Fabrication of sponge biomass adsorbent through UV-induced surface-initiated polymerization for the adsorption of Ce(III) from wastewater
Chen Liu, Chunjie Yan, Sen Zhou and Wen Ge

ABSTRACT
The recovery of rare earth ions from industrial wastewater has aroused wide concern in recent years. In present work, we synthesized a novel three-dimensional adsorbent (denoted as LF-AA) by grafting loofah fiber with acrylic acid via ultraviolet radiation. The LF-AA was washed by boiling water and subjected to soxhlet extraction with acetone and then fully characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and scanning electron microscopy (SEM). Rare earth ion (Ce(III)) was selected as a model to validate its adsorption property. The saturation adsorption capacity for Ce(III) reaches 527.5 mg/g. Not only was this material highly efficient at adsorbing Ce(III) from aqueous solutions, it also proved to have ideal performance in regeneration; the total adsorption capacity of LF-AA for Ce(III) after six successive cycles decreased only 6.40% compared with the initial capacity of LF-AA. More importantly, the LF-AA can be easily separated from aqueous solutions because of its three-dimensional sponge natural structure. This study provides a new insight into the fabrication of biomass adsorbent and demonstrated that the LF-AA can be used as excellent adsorbent for the recovery of rare earth ions from wastewater.

Key words | biomass adsorbent, Ce(III) adsorption, recycling, surface modification, wastewater treatment

INTRODUCTION
Rare earth elements (REEs) are becoming one of the most important and indispensable strategic resources in the development of advanced materials science, due to their outstanding physical, chemical and nuclear properties (Uda et al. 2000; Chen 2011; Jordens et al. 2013; Madhukar Reddy et al. 2015). However, abundant wastewater containing rare earth ions is produced in rare earth separation and extraction processes. The REEs concentrations of wastewaters from rare earth smelting enterprises ranged from 150.0 mg/L to 300.0 mg/L according to our investigations. This means that rare earth resources are heavily wasted with the wastewater discharged (Wübbeke 2013; Yang et al. 2013). Although REEs are not typically considered water contaminants, it has been reported that REEs have many toxic effects in bacteria (GAO et al. 2015), plants (Brioschi et al. 2013), animals (Feng et al. 2006; Zhao et al. 2011) and human beings (Fan et al. 2004; Babula et al. 2008; Liu et al. 2014). Therefore, it is of great realistic significance to recycle rare earth ions from the waste water (Wu et al. 2012).

Up to now, various technologies have been developed for the effective recovery of rare earth ions, such as chemistry precipitation, solvent extraction, reverse osmosis, adsorption or ion-exchange and so on (Xie et al. 2014). However, most of these methods are usually of poor efficiency, high cost and generation of secondary contamination (Binnemans et al. 2013). Adsorption, with advantages of low investment, high efficiency and easy operation, is considered to be the most reliable treatment approach for the recovery of REEs from aqueous solutions. The commercially used adsorbent for rare earth ions removal is ion exchange resin, which is costly and produced with unsustainable fossil raw material. Many other novel adsorbents were also tested, such as clay minerals (attapulgite, diatomite), alumina, iron(III) hydroxide and active carbon. However, the main shortcomings of these adsorbents are poor physical strength, low adsorption
capacities or not ideal performance in regeneration (Zhou et al. 2014). Consequently, it is quite necessary to develop new types of highly efficient adsorbents.

Recently, the use of low cost, renewable and biodegradable agricultural and forest residues, such as biomass fiber, in the development of novel adsorbents has drawn wide attention due to increasing concern over environmental protection and sustainable development (Basha et al. 2009; Hameed & Ahmad 2009; Bilal et al. 2013). There are many methods in the development of biomass adsorbents, such as heat-treatment to preparation of activated carbon, acid or alkali treatment, grafting polymers, loaded with metal oxides and coating organic compounds. Among them, UV-induced surface-initiated polymerization as well as grafting polymer is considered to be one of the most effective measures to improve adsorption capacity of biomass materials (Zhou et al. 2016b). Loofah sponge fiber (LF), fruit of luffa cylindrical plants with three-dimensional natural structure, has been proved to have excellent mechanical properties and versatile surface chemistry. Recently, increasing attention has been focused on the modification of LF, especially in the fields of new energy, biofuel cells, supercapacitors and dye/metal cation removal process (Altinisik et al. 2010; Yuan et al. 2015; Li et al. 2014; Thakur & Thakur 2014; Liu et al. 2015). However, natural LF mainly consists of cellulose, hemicelluloses and lignin (Ghali et al. 2009), indicating that it has no functional groups which can work in metal cations adsorption process. Therefore, grafting LF with functional groups is of great significance in wastewater treatment. Poly(acrylic acid) has an advantage in adsorption due to the numerous carboxyl groups, but the polymer structure of poly(acrylic acid) can be easily destroyed by boiling water or organic solvent. Therefore, single poly (acrylic acid) without stable structure is not an ideal adsorbent for heavy metal ions removal from wastewater.

Considering the outstanding properties and special structure of LF, and excellent adsorption capacity of poly(acrylic acid) (PAA), in this paper a novel biomass adsorbent (LF-AA) was prepared by grafting loofah sponge fiber with acrylic acid (AA) via ultraviolet radiation grafting route. Rare earth ion (Ce(III)) was selected as a model to validate the adsorption process for subsequent use.

**Preparation of LF-AA**

The LF-AA was prepared in two steps, as shown in Figure 1. Firstly, the LF&BP was prepared by soaking LF in BP solution of ethanol. Typically, the LF&BP was obtained by adding LF strip into 25 mL of 0.1 wt.% BP solution of ethanol and then drying at 323.15 K. Secondly, the graft polymerization of LF&BP was achieved by the hydrogen abstraction reaction of AA and LF via ultraviolet radiation grafting route. In a typical reaction, one strip of LF&BP (with a total weight of about 1.0 g) was introduced in 25 mL of water, and AA solution (5 mL in 50 mL water) was added into a quartz tube, ensuring the LF was immersed in AA solution, and then the polymer grafting occurred by the UV-irradiation (UV lamp, power of 7 W, wavelength of 254 nm) for 6 h. Afterwards, the product was washed by boiling water and subjected to soxhlet extraction with acetone for 24 h to remove the homopolymers likely to be formed. Finally, the product (LF-AA) was dried in a vacuum oven at 333.15 K.

**Characterization**

Observations of the morphology of LF and LF-AA were characterized by field emission scanning electron microscope (FE-SEM) (SU8010, Hitachi, Ltd, Japan). The surface functional groups of LF and LF-AA were detected by FTIR (Nicolet iS50, Thermo Fisher Scientific Inc., USA), where the spectra were performed by ATR and recorded from 4,000 to 400 cm\(^{-1}\).

**MATERIAL AND METHODS**

**Chemicals and materials**

Acrylic acid (AA, monomer), benzophenone (BP, photosensitizer), acetone (ACE), sodium chloride (NaCl), and Ce(NO\(_3\))\(_3\)·6H\(_2\)O were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The stock solution of Ce(III) used in this study was prepared by dissolving Ce(NO\(_3\))\(_3\)·6H\(_2\)O in double distilled water. All substances were analytical grade and used without further purification.

Loofah sponge fiber was obtained from Hubei province, China. Protogenic loofah sponge fiber was cooked by boiling water for 30 min after cutting into strips, then washed with distilled water and dried under 333.15 K in vacuum environment for subsequent use.

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Batch adsorption experiments

The Ce(III) adsorption properties of LF-AA were primarily evaluated by using a batch adsorption experiment. Typically, 20 mL of Ce(III) solution with desired concentration and 10 mg of LF-AA were added to a vial and then shaken with a speed of 150 shakes·min⁻¹ in a thermostat shaker at 303.15 K for 4 h. Then the adsorbent was separated and the composition of solutions was determined by ICP (DGS-III, Shanghai Tailun Spectrometry Co. Ltd, China) to monitor the change of Ce(III) concentration before and after adsorption. The effect of pH on Ce(III) was adjusted in the range from 1.0 to 6.0 and maintained by 1 M NaOH or HCl, respectively. The effect of ionic strength (NaCl) was also studied by adjusted solution at various Ce(III) concentrations (50–500 mg/L) and different ionic strength (1–80 mmol/L) at optimal pH. The adsorption kinetic was conducted at three initial Ce(III) concentrations (100, 200 and 300 mg/L) by varying the contact time from 5 to 300 minutes at optimal pH. The adsorption isotherm on the adsorption of LF-AA toward Ce(III) was studied with a range of initial Ce(III) concentrations at optimal pH from 50 to 400 mg/L at 303.15, 313.15 and 323.15 K, respectively. The adsorption capacity was calculated as follows:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]  

(1)

where \(q_e\) (mg/g) is the adsorption capacity of Ce(III) at equilibrium, \(V\) (L) is the volume of solution and \(m\) (g) is the amount of adsorbent, \(C_0\) (mg/L) and \(C_e\) (mg/L) are the concentrations of Ce(III) at initial and equilibrium, respectively.

Reusability of LF-AA

To evaluate the reusability of LF-AA, a set of adsorption/desorption was performed. Typically, 10 mg of LF-AA was added to 20 mL of Ce(III) solution (300 mg/L), and the mixture was shaken in a shaker at 150 shake·min⁻¹ for 4 h. Then the Ce(III)-adsorbed LF-AA was separated and desorbed by being dispersed into 0.2 M HCl to be shaken for 4 h. After desorption, the LF-AA was separated and activated by 2% NaOH solution for 15 min, then washed with distilled water to neutralize for the next cycle.

The desorption rate was calculated as follows:

\[
\text{Desorption rate } \% = \frac{C_nV}{mq_{n-1}} \times 100\%
\]

(2)

where \(m\) (g) is the quality of the adsorbent, \(q_n\) (mg/g) is the situated adsorption capacity and \(C_n\) (mg/L) is the equilibrium concentration of Ce(III) at regeneration cycle time \(n\), \(V\) (L) is the volume of the solution.
Theory

To further investigate the adsorption efficiency of the adsorbent, the pseudo-first-order (Equation (3)) and pseudo-second-order (Equation (4)) rate equations were evaluated based on the experimental data.

\[ q_t = q_e \left(1 - e^{-k_1 t}\right) \]  
\[ q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \]

where \( q_t \) (mg/g) is the adsorption capacity at time \( t \) (min); \( q_e \) (mg/g) is the adsorption capacity at adsorption equilibrium; \( k_1 \) (min\(^{-1}\)) is the kinetic rate constant of the pseudo-first-order, and \( k_2 \) (g·mg\(^{-1}\)·min\(^{-1}\)) is the kinetic rate constant of the pseudo-second-order model.

The equilibrium adsorption data are analyzed by fitting them to Langmuir (Langmuir 1917) and Freundlich (Jaroniec et al. 1983) models, expressed by Equations (5) and (6), respectively.

\[ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \]  
\[ q_e = K_F C_e^{1/n} \]

where \( C_e \) is the equilibrium concentration of Ce(III) (mg/L), \( q_e \) (mg/g) is the adsorption capacity at adsorption equilibrium; \( q_m \) is the maximum adsorption capacity (mg/g), \( K_L \) (L/mg) is the Langmuir isotherm constant; \( K_F \) (mg\(^{1-1/n}\)·L\(^{1/n}\)·g\(^{-1}\)) and \( n \) are Freundlich constants representing adsorption capacity and adsorption intensity, respectively.

RESULTS AND DISCUSSION

Characterization of adsorbent

Figure 2 shows the SEM images of LF and LF-AA. We observed that LF-AA (Figure 2(c)) keeps the basic structure of raw LF (Figure 2(a)). The significant difference is the surface morphology; the LF (Figure 2(b)) has a rough surface without shiny look and just like a dry branch, while the surface of LF-AA (Figure 2(d)) is full of smooth bumps and pronounced pleats, indicating that the LF has been successfully modified by PAA (Karlsson et al. 2000; Henriksson & Gatenhalm 2002; Kato et al. 2003).

![Figure 2](https://iwaponline.com/wst/article-pdf/75/12/2755/452351/wst075122755.pdf)
The surface chemical structures of pristine (LF) and modified LF (LF-AA) were studied by ATR-FTIR, as shown in Figure 3. For pristine LF, the peak 3,337 cm\(^{-1}\) corresponds to the stretching vibration of –OH and –NH\(_2\) groups on the surface of LF. The absorption peaks at 2,892 and 1,638 cm\(^{-1}\) corresponded to the stretching vibrations of C–H bond and carbonyl stretching of para-substituted ketones or aryl aldehydes (Tarley & Arruda 2004). The peak at 1,162 cm\(^{-1}\) is assigned to asymmetric bridge of C–O–C stretching, and the peaks at 1,018 and 895 cm\(^{-1}\) correspond to C–H deformation and β-glucosidic linkage, respectively (Gupta et al. 2013). Compared with pristine LF, the FTIR–ATR spectra of LF-AA showed three new characteristic absorption peaks at 1,696, 1,450 and 1,162 cm\(^{-1}\), which are related to the stretching vibration of C=O, stretching vibration and symmetrical stretching of –COO groups, respectively (Pourjavadi et al. 2013). All these results show that carboxyl groups have been successfully grafted to the surface of LF.

**Batch study**

**Effect of pH**

To evaluate the effect of pH, we studied the adsorption of Ce(III) over the pH range 1.0 to 6.0. As results displayed in Figure 4(a), the adsorption capacity of Ce(III) was increased with the pH increase from 1.0 to 6.0. Apparently, these results were thanks to the effective grafting between natural LF and carboxyl groups. The equilibrium pH values were also determined, and the maximum adsorption capacity was achieved at equilibrium pH 5.1 (corresponds to initial pH 6.0). To further study the adsorption mechanism, a zeta potential analysis of LF-AA was investigated. As shown in Figure 4(b), the surface of LF-AA was negatively charged, the zeta potential of LF-AA was near 0 at pH 1.0 and then becomes stronger with the rising of solution pH, which is beneficial for adsorbing metal cations. These phenomena can be explained as follows: At low pH, the concentration of H\(^+\) is high and the surface of the adsorbents presents in carboxyl form (Ge et al. 2015). The lower adsorption efficiency at low pH may result from the strong coulomb repulsion and the competition between the H\(^+\) and Ce(III). As expected, with the pH value increased, the adsorption capacity of LF-AA sharply increased and reaches a high level at higher pH values. At higher pH values, the weakly acidic carboxyl groups will be deprotonated and resulting in more negative binding sites; therefore, the attraction of positively charged metal ions would be enhanced, thus improving the adsorption capacity (Bayramoglu & Yakup Arica 2009; Badruddoza et al. 2011).

**Effect of ionic strength and adsorption of different rare earth ions**

Alkaline metal ions are often present together with rare earth ions in water systems. Therefore, studying the effect of solution ionic strength is of significance in adsorption process. The effect of ionic strength on the adsorption of Ce(III) was studied at pH 6.0 with NaCl as background electrolyte. The batch adsorption results are presented in Figure 4(c); the adsorption capacity of LF-AA was not greatly affected by the ionic strength, indicating that the binding affinity of Ce(III) with carboxyl groups is stronger than for sodium ions, and ion exchange is more prone to occur between Ce(III) and carboxylate of adsorbent surface. The adsorption performance of rare earth ions with different ionic radius was also studied at pH 6.0, as shown in Figure 4(d); LF-AA possessed different adsorption capacity towards different rare earth ions and followed the order Dy(III) > Ce(III) > La(III) > Eu(III) > Y(III), which suggests that LF-AA amount adsorbed is related to ionic radius.

**Adsorption kinetics**

Figure 5(a) reveals the effect of contact time on Ce(III) adsorption onto the adsorbent LF-AA under three initial concentrations (100 mg/L, 200 mg/L, 300 mg/L) at pH 6.0. It has a rapidly increasing speed for the first 50 min, which achieves most of the adsorption capacity, and then gradually moves into a slower stage as the contact time
increases until it reaches adsorption equilibrium. The adsorption capacities were equal to 190.2, 387.4 and 516.2 mg/g at initial concentrations of 100, 200, and 300 mg/L, respectively.

This phenomenon could be attributed to the countless active sites (–COO– groups) from grafting and the porous structure of LF base. Specifically, metal cation was firstly migrated

Figure 4 | Effect of pH (a) and ionic strength (c) on the adsorption capacity of LF-AA toward Ce(III). (b) The zeta potentials of the adsorbent at different pH values. (d) The adsorption of different rare earth ions.

Figure 5 | (a) Effect of time on the adsorption of metal ions and (b) nonlinear fitting of pseudo-first-order and pseudo-second-order models.
and adsorbed on the surface of LF-AA, which mainly resulted from ion exchange and charge neutralization. When the surface adsorption reached saturation, the rare earth cation would gradually diffuse to the interior of LF-AA and then be adsorbed on the interior of LF-AA, which made the subsequent diffusion (i.e. inner diffusion) more difficult; this stage should take a relatively long time (Ghaedi et al. 2014; Wang et al. 2014).

The pseudo-first-order and the pseudo-second-order plots for the adsorption of the Ce(III) on the LF-AA are shown in Figure 5 and the kinetic constants of these models are given in Table 1. It is clear that the $R^2$ of pseudo-second-order adsorption model was more close to 1 than pseudo-first-order model, and the values of $q_{e,exp}$ (experimental values of adsorption capacities) are closer to $q_{e,cal,2}$ (calculated by pseudo-second-order equation) than that of $q_{e,cal,1}$ (calculated by pseudo-first-order equation). This result suggests that the pseudo-second-order adsorption model was more suitable for the adsorption of Ce(III), and the metal ions adsorption onto LF-AA may take place through a chemical process involving valence forces through sharing or exchange of electrons (Li et al. 2013).

### Adsorption isotherms

As an important parameter of heavy metal adsorption at liquid–solid interfaces, the effect of temperature (303.15, 313.15, and 323.15 K) on adsorption of Ce(III) onto LF-AA was examined at pH 6.0 as shown in Figure 6. The maximum adsorption capacity of Ce(III) was achieved at 323.15 K. The adsorption capacity led to an inconspicuous increase with the temperature increasing from 313.15 K to 323.15 K. Increasing adsorption temperature is known to enhance the possibility of interaction between metal ions and the adsorbent, and it is favorable for the transfer and diffusion of adsorbate from bulk solution to adsorbent surface. However, the increase of temperature may also cause greater mobility of the adsorbate molecules previously...
adsorbed (Li & Lei 2012; Li et al. 2015). It indicated that the temperature has no significant influence on adsorption of Ce(III) onto LF-AA based on the above two considerations.

The adsorption isotherm and non-linear fitting of the adsorption isotherm models are shown in Figure 7. The $q_e$ of the metal ions was increased with increasing concentrations until reaching equilibrium. The parameters of Langmuir and Freundlich isotherm models were calculated and summarized in Table 2. Obviously, the Langmuir equation fitted the isotherm data well, with all $R^2$ value, more close to 1, which indicates that the binding sites of LF-AA are uniformly distributed on its surface, and the adsorption of Ce(III) is regarded as monolayer adsorption (Li et al. 2015). Comparison with several reported biomass adsorbents is listed in Table 3, revealing that LF-AA exhibits excellent adsorption ability for the recovery of Ce(III) from aqueous solutions.

**Regeneration and reusability**

The regeneration and reusability are important factors of a new adsorbent from a practical point of view. To evaluate the reusability of the adsorbent, six consecutive adsorption/desorption cycles were conducted and the results are presented in Figure 8. The adsorbent (LF-AA) achieved high and stable adsorption efficiency in the regeneration and reuse processes. Specifically, the total adsorption capacity of LF-AA for Ce(III) after six consecutive cycles decreased slightly from 515.8 to 482.7 mg/g, which is only a 6.40% reduction compared with the initial capacity of LF-AA, and it is still better than that for other polymeric absorbents that are freshly prepared. Moreover, desorption efficiency was also above 97.0% throughout the six cycles with 0.2 M HCl. Clearly, LF-AA in our study has good potential for repeated utilization for the adsorption and recycling of rare earth ions (Ce(III)) from water.

**CONCLUSIONS**

In this study, an efficient adsorbent was successfully synthesized on the basis of natural loofah sponge fiber via ultraviolet radiation grafting route. The LF-AA composites obtained were found to retain properties of their components, namely ideal structure for application (from LF), excellent adsorption/desorption capability for metal ions (from AA). In addition, the LF-AA exhibits excellent reuse
ability, with maximum adsorption capacity of 527.5 mg/g for Ce(III), which could be used as a reusable adsorbent with convenient conditions. According to the characterization analysis, the main adsorption mechanism should be ion exchange happening on the -COO- sites and then forming a bidentate chelate. Therefore, this adsorbent with excellent performances can be applied in the recovering of rare earth and other metal ions from water.

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