Adsorption of La$^{3+}$, Ce$^{3+}$ from Aqueous Solutions by Bayberry Tannin Grafted Chitosan

Ying Jing$^{1*}$, Yunzhu Chen$^1$, Xuemei Wang$^1$, Lichao Nengzi$^1$
$^1$School of Environment & Resource, Xichang University, Xichang 615000
*e-mail address: 229085116@qq.com

Abstract. Bayberry tannin grafted with chitosan (CS-BT) had been successfully prepared and their adsorption performance had been studied La$^{3+}$, Ce$^{3+}$ rare earth ions aqueous solutions. The as-prepared absorbents were characterized by Fourier transform infrared spectrometer and scanning electron microscopy. The result showed under optimal conditions [T=40℃; C=2.0 g/L; pH=3.0 (La$^{3+}$), pH=4.0 (Ce$^{3+}$);] that the saturation adsorption capacities of CS-BT to La$^{3+}$, Ce$^{3+}$ were 58.42 mg/g, 800.08 mg/g, respectively, when [T=30 ℃; C=1.0 g/L; pH=4.0 (La$^{3+}$), Ce$^{3+}$;] the difference of adsorption quantity between La$^{3+}$ and Ce$^{3+}$ reach up to 101.5 mg/g by using the absorbent (CS-BT). The adsorbent exhibited better adsorption capacity to Ce$^{3+}$ than that of La$^{3+}$. The CS-BT had high adsorption rate and could achieve basic saturated adsorption in about 5 min. It was found that the adsorption kinetics was well described by the adsorption isotherms followed Freundlich (La$^{3+}$, Ce$^{3+}$) adsorption model and the pseudo-second order kinetic model. The research indicated CS-BT could be used as the cheaper and friendly absorbent in enrichment and separation of RE$^{3+}$ in aqueous solution.

1. Introduction

Rare earth is a valuable resource. However, the rare earth ions in water often cause eutrophication, and be pernicious to the health of the human beings$^{[1-3]}$. At present, several of methods have been established to remove the RE$^{3+}$ in waste water, such as solvent extraction$^{[4,6]}$, ion exchanging$^{[7]}$ and adsorption$^{[8,9]}$. Among these methods, solvent extraction requires a large amount of organic solvents, which are toxic and unfriendly to the environment$^{[10]}$. Ion exchanging has overcome these drawbacks but usually exhibit low efficiency. Adsorption has attracted much attention for its environment friendly and high efficiency. Various metal ions have been removed from water successfully by using adsorption methods$^{[11-13]}$. The property of the adsorbents is the most important issue in adsorption process. The adsorbents could be divided into two categories, including artificial products and natural ones. Due to the nature of environmental friendly, renewable and have no secondary pollution, modified biomass are used for adsorption of rare earth ions in wastewater. Typical natural products such as chitosan$^{[14,15]}$, microorganisms$^{[9]}$, plant tannin$^{[16-18]}$ and biological materials$^{[19,20]}$ have been used as adsorbents for removing metal ions in water.

Chitosan and its derivatives have been used as antimicrobial agents, biosorbents and polymers for controlled drug release due to their excellent biodegradability, non toxicity and adsorption properties. Chitosan is also capable of adsorbing a number of metal ions as its amino groups can serve as chelation sites. Because their high nitrogen content and porosity, chitosan based adsorbents have exhibited relatively high adsorption and kinetics for most heavy metals$^{[14]}$. The presence of amino groups makes chitosan an efficient metal scavenger, capable of retaining metal ions from waste water. Nevertheless, the poor stability of chitosan in aqueous acidic media restricts its application as...
abiosorbent, as many industrial effluents tend to be acidic. Chemical modifications of chitosan are thereby essential to improve its chemical stability, mechanical strength and adsorption capacity in acidic media.

Plant tannin, one of the most abundant biomasses, is kind of natural polyphenols which widely exist in roots, barks, leaves and fruits of plants. There are large amount of phenolic hydroxyls in tannin’s structure. These phenolic hydroxyls could from five-members chelating ring with various metal ions, endowing high affinity of tannin toward metal ions. However, tannin could not be used as adsorbents for its water solubility \([16-18]\). Support matrix is necessary for immobilizing tannin during the adsorbent preparation.

Therefore, we have the task of the group to chitosan be grafted with tannin, the advantages of both the chitosan and bayberry tannin preparation of a larger adsorption capacity of the adsorbent, the adsorption of rare earth ions in industrial water. The modified material could concentrate the rare earth ions, and the used absorbents can be transformed into rare earth oxide by calcination. In this study, bayberry tannin adsorbent (CS-BT) was obtained by grafting chitosan using glutaraldehyde as cross-linking agent. Subsequently, the adsorbent was utilized in removing \(\text{RE}^{3+}\) in water. The properties of these adsorbents were systematically investigated under different conditions, such as pH, concentrations, temperature and time, etc.

2. Materials and methods

2.1. Reagents and instrument

\(\text{Ce}_2(\text{CO}_3)_3\), \(\text{La}_2\text{O}_3\) and other reagents were of analytical grade, which were purchased from Kelong chemical reagents factory (Chengdu, China) and used without further purification. Deionized water was used for the preparation of all solutions. The pH adjustment of solutions was carried out using 0.1mol/L \(\text{HNO}_3\) and \(\text{HCl}\) or 0.1 mol/L \(\text{NaOH}\) solutions. The bayberry tannin (BT) was obtained from the barks of bayberry trees. Chitosan with 95% degree of deacetylation (DD) was purchased from Aladdin (CAS: 9012-76-4).

The content of aqueous solution (\(\text{La}^{3+}, \text{Ce}^{3+}\)) and mixed aqueous solution (\(\text{La}^{3+}, \text{Ce}^{3+}\)) rare earth solution was determined by in Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Optima, 8000DV, Perkin-Elmer, US). The morphology of the samples was observed with scanning electron microscope (SEM, FEI Quanta 250). And these absorbents were characterized by Fourier transform infrared spectroscopy (FT-IR, Nicolet 2005).

2.2. Preparation of adsorbent

2.2.1. Preparation of the adsorbent (CS-BT)

0.10.0 g of bayberry tannin was dissolved in 100mL distilled water, and the initial pH of solution was adjusted to 7 (0.1mol \(\text{NaOH}\)). After add 5.0 g chitosan mixture was stirred at 318K for 6 hours. After reaction, the product was thoroughly washed with deionized water Neutral, Then add 300mL glutaraldehyde (20 g/L), and the initial pH of solution was adjusted to 6.5 (0.1mol \(\text{NaOH}\)) mixture was stirred at 323K for 6h. Subsequently, the product was thoroughly washed with deionized water and dried in vacuum at 318 K for 24 hours, and finally the CS-BT adsorbent was obtained.

2.2.2. Effect of initial pH on adsorption capacity of the adsorbent

0.1 g of adsorbent (CS-BT) was suspended in 50 mL of \(\text{La}^{3+}, \text{Ce}^{3+}\) aqueous solutions (\(\text{La}^{3+}, \text{Ce}^{3+} 200\,\text{mg/L}\)) and \(\text{RE}^{3+}\) (\(\text{La}^{3+}, \text{Ce}^{3+}\)) mixed aqueous solutions (\(\text{La}^{3+} 100\,\text{mg/L}, \text{Ce}^{3+} 100\,\text{mg/L}\)), respectively. The pH of the solutions was ranged from 2.0 to 5.5. The adsorption process was conducted at 303K with constant stirring for 1 hour. When the adsorption was completed, the suspension was filtered and the concentration of \(\text{La}^{3+}\) and \(\text{Ce}^{3+}\) in filtrate was analyzed by ICP-OES. The adsorption capacity \((q_{e}, \text{mg/g})\) of the adsorbent (CS-BT) to \(\text{La}^{3+}\) and \(\text{Ce}^{3+}\) was obtained by mass balance calculations of \(\text{La}^{3+}\) and \(\text{Ce}^{3+}\) in solution before and after adsorption.
2.2.3. Effect of initial temperature on adsorption capacity of the adsorbent. 0.1 g of adsorbent (CS-BT) was suspended in 50.0 mL La\(^{3+}\), Ce\(^{3+}\) of aqueous solutions with initial concentration ranging from 0.2 to 2.5 g/L. The pH of La\(^{3+}\) and Ce\(^{3+}\) aqueous solutions was adjusted to 3.0, 4.0. The adsorption experiments were conducted by constant shaking at 303 K, 308 K, 313 K, 318 K for 1 hour, respectively. Then the suspension was filtered and the concentration of La\(^{3+}\) and Ce\(^{3+}\) in filtrate was analyzed.

0.1 g of adsorbent (CS-BT) was suspended in 50.0 mL RE\(^{3+}\) (La\(^{3+}\), Ce\(^{3+}\)) of mixed aqueous solutions with initial concentration ranging from 0.2 to 1 g/L (La\(^{3+}\) and Ce\(^{3+}\) were the same concentration). The pH of La\(^{3+}\), Ce\(^{3+}\) mixed aqueous solutions was adjusted to 4.0. Then the suspension was filtered and the concentration of La\(^{3+}\) and Ce\(^{3+}\) in filtrate was analyzed. Uptake experiments were performed by placing 0.1 g of CS-BT in a series of flasks containing 50 mL (La\(^{3+}\) 100 mg/L, Ce\(^{3+}\) 100 mg/L) of the rare earth ion solution at pH 5.5. The flasks were agitated on a shaking for 30 min while keeping the temperature at 303 K, 313 K, 323 K, 333 K.

2.2.4. Adsorption kinetics. Measurements of metal ion uptake using a batch method were conducted by placing 0.1 g of CS-BT in a flask containing 50 mL (La\(^{3+}\), Ce\(^{3+}\) 200 mg/L) rare earth ion solution at pH 3.0 (La\(^{3+}\)), 4.0 (Ce\(^{3+}\)) and 50 mL (La\(^{3+}\) 100 mg/L, Ce\(^{3+}\) 100 mg/L) mixed rare earth ion solution at pH 4.0, respectively. The contents of the flask were agitated on a shaking 303 K. Then the suspension was filtered and the concentration of La\(^{3+}\) and Ce\(^{3+}\) in filtrate was analyzed.

3. Results and discussions

3.1. Characterization of adsorbents

The SEM micrographs spectra of CS (a), CS-BT (b) are shown in Fig.1. The result demonstrates adsorbents have the good particulate structure. We can observe that the particle morphology of CS have significant changes compared with CS-BT. The particle of CS was distributed for grafting tannin and the surface of prepared absorbents was rough, which can be helpful to absorption performance. While the tannin and hydroxyl ball can form hydrogen bonds to cause a little trend of aggregation, so the particle of CS-BT was seen to be bigger than CS.

FTIR spectra of the CS (a), CS-BT (b), BT (c) are shown as Fig. 2. As Fig. 2 is shows, FTIR spectrum is a useful tool to identify functional groups in molecules, and can obtain structural and bond information on a complex. FTIR spectrum of this composite is shown in Fig. 2(b). The major bands for bayberry tannin immobilized on chitosan (CS-BT) can be assigned as follows: 3434.16 cm\(^{-1}\) (-OH and -NH\(_2\) stretching vibrations), which are on the surface of bayberry tannin (-OH) and chitosan (-OH and -NH\(_2\)). 2925.43 cm\(^{-1}\) (-CH stretching vibration in -CH and -CH\(_2\)), 3434.16 cm\(^{-1}\), 2925.43 cm\(^{-1}\), 1633.16 cm\(^{-1}\) (N-H bending vibration), 1456.02 cm\(^{-1}\) (-CH symmetric bending vibrations in -CHOH-), The benzene skeleton vibration of 1633.16 cm\(^{-1}\) and 1456.02 cm\(^{-1}\) peaks in Bayberry tannin molecules in peak benzene skeleton vibration absorption structure; benzene ring phenol hydroxy 1399.86 cm\(^{-1}\) peak in Bayberry tannin molecules in the in-plane bending vibration absorption
peak[16,18]. These analysis results showed that the CS-BT was prepared successfully cured onto the surface of the carrier.

Fig 1. SEM images of (a) chitosan; (b) bayberry tannin grafted chitosan.

Fig 2. FTIR image of (a) CS, (b) CS-BT, (c)BT.

3.2. Adsorption performance of the adsorbent (CS-BT)

3.2.1. Effect of initial pH on adsorption capacity of the adsorbent. Fig. 3(a) shows the influence of initial pH on the adsorption capacity of CS-BT to La$^{3+}$ and Ce$^{3+}$ aqueous solutions. The adsorption capacities of the adsorbent on La$^{3+}$ and Ce$^{3+}$ not significantly increased when the pH increased from 2.0 to 5.5. Fig. 3 (b) shows the influence of initial pH on the adsorption capacity of CS-BT to La$^{3+}$ and Ce$^{3+}$ in RE$^{3+}$ (La$^{3+}$ and Ce$^{3+}$) mixed aqueous solutions. There was a significant competition between the La$^{3+}$ and Ce$^{3+}$ on adsorbent. The optimal pH for adsorption of CS-BT on La$^{3+}$ and Ce$^{3+}$ which could reach the maximum capacity were 3.0 and 4.0, respectively. The result based on that the dissociation degree of phenolic hydroxyls in BT should be causes little impact by the pH of solution. However, due to the more -OH existing in the solution, the degree of hydrolysis of La$^{3+}$ and Ce$^{3+}$ increasing, and the oxidation in the tannin, the adsorption capacity of La$^{3+}$ and Ce$^{3+}$ was decreased by adsorbent. For the coordination of rare earth ions enhanced with the increase of the atomic number, the adsorbent showed better adsorption capacity to Ce$^{3+}$ than that of La$^{3+}$. Moreover, CS-BT exhibits higher adsorption capacity than CS, probable for potential active functional groups of bayberry tannin. The adsorbents can be new cheaper materials to separate rare earth for the deference of adsorption properties.

Fig 3. Effect of pH on the uptake of La$^{3+}$ and Ce$^{3+}$ ions by CS-BT (A. Initial concentration 200mg/L; B. Initial concentration 100mg/L; contact time 1 h; shaking rate 200 rpm, 30 °C).
3.2.2. Adsorption isotherms. Fig. 4 the initial concentration of Fig. 4(a, b) La$^{3+}$ and Ce$^{3+}$ was in the range of 0.2 to 2 g/L and Fig. 3 (c) La$^{3+}$ and Ce$^{3+}$ was in the range of 0.2 to 1 g/L. The adsorption amount of adsorbents to La$^{3+}$ and Ce$^{3+}$ adsorption capacity increased along with the increasing of concentrations. The adsorbent showed higher adsorption capacity with the higher Ce$^{3+}$ concentration. The result showed La$^{3+}$ under optimal conditions [T=40 ºC; C=2 g/L; pH=3.0 (La$^{3+}$)] and Ce$^{3+}$ under optimal conditions [T=40 ºC; C=1 g/L; pH=4.0 (Ce$^{3+}$)] was optimal the adsorption capacity by using the absorbent (CS-BT). Moreover, temperature had little effect of Ce$^{3+}$ on the adsorption capacity. When [T=30 ºC; C=1 g/L; pH=4.0 (La3+, Ce3+)] the difference of adsorption quantity to La$^{3+}$, Ce$^{3+}$ reach up to 101.5 mg/g by using the absorbent (CS-BT), The adsorbent exhibited better adsorption capacity to Ce$^{3+}$ than that of La$^{3+}$.

Adsorption isotherms dates were further fitted by Langmuir and Freundlich isothermal equations. The experimental La$^{3+}$ dates could be fitted by the classical Langmuir [21] and Freundlich equation. The experimental Ce$^{3+}$ dates could be fitted by Freundlich equation.

Then Langmuir and Freundlich equations are expressed as follows:

\[ q_e = q_{\text{max}} b C_e / (1 + b C_e) \]  \( \text{(1)} \)

\[ q_e = K_C C_e^{1/n} \]  \( \text{(2)} \)

where \( q_e \) is the adsorption capacity of La$^{3+}$ and Ce$^{3+}$ at equilibrium (mg/g), \( q_{\text{max}} \) is the maximum adsorption capacity (mg/g), \( C_e \) is the concentration of La$^{3+}$ and Ce$^{3+}$ at equilibrium (g/L), \( b \) and \( k \) are the Langmuir constant and the Freundlich constant, respectively. The Langmuir and Freundlich models La$^{3+}$ fitting results are summarized in Table 1 and the Freundlich models Ce$^{3+}$ fitting results are summarized in Table 2.

As shown in Table 1, Table 2 and Table 3 the Langmuir and Freundlich equation gives satisfied fitting to the isotherm data with correlation constant (R2) higher than 0.84, and the theoretical adsorption capacities are close to those determined by experiments. All these results suggested that La$^{3+}$ may be adsorbed in the form of monolayer and multi-layer on the surface of the adsorbent (CS-BT). However, Ce$^{3+}$ Freundlich equation parameter \( 1/n \) is a constant related to the adsorption force. The \( 1/n \) value is smaller and adsorption is stronger, so the Freundlich equation parameters in Table 1, Table 2 and Table 3 are less than 2, which indicates that the adsorption of La$^{3+}$ and Ce$^{3+}$ by the adsorbent (CS-BT) can be carried out under mild conditions.

![Fig 4](image_url)

**Fig 4.** Effect of initial concentration and temperature on the adsorption capacity of La$^{3+}$ and Ce$^{3+}$ concentrations and La$^{3+}$ and Ce$^{3+}$ in the mixed concentrations.

**Table 1.** The Langmuir and Freundlich model parameters of the adsorption of La$^{3+}$ in the concentrations.

| Adsorbents | La$^{3+}$ | Langmuir | Freundlich |
|------------|-----------|-----------|------------|
|            | R²        | qmax      | RL         | KL         | R²        | KF        | 1/n        |
| CS-BT      | 30°C      | 0.8486    | 62.50      | 0.3650     | 8.7*10⁻⁴  | 0.9160    | 0.1498     | 0.7608     |
|            | 35°C      | 0.9772    | 66.67      | 0.2270     | 1.7*10⁻³  | 0.8811    | 0.1043     | 0.8611     |
|            | 40°C      | 0.9833    | 68.49      | 0.1818     | 2.4*10⁻³  | 0.9322    | 0.7992     | 0.5872     |
|            | 45°C      | 0.9880    | 32.89      | 0.1163     | 3.8*10⁻³  | 0.8985    | 1.4087     | 0.4178     |
Table 2. The Freundlich model parameters of the adsorption of Ce\(^{3+}\) in the concentrations.

| Adsorbents | Ce\(^{3+}\) | Freundlich |
|------------|-------------|------------|
|            | R\(^2\)     | K\(F\)     | 1/n        |
| CS-BT      |             |            |            |
| 30°C       | 0.9945      | 3.804\(\times\)10^{-2} | 1.3108     |
| 35°C       | 0.9886      | 3.976\(\times\)10^{-2} | 1.3139     |
| 40°C       | 0.9979      | 1.215\(\times\)10^{-2} | 1.4764     |
| 45°C       | 0.9683      | 9.979\(\times\)10^{-3} | 1.4902     |

Table 3. The Freundlich model parameters of the adsorption of La\(^{3+}\), Ce\(^{3+}\) in the mixed concentrations.

| Adsorbents | RE\(^{3+}\) | Freundlich |
|------------|-------------|------------|
|            | R\(^2\)     | K\(F\)     | 1/n        |
| CS-BT      |             |            |            |
| La\(^{3+}\) | 0.9609      | 9.913\(\times\)10^{-3} | 1.3009     |
| Ce\(^{3+}\) | 0.9970      | 1.628\(\times\)10^{-1} | 1.0015     |
| La\(^{3+}\), Ce\(^{3+}\) | 0.9940 | 1.605\(\times\)10^{-1} | 1.0570     |

3.2.3 Adsorption kinetics. Fig. 5 indicated that the adsorbent showed increase adsorption capacity with prolonged adsorption time on the four RE\(^{3+}\) (La\(^{3+}\), Ce\(^{3+}\)), which could achieve equilibrium adsorption in about 5 min. At the beginning of the adsorption process, adsorption capacity increased fast and then gradually reaches an equilibrium value in approximate. The initial concentration of La\(^{3+}\) and Ce\(^{3+}\) has no significant effect on the time needed to attain adsorption equilibrium. Therefore, it is reasonable to predict that the adsorption of La\(^{3+}\) and Ce\(^{3+}\) should take place at the outer surface of two adsorbents and the intraparticle diffusion resistance can be neglected. To further understand the adsorption process, the pseudo-first-order rate, pseudo-second-order rate, and intraparticle diffusion rate models were used to fit the adsorption kinetic data. The pseudo first-order rate (3), pseudo second-order rate (4) models are given as:

\[
\log (q_e - q_t) = \log q_e - k_1t/2.303
\]

\[
T/qt = 1/(k_2q_e^2) + t/q_e
\]

Where \(q_e\) and \(q_t\) are the amount of La\(^{3+}\) and Ce\(^{3+}\) adsorbed (mg/g) at equilibrium and at time \(t\) (min) respectively, and \(k_1\) and \(k_2\) are the rate constants of the pseudo-first-order-rate model (min\(^{-1}\)), pseudo-second-order-rate model (mg/g min\(^{-1}\)), respectively. The absorption reaction is in accordance with the pseudo-second order kinetic equation (Table 4), and it can be considered as the chemical adsorption reaction\(^{[22]}\).

Fig 5. Effect of time on the uptake of La\(^{3+}\) and Ce\(^{3+}\) ions by CS-BT (a. Initial concentration 200mg/L; b. Initial in mixed concentration 100mg/L; 30°C).
4. Conclusion
In this study, Bayberry tannin immobilized on chitosan (CS-BT) had been successfully prepared and applied for adsorbing mixed rare earth ions (La$^{3+}$, Ce$^{3+}$) aqueous solutions. The result showed the adsorbent exhibited better adsorption capacity to Ce$^{3+}$ than that of La$^{3+}$. The adsorption kinetics was in accordance with the pseudo two order rate equation and the resolution rate could reach 95.00% by 0.1 mol/L HNO$_3$ solution, so the reaction was the endothermic and chemical adsorption reaction. The CS-BT exhibited selectivity to Ce$^{3+}$ among these two rare earth ions (La$^{3+}$, Ce$^{3+}$), which have potential applications in enrichment and separation of RE$^{3+}$ in aqueous solution. The adsorbent (CS-BT) could concentrate the rare earth ions, and the used absorbents can be transformed into rare earth oxide by calcination.

References
[1] S Liu, Y Huang, X Zhu, X Liu. Environmental Effects of Ion-absorbed Type Rare Earth Extraction on the Water and Soil in Mining Area and Its Peripheral Areas. Environmental Science & Technology,2015.
[2] J Qin, X Chen, LI Zeng. Effects of rare earth on human health. Trace Elements Science,2002-06.
[3] QY Cai, Environmental Issues and Ecological Restoration of Ion-absorbed-type Rare Earth Deposit in South China, Territory & Natural Resources Study,2013.
[4] Y Wang, C Huang, F Li, Y Dong, X Sun. Process for the separation of thorium and rare earth elements from radioactive waste residues using Cyanex®; 572 as a new extractant, Hydrometallurgy,2017,169:158-164.
[5] MT Khaironie, M Masturah, MY Meor Sulaiman, S Nazaratul Ashifa. Solvent Extraction of Light Rare Earth Ions Using D2EHPA from Nitric Acid and Sulphuric Acid Solutions, Advanced Materials Research,2014,970(970):209-213.
[6] Z Chen, W T Wang, F N Sang, J H Xu, G S Luo. Fast extraction and enrichment of rare earth elements from waste water via microfluidic-based hollow droplet, Separation and Purification Technology,2017,174:352-361.
[7] DL Ramasamy, E Repo, V Srivastava, M Sillanpä. Chemically immobilized and physically adsorbed PAN/acetylacetone modified mesoporous silica for the recovery of rare earth elements from the waste-water-comparative and optimization study, Water Research,2017,114:264–276.
[8] Y Andrés, C Gérento. Removal of Rare Earth Elements and Precious Metal Species by Biosorption, Springer Netherlands,2011:179-196.
[9] H Moriwaki, H Yamamoto. Interactions of microorganisms with rare earth ions and their utilization for separation and environmental technology. Applied Microbiology and Biotechnology,2013,97(1):1-8.
[10] S Liu, Y Huang, X Zhu, X Liu. Environmental Effects of Ion-absorbed Type Rare Earth Extraction on the Water and Soil in Mining Area and Its Peripheral Areas, Environmental Science & Technology, 2015.

Table 4. the parameters of Pseudo-second-order model.

| Adsorbents         | RE$^{3+}$ | qe (calculated value) mg/g | qe (measured value) mg/g | Er     | k2 (g/mg.min) | R$^2$ |
|--------------------|-----------|----------------------------|--------------------------|--------|--------------|-------|
| CS-BT              | La$^{3+}$ | 9.59                       | 9.54                     | 0.52%  | 9.64*10-2    | 0.9958|
|                    | Ce$^{3+}$ | 98.63                      | 98.62                    | 0.010% | 1.71         | 1.0000|
| CS-BT (the mixed   | La$^{3+}$ | 7.59                       | 7.62                     | 2.49%  | -3.9*10-3    | 0.9998|
| concentrations)    | Ce$^{3+}$ | 49.31                      | 49.38                    | 0.016% | -1.42*10-3   | 1.0000|
[11] G.S. Lee, M. Uchikoshi, K. Mimura, M. Isshiki, Distribution coefficients of La, Ce, Pr, Nd, and Sm on Cyanex 923-, D2EHPA-, and PC88A-impregnated resins, Sep. Purif. Technol. 67 (2009) 79–85.

[12] C.H. Xiong, C.P. Yao, Preparation and application of acrylic acid grafted polytetrafluoroethylene fiber as a weak acid cation exchanger for adsorption of Er(III), J. Hazard. Mater. 170 (2009) 1125–1132.

[13] G.A. Moldoveanu, V.G. Papangelakis, Recovery of rare earth elements adsorbed on clay minerals: I. Desorption mechanism, Hydrometallurgy 117–118 (2012) 71–78.

[14] Roosen J, Spooren J, Binnemans K. Adsorption performance of functionalized chitosan-silica hybrid materials toward rare earths. J Mater Chem A, 2014, 2 (45): 19415-19426.

[15] Nagan Prakash & Srinivasan Latha & Persu N. Sudha &N. Gopalan Renganathan, Influence of clay on the adsorption of heavy metals like copper and cadmium on chitosan copper and cadmium on chitosan, Environ Sci Pollut Res. 2013, 20:925-938.

[16] Yang R L, Liu Y C, Liu Q, Xu T T, Zhu K, Liao Y, Mao H, Zhao S L. Tannin grafted aminated silicon adsorbents: adsorption performance of RE3+ coexistence, Desalin Water Treat. 2016, 57(56): 27386–27395.

[17] Xu T T, Huang C R, Luo Y Y , Du Q, Zhao S L. Adsorption properties of Pr3+ and Nd3+ using silica grafted with larch tannin[J]. Adv Mater Res. 2012, 550-553:1561-1565.

[18] Shen Y Y, Yang R L, Liao Y, Ma J, Mao H, Zhao S L. Tannin modified aminated silica as effective absorbents for removal of light rare earth ions in aqueous solution, Desalin Water Treat. 2016, (57) :18529–18536.

[19] Wang D J, Chen H, Xu H, Sun J M, Xu Y Y. Preparation of wheat straw matrix-g-polyacrylonitrile-based adsorbent by SET-LRP and Its applications for heavy metal ion removal. Acs Sustainable Chemistry & Engineering, 2014, 2 (7):1843–1848.

[20] Inoue K, Alam S. Refining and mutual separation of rare earths using biomass wastes, JOM. 2013, 65(10): 1341-1347.

[21] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[22] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[23] G. Gamez, J.L. Gardea-Torresdey, K.J. Tiemann, J. Parsons, K. Dokken, M.J. Yacaman, Recovery of gold(III) from multi-elemental solutions by alfalfa biomass, Adv. Environ. Res. 7 (2003) 563–571.