Polyacrylic acid grafted silica fume as an excellent adsorbent for dysprosium(III) removal from industrial wastewater

Tian Liang, Chunjie Yan, Xujian Li, Sen Zhou and Hongquan Wang

ABSTRACT

In the development of industrial life, an enormous amount of silica fume (SF) has been accumulated and cannot be reused properly, and a large quantity of rare-earth elements in industrial wastewater has been inappropriately discharged, both of which pose a threat to human health and the environment. By using UV photocatalytic grafting technology, a polymer brush grafted from modified SF, which can be used as a high efficiency adsorbent, can solve both problems at the same time. Specifically, SF was firstly silanol-functionalized by γ-methacryloxypropyltrimethoxysilane (KH570), then grafted with polyacrylic acid brushes by UV photocatalytic grafting to finally obtain the adsorbent. Under optimal conditions, adsorption capacity of the adsorbent for dysprosium(III) (Dy³⁺) could reach 278.49 mg/g. It took 1 min for the adsorbent to reach adsorbing equilibrium at a relatively low concentration of Dy³⁺ (40 mg/L), and only 3 min at a medium and high concentration (130 mg/L and 200 mg/L). After six adsorption–desorption cycles, the adsorbent still possessed high adsorption capacity for Dy³⁺ (251.20 mg/g). The adsorption behavior of the adsorbent fit the Langmuir isotherm model (R² > 0.97) and pseudo-second-order kinetic model (R² > 0.98) well. The functional group of carboxylate anion, -COO⁻, played a central role during the adsorption process, which was verified by Fourier transform infrared and X-ray photoelectron spectroscopy analyses.

Key words | Dy³⁺ removal, grafting from, modified silica fume, nanocomposite, UV photocatalytic grafting

INTRODUCTION

Silica fume (SF) is a by-product of the ferroalloys industry in smelting ferrosilicon and industrial silicon (metallic silicon) (Boonsri et al. 2012). With the prosperous development of the Chinese ferroalloys industry, SF has increased rapidly and caused harm to the environment and human health. The rare-earth elements (REEs) have an unfilled 4f electronic layer structure and possess unique abundant electronic energy levels, which enable them to have excellent light, magnetic, electrical, acoustic and thermal performance. They are strategic resources and play an indispensable role in different areas such as military, petrochemical, ceramic and glass, machinery, electronics, agriculture, and new materials; thus they are praised as ‘industrial vitamins’ (Chen 2011; Awual et al. 2015). But a high concentration of rare-earth ions in domestic water will cause harm to human health. Residents near the rare-earth mining areas are vulnerable to cancer, leukemia or congenital defects. At present, China possesses 23% of the world’s rare-earth resources, yet it has to meet more than 90% of the global market’s demand, which causes a serious imbalance between demand and supply.

Faced with these severe problems, the recycling of REEs has become an extremely important and urgent task. The methods of recycling REEs mainly include chemical precipitation, precipitate flotation, solvent extraction, membrane separation and biosorption (Bou-Maroun et al. 2006a, 2006b; Chen et al. 2012; Binnemans et al. 2013; Roosen & Binnemans 2014). But these methods are either overpriced, causing secondary pollution, or function well only in harsh conditions (e.g., aqueous solution containing high concentration of metal ions). The adsorption method, however, has fine selectivity towards metal ions, is easy to operate, consumes a small amount of energy, works with high efficiency and brings about little secondary pollution, which is considered to be an ideal approach for metal ions removal in wastewater (Wang et al. 2015; Ogata et al. 2015a, 2015b).
The development of cost-effective and efficient rare-earth ion adsorbents has huge economic benefits and profound practical significance to the sustainable use of rare-earth resources and protection of the environment. Based on the ionic state of REEs in industrial wastewater, plus the massive amount of SF that causes severe environment and health problems, it becomes a natural choice to synthesize an SF-based adsorbent to treat the wastewater by adsorption method. Functionalizing inorganic substrate with polymer brushes is an important way to realize the high value-added utilization of inorganic material. At present, the application of polymer brushes is mainly focused on water treatment, organic–inorganic composite materials, separation and purification of biological macromolecules, colloid modification, chemical valves, lubricants, adhesives, polymer surfactants and compatibilizers, etc. (Kumar et al. 2013; Li et al. 2013; Borozenko et al. 2014; Liu et al. 2016). In view of very few reports on inorganic substrate grafted polymer brushes, a new adsorbent of polyacrylic acid (PAA) brushes functionalized SF was designed and synthesized in this work. The ‘grafting from’ approach was adopted to complete this task (Borozenko et al. 2014). SF was modified with silane coupling agent to obtain the modified SF (MSF), and then functionally grafted with acrylic acid (AA) using UV photocatalytic grafting method to get the PAA grafted MSF (PAA-g-MSF). Considering the wide range of application of dysprosium (Dy), Dy³⁺ was chosen as a typical adsorbate to evaluate adsorbing performance and features of PAA-g-MSF. The effect of pH and foreign cations on the adsorption was investigated, as were the repeated use performance, adsorption kinetics and adsorption isotherms. The PAA-g-MSF adsorbent was also compared with other adsorbents (Guangyao et al. 1992; Riaz & Javed 1995; Wang & Gao 2007; Aghayan et al. 2013; Wu et al. 2013; Kondo et al. 2015; Smith et al. 2016; Awual et al. 2017). By comparison, a conclusion could be drawn that the adsorbent prepared in this work is better than most adsorbents of previous reported studies. In short, this new adsorbent has a bright prospect for application to the recovery of Dy³⁺.

**EXPERIMENTAL**

**Materials and chemical reagents**

SF was supplied by Shanghai Aikai Silica Fume Material Co., Ltd, China. γ-methacryloyloxypropyltrimethoxysilane (KH-570, silane coupling agent) was provided by Aoup Chemical Reagent Co., Ltd (Wuhan, China). Hydrochloric acid, ammonium iron(II) sulfate hexahydrate ((NH₄)₂Fe(SO₄)₂·6H₂O) (inhibitor), benzophenone (BP, photo-initiator), and acrylic acid (AA) were purchased from Fuchen Chemical Reagent Co., Ltd (Tianjin, China). To remove the polymerization inhibitor, AA was purified by distillation under reduced pressure. Other chemicals and reagents were of analytical grade and used as received, all of which were supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All aqueous solutions were formulated with deionized water.

**Synthesis route and mechanism**

The procedure of synthesizing PAA-g-MSF is shown in Figure 1(a). Firstly, SF was acid-activated using hydrochloric acid. Original SF was added into 2.0 mol/L HCl solution, and stirred at 45 °C for 5 h to obtain the acid-activated SF (ASF). Then ASF was modified by KH-570. Specifically, 3 g ASF and 0.3 mL KH-570 were added into 60 mL toluene, melted BP was not miscible with water, the solvophobic effect would lead BP to adhere to MSF. Finally, a UV photocatalytic grafting method was adopted to synthesize the PAA-g-MSF nanocomposite. (NH₄)₂Fe(SO₄)₂·6H₂O was added into the mixture and then cleansed with nitrogen to remove oxygen. Subsequently, the solution was UV-irradiated by a 500 W high-pressure mercury lamp (wavelength of 210 nm). The final product (PAA-g-MSF) was filtered and washed alternately with deionized water and ethanol to get rid of the unreacted AA and self-polymerized PAA. The obtained PAA-g-MSF was stirred in NaOH solution to remove the Fe²⁺ adsorbed by -COO⁻. After this, the protonated PAA-g-MSF was stirred in NaOH solution and neutralized with deionized water. The Na-transformed PAA-g-MSF was prepared for adsorption studies.

Figure 1(b) illustrates the mechanism of modification of SF. The specific ‘grafting from’ approach is shown in Figure 1(c). Figure 1(d) demonstrates three ways of PAA-g-MSF adsorbing Dy³⁺. Chemical bonding (i.e., chelate coordination) is the main manner of adsorption in this case. The carboxylate anions in the Dy³⁺ adsorbed PAA-g-MSF complexes (PAA-g-MSF-Dy³⁺) may be in the same polymer chain or not as shown in Figure 1(d).
Adsorption and regeneration experiments

The adsorption procedures were conducted as follows. Ten milligrams of PAA-g-MSF was added into an adsorption bottle which had 20 mL Dy³⁺ solution (various concentrations and different pH) in it; then the bottle was shaken in an air bath thermostat oscillator at different temperature for different time. Afterwards, the PAA-g-MSF-Dy³⁺ was obtained by centrifuging the mixture. Inductively coupled plasma mass spectroscopy (ICP-MS) was utilized to detect the concentration of Dy³⁺ in aqueous solution. The adsorption amount of Dy³⁺ was calculated by the following equation:

\[Q_e = \frac{(C_i - C_e) \times V}{m}\]  (1)

where \(Q_e \) (mg/g) is the adsorption quantity of Dy³⁺ per unit mass of PAA-g-MSF at equilibrium, \(m\) (g) is the weight of PAA-g-MSF, \(V\) (L) is the volume of solution, and \(C_i\) and \(C_e\) (mg/L) are the initial and adsorption equilibrium concentrations of Dy³⁺, respectively.

The influence of pH towards adsorption was studied in the pH range from 1.0 to 6.0 by a similar procedure described above. The effect of foreign cations on the efficiency of adsorption was examined by increasing the concentration of K⁺, Ca²⁺ or Na⁺ in Dy³⁺ solution from 0 to 200 mmol/L at optimal pH. The kinetic experiments were carried out by changing the contact time from 0.5 to 120 min at various initial Dy³⁺ concentrations (40, 130, and 200 mg/L) to ascertain the rate and kinetic characteristics of adsorption.

The isothermal adsorption experiments were conducted at diverse temperatures (303.15, 313.15, and 323.15 K) in different initial Dy³⁺ concentration (ranged from 30 to 250 mg/L) to reveal the equilibrium adsorption features. To detect the repeated use efficiency of PAA-g-MSF, the nanocomposite was subjected to a six-cycle adsorption–desorption experiment. To ensure the accuracy, the six-cycle adsorption–desorption experiment was repeated for three times, and the final data were the average value of the three sets of experimental data.

In each cycle, 10 mg PAA-g-MSF was added into the Dy³⁺ solution (20 mL, 200 mg/L) and shaken in an air bath thermostat oscillator at 313.15 K for 60 min. The PAA-g-MSF-Dy³⁺ complexes were then centrifuged from the solution, washed with HCl solution (20 mL, 0.2 mol/L) for 1 h, and finally filtered. ICP-MS was utilized to detect the Dy³⁺ concentration in filtered solution; then the desorbed amount of Dy³⁺ was calculated. The acid-treated PAA-g-MSF was then washed with NaOH solution (20 mL, 0.1 mol/L) for 15 min and neutralized for the next cycle. The desorption ratio was calculated as follows:

\[D_r = \frac{V_d}{\left(\frac{C_i - C_e}{V}\right) \times 100\%}\]  (2)

where \(D_r\) (%) is the desorption ratio, \(V_d\) (L) is the volume of the desorption solution, \(C_d\) (mg/L) is the concentration of
Dy$^{3+}$ in the desorption solution; $C_e$, $C_e$ and $V$ are the same as defined above.

**Adsorption equations**

**Adsorption kinetics**

To investigate kinetics behavior of PAA-g-MSF, the pseudo-first-order and pseudo-second-order kinetic models were utilized. Their equations are expressed correspondingly as follows (Xiong & Yao 2009; Wu et al. 2013; Li et al. 2015):

$$Q_t = Q_e^* (1 - e^{-K_1 t})$$  (3)

$$Q_t = \frac{K_2 Q_e^2 t}{1 + K_2 Q_e t}$$  (4)

where $Q_e$ and $Q_t$ (mg/g) are the quantity of Dy$^{3+}$ adsorbed on the adsorbent at equilibrium and at different times $t$ (min), respectively, per unit mass of PAA-g-MSF; $K_1$ (1/min) and $K_2$ (g/(mg min)) are constants of the pseudo-first-order and pseudo-second-order kinetic models respectively.

**Adsorption isotherms**

Freundlich and Langmuir are widely utilized isotherm adsorption models and their equations are presented as follows (Xiong & Yao 2009; Wu et al. 2013; Li et al. 2015):

$$Q_e = K_F C_e^{1/n}$$  (5)

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$  (6)

where $K_F$ (mg$^{1-1/n}$ L$^{1/n}$/g) and $n$ are Freundlich constants that are related to temperature and the adsorption system, $Q_m$ (mg/g) is the theoretical maximum adsorption capacity of the Langmuir isotherm model, $K_L$ (L/mg) is the Langmuir constant, which is associated with the adsorption energy. The adsorption process is prone to proceed when $1/n$ is between 0.1 and 0.5 and is difficult to carry out when $1/n$ is more than 2. $Q_e$ and $C_e$ are the same as defined above.

**Structural and chemical characterization**

A Nicolet iS50 Fourier transform infrared (FT-IR) spectrometer in the range of 400–4,000 cm$^{-1}$ by means of the KBr pellet technique was used to record the FT-IR spectra. Thermogravimetry (TG) was performed on a NETZSCH STA449-F3 thermal analysis system. The microstructure of materials was displayed by using a field-emission scanning electron microscope (FE-SEM, Hitachi SU8010 at 5.0 kV). Energy dispersive spectroscopy (EDS, GENESIS, and EDAX America) was utilized to analyze the composition of the materials at the same time. The ICP-MS was employed to detect the concentration of Dy$^{3+}$ in aqueous solution. The chemical analyses of the original and Dy$^{3+}$-adsorbed PAA-g-MSF were conducted by X-ray photo-electron spectroscopy (XPS) (Thermo Fisher ESCALAB 250Xi XPS, UK).

**RESULTS AND DISCUSSION**

Characterization of materials

Figure 2(a) shows the IR spectra of original SF, MSF, PAA-g-MSF and PAA-g-MSF-Dy$^{3+}$. It can be seen from Figure 2(a) that MSF has an additional peak of 1,629.55 cm$^{-1}$ compared to that of SF, which corresponds to the infrared absorption peak of stretching vibration of C=C in olefin and the C=C group does exist in KH-570. PAA-g-MSF has two more IR adsorption peaks, located at 1,618.27 cm$^{-1}$ and 1,414.46 cm$^{-1}$, than SF. These two peaks correspond to COO$^-$ antisymmetric and symmetric vibration respectively. According to the experimental theory, the COO$^-$ group should exist in PAA-g-MSF if AA was successfully grafted onto the MSF, which was effectively confirmed by FT-IR. The adsorption peaks of 1,618.27 cm$^{-1}$ and 1,414.46 cm$^{-1}$ in PAA-g-MSF shifted to 1,543.71 cm$^{-1}$ and 1,423.13 cm$^{-1}$ in PAA-g-MSF-Dy$^{3+}$, which could be attributed to the COO$^-$ on the PAA brush and Dy$^{3+}$ forming complexes and thus changing the vibration frequencies of COO$^-$. Figure 2(b) displays the TG analyses of SF, MSF, PAA-g-MSF and PAA-g-MSF-Dy$^{3+}$. SF lost 3.46% of its weight when the temperature rose to 1,000 °C, which was caused by loss on ignition (H$_2$O, C, etc.). Meanwhile, MSF, PAA-g-MSF and PAA-g-MSF-Dy$^{3+}$ lost 8.01, 35.92 and 33.73% of their mass respectively under the same condition. MSF lost 4.55% more of its weight than SF, which might be caused by the thermal decomposition of the silane coupling agent at high temperature. And PAA-g-MSF had 27.91% more of its weight loss than MSF; this might be the reason that grafted PAA had been decomposed when the temperature was high. In addition, PAA-g-MSF-Dy$^{3+}$ had 2.19% less weight loss than PAA-g-MSF, which could be explained by
the adsorbed Dy\(^{3+}\) not burning away during the heating process. IR and TG analyses strongly supported the fact that SF had been successfully modified and grafted, and the adsorption was the process of Dy\(^{3+}\) coordinating with -COO\(^{-}\) to form complexes.

The morphology of the four samples rarely changed except that the other three have less irregular debris than SF (Figure 3). This might be because the acid activation process had removed a lot of impurities and the SF particle was so small that the changes brought by modification, grafting and adsorption were difficult to observe. It also demonstrated that the structure of SF had not been damaged during these processes. However, the insets display significant changes between the four samples. The same amount of the four samples was added into an equal volume of each solution. SF sank into H\(_2\)O while MSF floated on the surface, indicating that modification had introduced hydrophobic organic functional groups onto the surface of SF. PAA-g-MSF was much larger than SF due to the -COO\(^{-}\) groups being repelled from each other by electrostatic force, resulting in PAA-g-MSF swelling in H\(_2\)O. PAA-g-MSF-Dy\(^{3+}\) shrank in the high concentration of Dy\(^{3+}\) solution (200 mg/L) due to the chelate coordination of -COO\(^{-}\) and Dy\(^{3+}\), leaving little -COO\(^{-}\) to repel from each other and no swelling phenomenon occurred. The EDS detection conducted simultaneously could make up for the deficiency of SEM and proved the effectiveness of grafting and adsorption; the relevant results will be mentioned later.

**Adsorbing performance studies**

**The effect of pH on the adsorption**

Figure 4(a) displays the influence of pH on adsorption of Dy\(^{3+}\) by adsorbent. The experiment was carried out at the temperature of 313.15 K, Dy\(^{3+}\) concentration of 200 mg/L, and adsorbing time of 60 min. As shown in Figure 4(a), pH significantly affects the adsorption capacity of the adsorbent. The adsorbent hardly adsorbed Dy\(^{3+}\) when the pH was 1 or 2. Under such condition, -COO\(^{-}\) was protonated and preferentially bound to H\(^+\), so the adsorption capacity of Dy\(^{3+}\) was small. It could be concluded that the adsorption capacity of adsorbent towards Dy\(^{3+}\) increased as pH rose (from 1 to 6). As pH was increased from 5 to 6, the adsorption capacity increased by a little and reached the maximum value of 275.63 mg/L. Another phenomenon was that when the initial pH was increased from 1 to 5, the equilibrium pH was higher than the initial pH. This could be ascribed to the
protonation effect whereby -COO⁻ bound to H⁺ in preference to Dy³⁺, resulting in a decrease of H⁺ concentration and the increase of pH of the solution. In contrast, the equilibrium pH was less than the initial pH when the initial pH was 6. This might be due to a small amount of Dy³⁺ hydrolyzed in aqueous solution. The main hydrolysis processes of Dy³⁺ and their equations are as follows (Riaz & Javed 1995):

\[
\text{Dy}^{3+} + \text{H}_2\text{O} \Leftrightarrow \text{Dy(OH)}^{2+} + \text{H}^+ \tag{7}
\]

\[
\text{Dy(OH)}^{2+} + \text{H}_2\text{O} \Leftrightarrow \text{Dy(OH)}^{+} + \text{H}^+ \tag{8}
\]

Dy³⁺ hydrolyzed to Dy(OH)²⁺ and Dy(OH)⁺ to which -COO⁻ bound and formed complexes (PAA-g-MSF-Dy³⁺) so that the reaction equilibrium shifted to the right, thus the H⁺ concentration in the solution increased and the pH decreased. The solubility product constant (K_{sp}) of Dy(OH)₃ is 1.4 × 10^{-22}, which shows that Dy(OH)₃ is difficult to dissolve in aqueous solution.

The effect of foreign cations on the adsorption

Figure 4(b) illustrates the effect of common foreign cations (K⁺, Ca²⁺, Na⁺) on the adsorption of Dy³⁺ by adsorbent. The experiment was conducted in a series of solutions containing different concentration of foreign cations with pH of 6, temperature of 313.15 K and Dy³⁺ concentration of 200 mg/L (1.23 mmol/L). The maximum concentration of foreign cation was set as 200 mmol/L, which was 162.5 times the concentration of Dy³⁺. It is clear that K⁺ and Na⁺ have little effect on the adsorption of Dy³⁺ by adsorbent while Ca²⁺ has an obvious effect. The amount of Dy³⁺ adsorbed by adsorbent reduced with the increase of Ca²⁺ concentration. It was probable that some -COO⁻ and Ca²⁺ formed complexes, and the amount of -COO⁻ which can form complexes with Dy³⁺ reduced correspondingly, resulting in the decrease of the adsorption capacity of Dy³⁺ by adsorbent.

Adsorption kinetics

Figure 5(a) demonstrates the adsorption capacity of Dy³⁺ by adsorbent at different times at the pH of 6, temperature of 313.15 K and various initial Dy³⁺ concentrations. The pseudo-first-order and pseudo-second-order kinetic models have been employed to determine adsorption kinetic features of the adsorbent as shown in Figure 5(b). The intraparticle diffusion model also has been studied, as can be seen in the supplementary material (available with the online version of this paper). It took only 1 min for the adsorbent to reach adsorbing equilibrium at a relatively low concentration of Dy³⁺ (40 mg/L). The criterion of adsorption equilibrium is determined by the difference between the adsorption capacity at various times (Q_t) and the theoretical equilibrium adsorption capacity (Q_e) under the same Dy³⁺ concentration. We consider that the adsorption reaches its equilibrium when the difference is within 5% ((Q_e - Q_t)/Q_e < 5%). In the medium and high concentration (130 mg/L and 200 mg/L) of Dy³⁺, the adsorbent achieved its equilibrium within 3 min. The adsorption capacity for Dy³⁺ of the adsorbent could reach 278.49 mg/g under the condition of Dy³⁺ concentration of 200 mg/L and adsorbing time of 90 min. It was confirmed by the results that the three groups of experimental data were more in line with the pseudo-second-order kinetic model than the pseudo-first-order kinetic model.

The calculated parameters of the pseudo-first-order and pseudo-second-order kinetic models are listed in Table 1. Q_{e-exp} is the experimental data of adsorption capacity at
equilibrium, $Q_{e-1}$ and $Q_{e-2}$ are the theoretical value of adsorption capacity of pseudo-first-order and pseudo-second-order kinetic models respectively. $R^2$ is the coefficient of determination of the models; in this work, the greater the value is, the better the data fitting to the models (Xiong & Yao 2009; Wu et al. 2013; Li et al. 2013). Table 1 shows that the adsorption kinetics features of PAA-g-MSF are more consistent with the pseudo-second-order kinetic model than the pseudo-first-order kinetic model.

**Adsorption isotherms**

Figure 6(a) shows the adsorption capacity of Dy$^{3+}$ by adsorbent at different temperature under the condition of the pH of 6, adsorbing time of 60 min, and various initial Dy$^{3+}$ concentrations. The Freundlich and Langmuir isotherm models have been utilized to analyze adsorption isotherm features of the adsorbent as shown in Figure 6(b)–6(d). Other isotherm models such as Temkin and Dubinin–Radushkevich have also been used to determine the adsorption features, as can be seen in the supplementary material. The amount of Dy$^{3+}$ adsorbed by the adsorbent did not vary much when the other experimental conditions remained the same while the temperature changed. The result suggested that the change of temperature within a certain range (from 303.15 K to 323.15 K) had little influence on the adsorption performance of the adsorbent. Thermodynamic studies have been conducted based on this result, as shown in the supplementary material. The results in Figure 6(b)–6(d) indicate that the behavior of PAA-g-MSF adsorbing Dy$^{3+}$ was more consistent with the Langmuir isotherm model than the Freundlich isotherm model. This revealed that the adsorption of Dy$^{3+}$ by adsorbent was monolayer adsorption and each adsorption center could only be occupied by an adsorbed molecule. It also indicated that the adsorbent had an ideal uniform surface and each adsorption center had an equal adsorption energy.

Table 2 shows the calculated parameters of the Freundlich and Langmuir isotherm models which were defined as above. It is known from Table 2 that the adsorption isotherm features of PAA-g-MSF are more in accordance with the Langmuir isotherm model than the Freundlich isotherm model. The values of $1/n$ are all between 0.1 and 0.5, which indicates that the adsorption process of Dy$^{3+}$ by PAA-g-MSF is easy to carry out.

**Desorption and repeated use**

Figure 7 displays the adsorbed capacity and desorbed ratio of Dy$^{3+}$ for each repeated use of adsorbent. The

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Parameters of pseudo-first-order and pseudo-second-order kinetic models for PAA-g-MSF adsorbing Dy$^{3+}$</th>
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<tr>
<td>$C_i$ (mg/L)</td>
<td>$Q_{e-exp}$ (mg/g)</td>
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</tr>
<tr>
<td>40</td>
<td>79.4</td>
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<td>130</td>
<td>253.6</td>
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<td>200</td>
<td>278.3</td>
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adsorbed capacity reduced as the cycle number increased. The adsorption capacity was 277.20 mg/g for the first adsorption and 251.20 mg/g for the sixth. Although the adsorption capacity was decreased, it was still 90.62% of that for the first time. The desorption ratio changed irregularly but all of them were more than 95% as shown in Figure 7. It could be concluded that the desorption of PAA-g-MSF-Dy$^{3+}$ was convenient and efficient, and the adsorbent could be used repeatedly for at least six times.

**Comparison with other adsorbents**

When assessing the performance of an adsorbent, the time to reach equilibrium, pH, temperature and adsorption capacity are indispensable aspects. Table 3 lists these parameters of various adsorbents when adsorbing Dy$^{3+}$. It can be seen from Table 3 that although PAA-g-MSF did not have the maximum adsorption capacity of Dy$^{3+}$, it was the quickest one to reach adsorption equilibrium. Moreover, PAA-g-MSF functioned best when pH was 6.0 and

**Table 2 | Parameters of Freundlich and Langmuir isotherm models**

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Freundlich isotherm model</th>
<th>Langmuir isotherm model</th>
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<tr>
<td></td>
<td>$K_F$ (mg$^{1-1/n}$ L$^{1/n}$/g)</td>
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</tr>
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<td>303.15</td>
<td>129.85</td>
<td>0.185</td>
</tr>
<tr>
<td>313.15</td>
<td>127.97</td>
<td>0.189</td>
</tr>
<tr>
<td>323.15</td>
<td>124.71</td>
<td>0.192</td>
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</table>
temperature was 313.15 K, both of which were easy to accomplish. In general, PAA-g-MSF has a great advantage compared with other adsorbents.

Adsorption mechanism

XPS and EDS analyses were utilized to further explore the adsorbing mechanism of \( \text{Dy}^{3+} \) by adsorbent. The results of XPS and EDS analyses are presented in Figure 8. Figure 8(a) shows that the two peaks appearing at 497.01 eV and 1,071.01 eV in PAA-g-MSF disappear in PAA-g-MSF-\( \text{Dy}^{3+} \), and PAA-g-MSF-\( \text{Dy}^{3+} \) has two more peaks at 1,297.01 eV and 1,336.01 eV compared to PAA-g-MSF. By searching the NIST XPS database, it can be known that 497.01 eV is the Auger electron energy of Na, 1,071.01 eV is the binding energy of sodium oxalate, and 1,297.01 eV and 1,336.01 eV are the binding energy of Dy. It could be inferred that after being washed with NaOH, the -COOH in original adsorbent transferred to -COONa, which was in accordance with the two peaks at 497.01 eV and 1,071.01 eV. During the process of PAA-g-MSF adsorbing \( \text{Dy}^{3+} \), \( \text{Dy}^{3+} \) replaced Na\(^+\) to form complexes with -COO\(^-\) and thus obtained PAA-g-MSF-\( \text{Dy}^{3+} \). This could explain why the peak of Na disappeared while the peak of Dy appeared in the XPS spectrum of PAA-g-MSF-\( \text{Dy}^{3+} \). Of the EDS spectra in Figure 8(b), PAA-g-MSF has one more peak of Na than SF and MSF, while PAA-g-MSF-\( \text{Dy}^{3+} \) has one more peak of Dy and one less peak of Na than PAA-g-MSF. The results of EDS could also support the above inference derived from XPS spectra. In summary, the results of XPS, EDS and above-mentioned FT-IR effectively proved the existence of the functional group -COO\(^-\) in the adsorbent and reasonably explained the adsorption mechanism of \( \text{Dy}^{3+} \) coordinating with -COO\(^-\) to form complexes.

CONCLUSION

In this work, a kind of adsorbent with excellent adsorption performance towards \( \text{Dy}^{3+} \) was prepared using a convenient and effective approach. Firstly, silane coupling agent KH-570 was utilized to silanol-functionalize the acid-activated SF. Then the UV photocatalytic grafting technology was employed to graft AA onto MSF. The adsorption capacity of \( \text{Dy}^{3+} \) by adsorbent in this study could reach 278.49 mg/g under optimized condition (pH of 6, temperature of 313.15 K). The adsorption features of the adsorbent were in high accordance with the pseudo-second-order kinetic model and Langmuir isotherm model. Foreign cations such as \( \text{K}^+ \) and \( \text{Na}^+ \) had little impact on the adsorption of \( \text{Dy}^{3+} \) by adsorbent while \( \text{Ca}^{2+} \) had an obvious effect but PAA-g-MSF still adsorbed a considerable amount of \( \text{Dy}^{3+} \). The adsorbent still possessed high adsorption capacity for \( \text{Dy}^{3+} \) (251.20 mg/g) after six repeated use. The results of FT-IR, EDS and XPS not only confirmed the existence of

<table>
<thead>
<tr>
<th>Types of adsorbent</th>
<th>Equilibrium time</th>
<th>Other experimental conditions</th>
<th>Adsorption capacity for ( \text{Dy}^{3+} ) (mg/g)</th>
<th>References</th>
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<tr>
<td>Alumina-silica based composite</td>
<td>60 min</td>
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<td>Awual et al. (2017)</td>
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<tr>
<td>Microcapsules containing dibenzoylmethane</td>
<td>60 h</td>
<td>pH = 6.0; T = 303 K</td>
<td>70.85</td>
<td>Kondo et al. (2015)</td>
</tr>
<tr>
<td>D113 resin</td>
<td>Unknown</td>
<td>pH = 6.0; T = 298 K</td>
<td>292.7</td>
<td>Wang &amp; Gao (2007)</td>
</tr>
<tr>
<td>Macroporous poly(vinylphosphoramidic acid) resin</td>
<td>Unknown</td>
<td>pH = 4–5</td>
<td>101</td>
<td>Guanqyao et al. (1992)</td>
</tr>
<tr>
<td>Zr-modified mesoporous silica supported H4[PMo11VO40]</td>
<td>60 min</td>
<td>pH = 5.0; T = 308 K</td>
<td>52.63</td>
<td>Aghayan et al. (2013)</td>
</tr>
<tr>
<td>PAA-g-MSF</td>
<td>3 min</td>
<td>pH = 6.0; T = 313.15 K</td>
<td>278.49</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 3 | PAA-g-MSF compared with other adsorbents

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functional groups -COO in the adsorbent, which were in conformity with the theory of the synthesis of the material, but also gave a reasonable explanation of PAA-g-MSF adsorbing Dy$^{3+}$. Overall, the PAA-g-MSF nanocomposite obtained in this work has a strong competitive edge compared with other adsorbents and it also has a great prospect for recycling REEs from industrial wastewater.

ACKNOWLEDGEMENT

This study was supported by Public Service Project of the Chinese Ministry of Land and Resource (201311024). The authors would also like to thank the Fundamental Research Funds for the Central Universities, China University of Geosciences (Wuhan) (CUGL150803).

REFERENCES


Bou-Maroun, E., Chebib, H., Leroy, M. J. P., Boos, A. & Goetz-Grandmont, G. J. 2006a Solvent extraction of lanthanum(III), europium(III) and lutetium(III) by bis(4-acyl-5-hydroxyypyrazoles) derivatives. Separation and Purification Technology 50, 220–228.


Figure 8  (a) XPS spectra of original and Dy$^{3+}$-adsorbed PAA-g-MSF and (b) EDS spectra of SF, MSF, PAA-g-MSF and PAA-g-MSF-Dy$^{3+}$.


First received 1 June 2017; accepted in revised form 5 January 2018. Available online 24 January 2018