta R, Saxena RK. Process Biochem 1999; 34: 77-85.
[12] Kazy SK, Das SK, Sar P. J Ind Microbiol Biot 2006; 33: 773- 783.
[13] Sert S, Kütahyali C, Inan S, Talip Z, Çetinkaya B. Eral M. Hydrometallurgy 2008; 90 :13-18.
[14] Vijayaraghavan K, Balasubramanian R. Chem. Eng. J 2010; 163 (3) : 337-343.
[15] Xu S X, Zhang S M, Chen K, Han J F, Liu H S, Wu K. J Rare Earth 2011; 29(3): 265-270.
[16] Palmieri MC, Volesky B, Garcia O. Hydrometallurgy 2002; 67: 31-36.
[17] Lalhruaitluanga H, Jayaram K, Prasad MNV, Kumar KK. J Hazard Mater 2010; 175: 311-318.
[18] Baral SS, Das SN, Rath P. Biochem Eng J 2006; 31:216-222.
[19] Verma A, Chakraborty S, Basu JK. Sep Purif Technol 2006; 50: 336-341.
[20] Langmuir I. J Am Chem Soc 1918; 40:1361-1403.
[21] Freundlich HMF. J Phys Chem 1906; 57:385-470.