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Original Research

Recovering rare earth elements via immobilized red algae from ammonium-rich wastewater

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ABSTRACT

Biotreatment of acidic rare earth mining wastewater via acidophilic living organisms is a promising approach owing to their high tolerance to high concentrations of rare earth elements (REEs); however, simultaneous removal of both REEs and ammonium is generally hindered since most acidophilic organisms are positively charged. Accordingly, immobilization of acidophilic *Galdieria sulphuraria* (*G. sulphuraria*) by calcium alginate to improve its affinity to positively charged REEs has been used for simultaneous bioremoval of REEs and ammonium. The results indicate that 97.19%, 96.19%, and 98.87% of La, Y, and Sm, respectively, are removed by *G. sulphuraria* beads (GS-BDs). The adsorption of REEs by calcium alginate beads (BDs) and GS-BDs is well fitted by both pseudo first-order (PFO) and pseudo second-order (PSO) kinetic models, implying that adsorption of REEs involves both physical adsorption caused by affinity of functional groups such as −COO− and −OH and chemical adsorption based on ion exchange of Ca^{2+} with REEs. Notably, GS-BDs exhibit high tolerance to La, Y, and Sm with maximum removal efficiencies of 97.9%, 96.6%, and 99.1%, respectively. Furthermore, the ammonium removal efficiency of GS-BDs is higher than that of free *G. sulphuraria* cells at an initial ammonium concentration of 100 mg L^{-1}, while the efficiency decreases when initial concentration of ammonium is higher than 150 mg L^{-1}. Last, small size of GS-BDs favors ammonium removal because of their lower mass transfer resistance. This study achieves simultaneous removal of REEs and ammonium from acidic mining drainage, providing a potential strategy for biotreatment of REE tailing wastewater.

1. Introduction

Rare earth elements (REEs), composed of 15 lanthanide elements and two pseudolanthanide elements (Sc and Y), are present in small quantities with vast applications in manufacturing, the nuclear industry, electronic devices, and medicine [1]. REEs primarily exist in ore from specific regions of the world, which means that their extraction requires a series of specific processes, including physical meshing, floating, magnetic separation, and subsequent chemical processes, such as liquid–liquid or solid–liquid hydrometallurgical methods [2,3]. Accordingly, in situ chemical leaching with ammonium salts without extensive physical pretreatment is generally applied in REE mining operations, as a result of which local surface and groundwater are unavoidably contaminated by ammonium sulfate-rich effluent [4]. REE wastewater has been reported to be an acidic pollutant (pH value of 3.5–5.0) composed of NH_4^+ (50–200 mg L^{-1}), NO_3^- (10–80 mg L^{-1}), SO_4^{2-} (200–700 mg L^{-1}), trace organics (<10 mg chemical oxygen demand (COD) per L), and residual REEs, leading to serious environmental pollution problems [5]. Therefore, REE wastewater treatment is significant to local environmental protection.

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Considering the strategic properties and potential metal pollution of REEs, many studies regarding the recovery of REEs from REE wastewater through sorption to active carbon [6,7], biosorbents [8,9], nanoparticles [10,11], and clay minerals [12] and through precipitation with Fe oxyhydroxides, Al−Fe hydroxides, and even carbonates at high pH values have been conducted [13−15]. However, these strategies are extremely limited in practical applications since the adsorption capacity and precipitation efficiency are pH dependent and low recovery efficiencies are obtained under acidic conditions [16]. Additionally, alkali and alkaline metals such as Na^+, K^+, Ca^{2+}, and Mg^{2+} may compete with REEs for adsorption sites, leading to a limited recovery efficiency of REEs [17]. Accordingly, nanofiltration (NF), a pressure-driven process that can discriminate monovalent and multivalent ions, has alternatively been investigated for the recovery of REEs. However, membranes generally exhibit poor chemical stability under low pH conditions, leading to low REE rejection rates after filtration [18]. Therefore, the fabrication of acid-tolerant membranes has been extensively investigated to reduce the cost of membrane replacement [19]. Although NF can recover multivalent REEs under appropriate conditions, the high transmembrane pressure and loss of selectivity after long-term use in acid wastewater hinder their practical applications [20].

Biosorption of REEs via acidophilic living organisms has been investigated for the recovery of REEs owing to the high tolerance of such organisms to REEs under acidic conditions [21]. Initially, bacteria such as *B. subtilis*, *L. methylohalidivorans*, and *P. inhibens* were employed for the biosorption of REEs under acidic conditions [22]; however, extensive organic carbon is consumed by the metabolism of heterotrophic bacteria, making bacteria-based biosorption an energy-intensive methodology [23]. Therefore, autotrophic algae with CO_2 as a carbon source have attracted the attention of researchers. Furthermore, algal cell walls are generally composed of functional groups that act as active sites for binding REEs, such as −OH, −COOH, $-NH_2$, oxygen-containing groups, and other sulfated groups [24]. Nevertheless, both macroalgae and microalgae exhibit limited REE tolerance below 25 mg L^{-1} and a relatively low recovery efficiency of 70% [25]. The biosorption of positively charged ciprofloxacin via electrostatic attraction by *Chlamydomonas* sp. Tai-03 with 100% removal efficiency strongly inspired our interest in REE adsorption [22]. Chemical modifications to change the electrostatic interactions of biosorbents and REEs, including functional group grafting [26], acid or base treatment [27], and alginate base immobilization [28,29], have been investigated for enhancing metal removal from wastewater, but ammonium nitrogen, another primary pollutant in REE acidic mining effluent, is rarely reduced or recycled simultaneously.

However, some research on the biotreatment of ammonium/nitrate nitrogen-rich REE mining drainage by living microalgae has been reported owing to the remarkable nitrogen-fixation abilities of these organisms [8]. In addition to inorganic nitrogen, organic nitrogen, such as sulfamethoxazole, can be effectively biotransformed by microalgae [30]. Acidophilic microalgae, such as *Chlorococcum* sp., *Galdieria sulphuraria* (*G. sulphuraria*) [31], *Scenedesmus* sp. and *Parachlorella* sp. [5], are generally employed for deammonification owing to their high tolerance of REEs and low pH value. Although an ultrahigh ammonium recovery efficiency is reported in these studies, simultaneous recovery of REEs has rarely been reported. According to previous research, these acidophilic microalgae generally have a low removal efficiency ($\leq$25 mg L^{-1}), although they exhibit high REE tolerance. Based on our previous research, acidic microalgae are generally positively charged with a zeta potential of approximately 2−3 mV, which may hinder the adsorption of positively charged REEs [32]. Simultaneous recovery of high concentrations of REEs and ammonium from acidic mining drainage is still a great challenge for REE wastewater treatment. Calcium alginate-based immobilization is a promising strategy to functionalize the surface of microorganisms with specific functional groups or surface charges, potentially providing a path for the simultaneous recovery of REEs and ammonium [33].

On this basis, *G. sulphuraria*, a thermoacidophilic red algae, was immobilized by sodium alginate to simultaneously remove both REEs and ammonium nitrogen from acidic mining drainage. The biosorption efficiencies and adsorption kinetics of La, Y, and Sm on free *G. sulphuraria*, blank beads (BDs), and beads of immobilized *G. sulphuraria* (GS-BDs) were evaluated and simulated by a pseudo-first-order (PFO) kinetic model and pseudo-second-order (PSO) kinetic model. To explore the mechanism of adsorption of REEs, Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) analysis of the surface of preadsorption and postadsorption GS-BDs were investigated in detail. The bioaccumulation of ammonium in free *G. sulphuraria*, BDs, and GS-BDs with variable sizes was also studied under different initial concentrations of ammonium to achieve the simultaneous removal of REEs and high concentrations of ammonium nitrogen.

2. Materials and methods

2.1. Immobilization of *G. sulphuraria*

G. sulphuraria (UTEX 2919), denoted by Prof. Dong Wei of South China University of Technology, was initially cultivated in standard Allen's medium with 5 g L^{-1} glucose for seven days to obtain enough biomass. *G. sulphuraria* was cultivated at a light intensity of 12,000 lux with a light:dark ratio of 12 h:12 h, temperature of 45 °*C*, and agitation rate of 150 rpm with an initial inoculation concentration of 0.44 g L^{-1}. The *G. sulphuraria* cells were then centrifuged and starved for one day to consume residual ammonia nitrogen. Then, the algal cells were evenly resuspended in fresh Allen medium (without ammonium) with 10 g L^{-1} glucose and 4% (w/v) sodium alginate (AR, 90%, Shanghai Macklin Biochemical Co., Ltd., Shanghai, China). BDs and GS-BDs with algae densities of 5 and 15 g L^{-1}, named GS-BDs-5 and GS-BDs-15, respectively, were finally obtained by dropping algae solution into 2% (w/v) $CaCl_2$ (AR, Aladdin Industrial Corporation, Shanghai, China) solution with a sterile syringe. To explore the effect of particle size on the removal efficiency of ammonia nitrogen, GS-BDs-5 samples with variable diameters of 1.5, 3, and 6 mm were fabricated by manual titration with a specific sterile syringe.

2.2. Treatment of rare earth tailwater with algae beads

2.2.1. Synthetic rare earth tailwater

Synthetic wastewater samples with La, Y, and Sm ($La(NO_3)_3 \cdot 6H_2O$, 99.9%, Shanghai Macklin Biochemical Co., Ltd.; $Y(NO_3)_3 \cdot 6H_2O$, AR, 99.5%, Shanghai Macklin Biochemical Co., Ltd.; $Sm(NO_3)_3 \cdot 6H_2O$, 99.9%, Shanghai Macklin Biochemical Co., Ltd.) were prepared for investigation of the removal of REEs. To explore the REE bioremoval capacities of GS-BDs, the initial concentrations of La, Y, and Sm were 40, 80, 120, and 160 mg L^{-1}. Then, certain amounts of ammonium sulfate (AR, 99.9%, Shanghai Macklin Biochemical Co., Ltd.) were added to adjust the ammonium concentration to 100, 150, 200 and 250 mg L^{-1}. The pH value of the synthetic wastewater was then regulated to 2.5 with sulfuric acid (AR, Sinopharm Chemical Reagent Co., Ltd.).

2.2.2. Simultaneous removal of REEs and ammonium

First, 30 mL of BDs, GS-BDs-5, or GS-BDs-15 was mixed with 70 mL of REE wastewater in a 250-mL volumetric flask (30%, v/v). Then, the samples were kept at a temperature of 45 °C with a light:dark ratio of 12 h:12 h and light intensity of 12,000 lux in rare earth tailwater for five days. To explore the REE removal capacity of GS-BDs, mixtures of 40, 80, 120, and 160 mg L^{-1} La, Y, and Sm were initially added during the cultivation of GS-BDs-15. Free *G. sulphuraria* and GS-BDs with particle sizes of 1.5, 3, and 6 mm were cultured in synthetic REE wastewater to test the effect of particle size on the bioremoval efficiency of NH_4^+. The variations in REEs within the REE wastewater, BDs, and GS-BDs were tested by inductively coupled plasma–optical emission spectrometry (ICP–OES) (iCAP 7000, Thermo Fisher Scientific, Waltham, MA, USA). The variation in the concentration of ammonia nitrogen was determined by Nessler's reagent spectrophotometry [34]. The surface functional groups of algal beads before and after adsorption of REEs were analyzed by Fourier transform infrared (FTIR) spectroscopy (Nicolet 8700, Thermo Scientific, U.S.). The XPS spectra of GS-BDs were recorded with an X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo Fisher Scientific, USA) to confirm the adsorption of La, Y, and Sm by GS-BDs.

2.2.3. Modeling of the adsorption process

The equilibrium adsorption capacities (q_e, μg g^{-1}) and removal efficiencies (R) of La, Y, and Sm were calculated as follows:

$$q_e = (C_0 - C_i) \times \frac{V}{M} \tag{1}$$

$$R = \frac{C_0 - C_5}{C_0} \times 100\% \tag{2}$$

where C_0 (mg L^{-1}) and C_i (mg L^{-1}) are the initial and equilibrium concentrations of REEs, respectively, and C_5 (mg L^{-1}) is the concentration of REEs after five days of cultivation. V (mL) is the volume of wastewater, and M (g) is the weight of the beads.

PFO (equation (3)) and PSO (equation (4)) kinetic models were used to fit the adsorption process [35]:

$$q_t = q'_e\left(1 - e^{-k_1 t}\right) \tag{3}$$

$$q_t = \frac{q_e'^2 k_2 t}{1 + q'_e k_2 t} \tag{4}$$

where q_t and q_e' (μg g^{-1}) are the fitted adsorption capacity and theoretical equilibrium adsorption capacity, respectively, t is the time (min), and k_1 (min^{-1}) and k_2 (g $μg^{-1}$ min^{-1}) are the rate constants of the PFO and PSO models, respectively.

2.2.4. Recovery of REEs

After being used for REE wastewater treatment, 1 mL of GS-BDs was mixed with 100 mL of sodium citrate solution (1.5 wt%) and allowed to stand overnight. Then, the mixture was ultrasonically treated to assist in the release of REEs from the post adsorption beads. The concentrations of REEs were measured by ICP–OES, and the recovery efficiency of REEs was calculated via the following equation:

$$E_{Rec} = \frac{C_{Rec} V_1}{\frac{V_2}{V_3}(C_0 - C_i) V_4} \times 100\% \tag{5}$$

where E_{Rec} is the recovery efficiency of REEs; V_1, V_2, V_3, and V_4 (mL) are the volumes of the GS-BD sample and sodium citrate solution, the GS-BD sample for the recovery of REEs, all GS-BDs after culture, and the REE wastewater; and C_{Rec} is the concentration of REEs in the dissolved solution.

3. Results and discussion

3.1. REE removal efficiencies of algae, BDs, and GS-BDs

Free *G. sulphuraria*, BDs, and GS-BDs were used to recover REEs from synthetic rare earth tailwater containing 40 mg L^{-1} La, Y, and Sm. Although *G. sulphuraria* exhibited remarkable biological activity in the synthetic rare earth tailwater, the concentrations of La, Y, and Sm remained at approximately 35.0 mg L^{-1} without a significant reduction during the cultivation of free *G. sulphuraria* algal cells in synthetic rare earth tailwater (Fig. 1a). Conversely, 95.47%, 94.15%, and 96.72% of La, Y, and Sm, respectively, were removed from REE wastewater containing 100 mg L^{-1} ammonium by blank beads (BDs). There are slight decreases in the removal efficiencies of La, Y, and Sm with increasing ammonium concentration from 100 to 250 mg L^{-1}. Analogously, 97.19%, 96.19%, and 98.87% of La, Y, and Sm, respectively, were removed by GS-BDs. The REE removal efficiencies of GS-BDs also decrease with increasing ammonium concentration from 100 to 250 mg L^{-1}. Notably, the REE removal efficiencies of GS-BDs are all higher than those of BDs, except at 200 mg L^{-1} ammonium (Fig. 1b–d). Unlike negatively charged microalgae such as *Chlorella* sp [36]. and *Chlamydomonas* sp. Tai-03 [22], *G. sulphuraria* are spheres with an average diameter of 5.84 μm and zeta potential of 2.69 mV. The electrostatic repulsion between the surface of algal cells and REE ions hinders the physical adsorption of REEs, similar to the electrostatic repulsion between *Dunaliella acidophila* and heavy metal ions [37], subsequently leading to constant REE concentrations during the cultivation of free *G. sulphuraria*. In contrast, GS-BDs composed of sodium alginate are rich in functional groups such as —OH and —COOH (Fig. S1). These functional groups provide abundant active sites for the adsorption of REEs, resulting in the high REE removal efficiency of BDs. However, a blueshift in the absorption peak of O—H and an obvious increase in the absorption peak of asymmetric vibrations of —COO are observed owing to monodentate complexation, bidentate complexation or bridging of functional groups with REEs after biotreatment of REE wastewater (Fig. S1). To confirm the existence of REEs in GS-BDs, XPS analysis of GS-BDs-15 after adsorption of REEs was conducted, and the results are presented in Fig. 2. Peaks are observed at 852.3 and 835.4 eV, attributed to La $3d_{3/2}$ and $3d_{5/2}$, respectively (Fig. 2b); 160.95 and 158.05 eV, attributed to Y $3d_{3/2}$ and $3d_{5/2}$ (Fig. 2c); and 1110.1 and 1083.1 eV, attributed to Sm $3d_{3/2}$ and $3d_{5/2}$ (Fig. 2d), implying the adsorption of REEs by GS-BDs. However, the REE removal efficiencies of both BDs and GS-BDs all decrease with increasing ammonium concentration, possibly due to competition of NH_4^+ with REEs for active sites on the BDs [38]. The REE removal efficiency of GS-BDs is slightly higher than the REE removal efficiency of BDs because the extracellular polymeric substances of algal cells are rich in functional groups, facilitating bioaccumulation in *G. sulphuraria* cells [39]. Even though the increase in the REE removal efficiency of GS-BDs is limited, their advantages in removing ammonium reduce the cost of ammonium removal from REE wastewater.

3.2. Kinetics of adsorption of REEs

To explore the mechanism of adsorption of REEs by BDs and GS-BDs, the adsorption kinetics of REEs were fitted by a PFO kinetic model and a PSO kinetic model. As demonstrated in Fig. 3, La, Y, and Sm are all quickly adsorbed by both BDs and GS-BDs within 3 min, while the adsorption rates slow after 3 min and finally reach equilibrium in 8 min. In comparison, a slight decrease in the adsorption rates of REEs by BDs and GS-BDs with increasing ammonium concentration is observed. REEs have been reported to be able to coordinate with carboxylic groups and hydroxylic groups

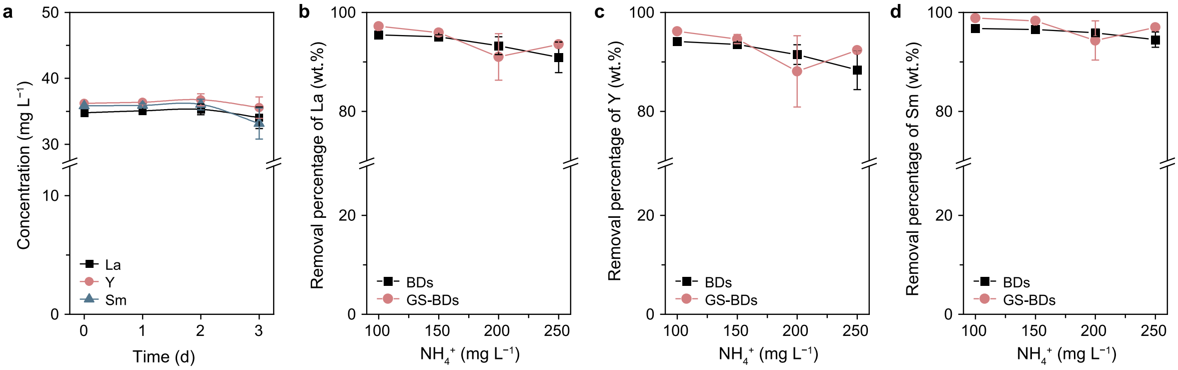

Fig. 1. **a**, Removal of La, Y, and Sm by free *G. sulphuraria*. **b–d,** Removal percentages of La (**b**), Y (**c**), and Sm (**d**) by BDs and GS-BDs-15.

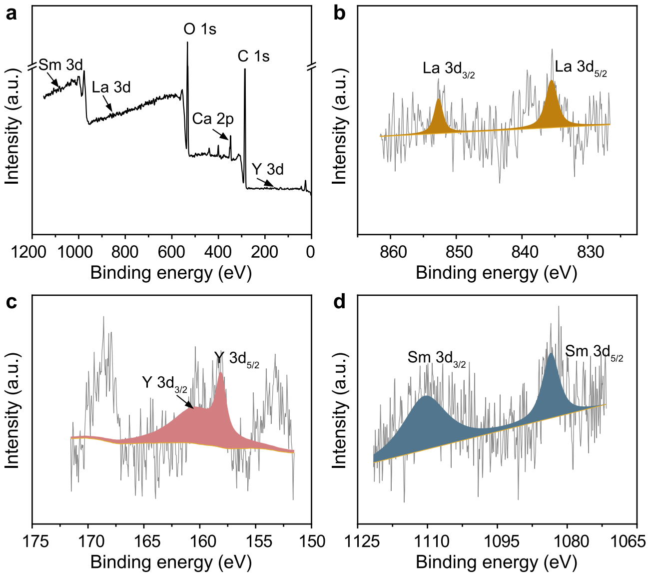

Fig. 2. XPS spectra of GS-BDs-15 after adsorption of REEs.

through monodentate complexation, bidentate complexation or bridging on the surface of BDs and GS-BDs, leading to the fast accumulation of REEs within 3 min [40]. The subsequent decrease in the adsorption efficiency of REEs is possibly due to the following two reasons. On the one hand, most of the active sites for the adsorption of REEs are occupied by La, Y, or Sm after 3 min, leading to decreases in the adsorption rates of REEs. On the other hand, the surface charges of BDs and GS-BDs become more positive with increasing concentrations of REEs, subsequently inhibiting further adsorption of REEs by enhanced electrostatic repulsion between the beads and REE ions. The decreases in the REE removal rates of BDs and GS-BDs are consistent with the variation in their relative removal efficiencies, possibly owing to the competition of NH_4^+ with REEs for active adsorption sites [41]. The parameters of the PFO model for the adsorption of La, Y and Sm by BDs and GS-BDs are listed in Tables 1 and 2, respectively. As presented, the adsorption of REEs by both BDs and GS-BDs is well fitted by the PFO model, with R^2 values above 0.98 (Table 1, Table 2), implying that the initial adsorption of REEs by both BDs and GS-BDs is a physical process.

Considering the possible ion exchange during the adsorption of REEs by BDs and GS-BDs, the kinetics of the adsorption of REEs were also simulated via the PSO model. According to Fig. 4, the adsorption of REEs by both BDs (Fig. 4a–c) and GS-BDs (Fig. 4d–f) is well fitted by the PSO model with average R^2 values of approximately 0.9906 (Table 3) and 0.9768 (Table 4), respectively, implying that chemical reactions also take place during the adsorption of REEs. Accordingly, the variations in the concentrations of REEs and Ca^{2+} with time were determined and are presented in Fig. 5. Remarkably, the concentration of Ca^{2+} increases from 24.1 to 260.9 mg L^{-1} with the adsorption of REEs from wastewater, while the concentrations of La, Y, and Sm decrease from 39.4, 37.1, and 37.5 mg L^{-1} to 3.09, 3.86, and 1.89 mg L^{-1}, respectively. According to stoichiometric analysis, approximately 0.872 mmol L^{-1} REEs are adsorbed by BDs, which implies that 1.31 mmol L^{-1} Ca^{2+} is released due to ion exchange during adsorption; this relationship indicates that an extra stoichiometric amount of Ca^{2+} is released in this process because of the release of Ca^{2+} from BDs or GS-BDs after the initial enrichment of Ca^{2+} from the culture medium. Overall, we propose that the adsorption of REEs from acidic mining drainage follows two processes: first, initial physical adsorption due to the affinity between REEs and functional groups of calcium alginate; and second, ion exchange between REEs and Ca^{2+}. Ion exchange of Ca^{2+} with REEs after physical adsorption is a limiting step for further bioaccumulation of REEs. REEs are stored in BDs or GS-BDs at an equilibrium concentration following these two processes.

The adsorption capacities and removal percentages of La, Y, and Sm by GS-BDs-15 with initial concentrations of 80, 120, and 160 mg L^{-1} were also tested. As demonstrated, La, Y, and Sm still have a high removal efficiency when a high initial concentration is used (Fig. 6), exhibiting losses of 11.3, 14.6, and 7.16 mg L^{-1}, respectively, after 40 min with an initial REE concentration of 160 mg L^{-1} in wastewater (Fig. 6c). The removal efficiencies of REEs at 80–160 mg L^{-1} are ranked as Sm > La > Y, with maximum removal efficiencies of 99.1%, 97.9%, and 96.6%, respectively (Fig. 6d). The removal rate of metal ions generally depends on the properties of the adsorbent, electronegativity of the metal ion, ionic radius, coordination number, and affinity constant between the metal and adsorbent [42,43]. Among these parameters, the affinity constants of La, Y, and Sm are $10^{6.8}$, $10^{6.8}$, and $10^{7.0}$, respectively, indicating that Sm has the highest affinity [44,45]. Accordingly, the removal percentages of Sm are higher than those of La and Y under the same conditions.

3.3. *Recovery of REEs*

The recovery of REEs from GS-BDs after adsorption was also tested by dissolving GS-BDs in sodium citrate. According to Fig. 7, the recovery percentages of La, Y, and Sm decrease from 72.7%, 76.1%, and 63.5% with an initial concentration of 80 mg L^{-1} to 65.1%, 66.4%, and 56.5%, with an initial concentration of 120 mg L^{-1}, respectively. However, they notably increase to 72.3%, 74.2%, and

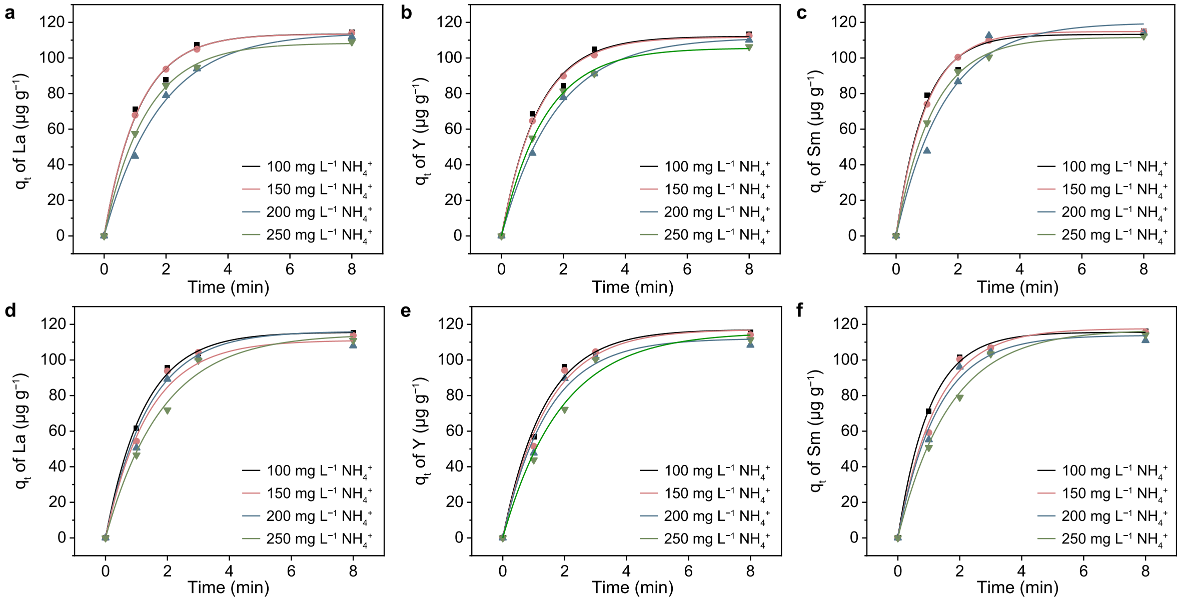

Fig. 3. Simulated PFO model of REE adsorption by BDs under different ammonium concentrations: **a**, La; **b**, Y; **c**, Sm. Simulated PFO model of REE adsorption by GS-BDs under different ammonium concentrations: **d**, La; **e**, Y; **f**, Sm.

Table 1
Parameters of the PFO model for the adsorption of La, Y, and Sm by BDs.

NH_3—N (mg L^{-1})	La			Y			Sm		
	$q_e^{'}$ (μg g^{-1})	k (min^{-1})	R^2	$q_e^{'}$ (μg g^{-1})	k (min^{-1})	R^2	$q_e^{'}$ (μg g^{-1})	k (min^{-1})	R^2
100	113.5	0.8876	0.9921	112.2	0.8412	0.9907	113.2	1.085	0.9918
150	113.4	0.8927	0.9997	111.7	0.8364	0.9995	114.9	1.035	1.0
200	114.2	0.5549	0.9970	111.5	0.5695	0.9990	119.8	0.6367	0.9774
250	108.4	0.7427	0.9992	105.6	0.7194	0.9989	111.6	0.8421	0.9991

Table 2
Parameters of the PFO model for the adsorption of La, Y, and Sm by GS-BDs.

NH_3—N (mg L^{-1})	La			Y			Sm		
	$q_e^{'}$ (μg g^{-1})	k (min^{-1})	R^2	$q_e^{'}$ (μg g^{-1})	k (min^{-1})	R^2	$q_e^{'}$ (μg g^{-1})	k (min^{-1})	R^2
100	115.6	0.8014	0.9978	117.1	0.7454	0.9942	115.5	0.9751	0.9985
150	116.1	0.7243	0.9931	117.2	0.6967	0.9887	117.7	0.8003	0.9915
200	111.1	0.7186	0.9904	112.1	0.6902	0.9850	113.9	0.7801	0.9897
250	114.6	0.5481	0.9896	115.6	0.5312	0.9897	117.0	0.5992	0.9942

64.3% with an initial concentration of 160 mg L^{-1}, respectively. We suppose that most REE ions are physically adsorbed by BDs and GS-BDs and may therefore be more easily detached by sodium citrate, while REEs might chemically bind with alginate via ion exchange with calcium ions, leading to decreases in the recovery efficiencies of REEs. However, we suppose that the amount of physically adsorbed REEs increases since extra REEs are physically adsorbed at an initial concentration of approximately 160 mg L^{-1}, subsequently enhancing the recovery of REEs from GS-BDs. Another point worth mentioning is that the recovery efficiencies of REEs at initial concentrations of 80–160 mg L^{-1} are ranked as Y > La > Sm, which is totally different from the relative removal efficiencies of GS-BDs from wastewater. The high affinity of REEs such as Sm for BDs possibly leads to low recovery efficiency, and vice versa. In addition to demonstrating potential for the recovery of REEs, immobilized *G. sulphuraria* can be harvested via filtration and resuspended for the next sequence of immobilization, possibly reducing the cost for the treatment of REE wastewater.

3.4. Removal of ammonium by GS-BDs

In addition to the adsorption of REEs from acidic mining wastewater, the bioremoval of ammonium, another important pollutant, was extensively investigated. According to Fig. 8a–d, ammonium at initial concentrations of 100, 150, 200, and 250 mg L^{-1} is initially adsorbed by BDs within 1–3 days, after which it is slowly released to reach equilibrium concentrations of 95.4, 128.0, 160.6, and 210.0 mg L^{-1}, respectively. Conversely, significant decreases in ammonium concentrations are observed with the addition of free *G. sulphuraria* and GS-BDs with initial biomass concentrations of 15 and 5 g L^{-1}, named GS-BDs-15 and GS-BDs-5, respectively. Notably, both GS-BDs-15 and GS-BDs-5 have higher ammonium removal efficiencies than free algae cells of *G. sulphuraria* at an initial ammonium concentration of 100 mg L^{-1}, while the ammonium removal rates of GS-BDs decrease with increasing initial concentration of ammonium. In addition, average equilibrium concentrations of 73.6, 88.5, 115.2, and 128.3 mg L^{-1}

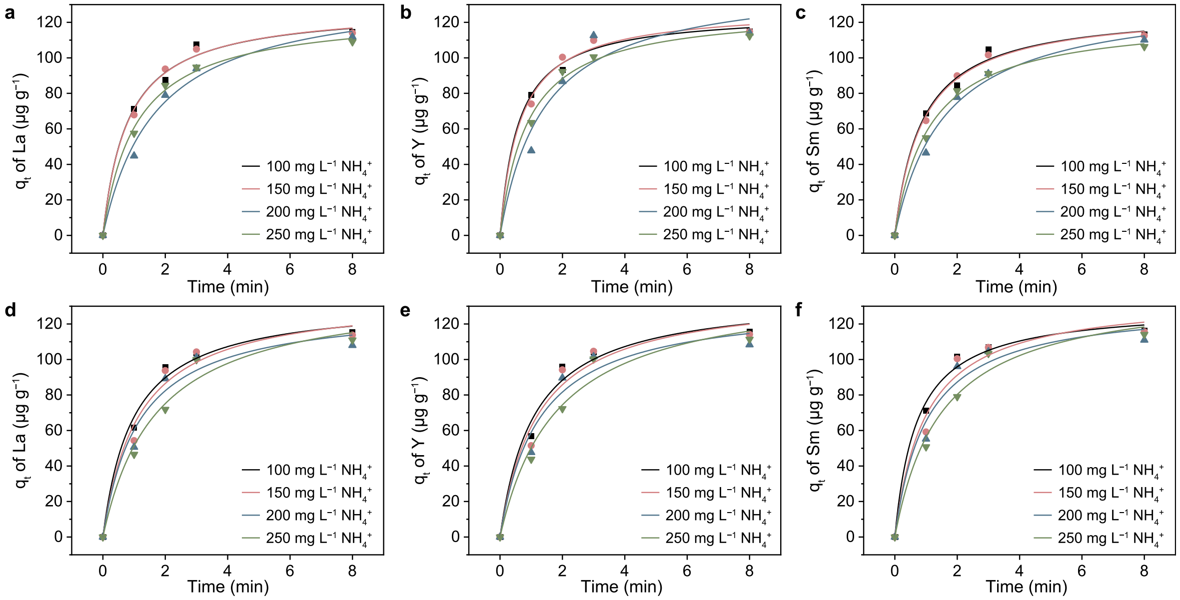

Fig. 4. Simulated PSO model of REE adsorption by BDs under different ammonium concentrations: **a**, La; **b**, Y; **c**, Sm. Simulated PSO model of REE adsorption by GS-BDs under different ammonium concentrations: **d**, La; **e**, Y; **f**, Sm.

Table 3
Parameters of the PSO model for the adsorption of La, Y, and Sm by BDs.

NH_3–N (mg L^{-1})	La			Y			Sm		
	$q_e^{'}$ (μg g^{-1})	$k_2 \times 10^3$ (g μg^{-1} min^{-1})	R^2	$q_e^{'}$ (μg g^{-1})	$k_2 \times 10^3$ (g μg^{-1} min^{-1})	R^2	$q_e^{'}$ (μg g^{-1})	$k_2 \times 10^3$ (g μg^{-1} min^{-1})	R^2
100	128.2	9.7	0.9930	127.4	9.09	0.9927	125.6	13.51	0.9923
150	128.6	9.61	0.9958	127.7	8.87	0.9966	128.1	12.18	0.9933
200	139.5	4.21	0.9880	135.2	4.56	0.9929	143.5	4.93	0.9538
250	125.8	7.41	0.9966	123.1	7.22	0.9970	127.6	8.79	0.9948

Table 4
Parameters of the PSO model for the adsorption of La, Y, and Sm by GS-BDs.

NH_3–N (mg L^{-1})	La			Y			Sm		
	$q_e^{'}$ (μg g^{-1})	$k_2 \times 10^3$ (g μg^{-1} min^{-1})	R^2	$q_e^{'}$ (μg g^{-1})	$k_2 \times 10^3$ (g μg^{-1} min^{-1})	R^2	$q_e^{'}$ (μg g^{-1})	$k_2 \times 10^3$ (g μg^{-1} min^{-1})	R^2
100	133.2	7.75	0.9892	136.5	6.71	0.9814	130.1	10.77	0.9922
150	136.0	6.43	0.9775	138.2	5.91	0.9710	135.9	7.50	0.9675
200	130.3	6.60	0.9718	132.5	6.05	0.9643	131.9	7.41	0.9709
250	140.0	4.14	0.9783	142.5	3.83	0.9746	140.6	4.73	0.9829

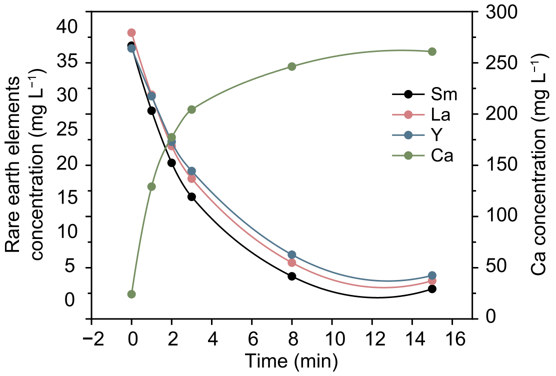

Fig. 5. Variations in the concentrations of REEs and Ca^{2+} with time.

ammonium are obtained after REE treatment with an initial ammonium concentration of 250 mg L^{-1} by BDs, free *G. sulphuraria*, GS-BDs-15, and GS-BDs-5, as demonstrated in Fig. 8a–d. As illustrated, NH_4^+ might be adsorbed by functional groups, such as –COO–, and –OH, during the adsorption of REEs, leading to a dramatic decrease in NH_4^+ concentration. Nevertheless, the adsorbed NH_4^+ would be released to reach an equilibrium NH_4^+ concentration owing to the competition of REEs for active sites. Ammonium is an important nitrogen source for the metabolism of *G. sulphuraria*. Accordingly, a continuous decrease in ammonium concentration is observed due to bioaccumulation by *G. sulphuraria*. However, a lower ammonium removal rate is observed for free algae cells than immobilized algae cells at an initial ammonium concentration of 100 mg L^{-1}, possibly owing to both the reduced charges of algae cells and the increased functional groups resulting from immobilization. Moreover, the ammonium removal rate decreases with increasing initial ammonium concentration since extra ammonium adsorbed by BDs would electrostatically repel further ammonium adsorption to algae cells. Furthermore, there is a slight increase in ammonium concentration at the 3rd or 4th day

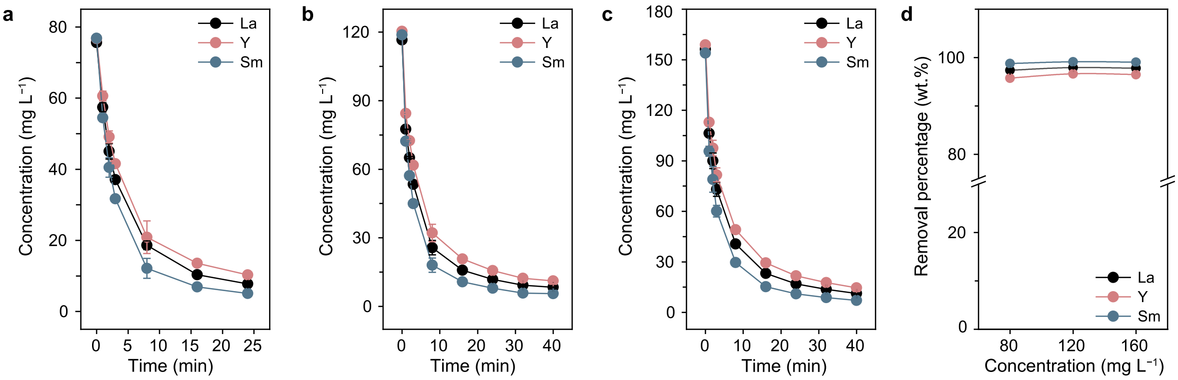

Fig. 6. Variations in the concentrations of REEs with time under different initial concentrations of REEs: **a**, 80 mg L^{-1}; **b**, 120 mg L^{-1}; **c**, 160 mg L^{-1} **d**, Removal percentages of REEs under different concentrations.

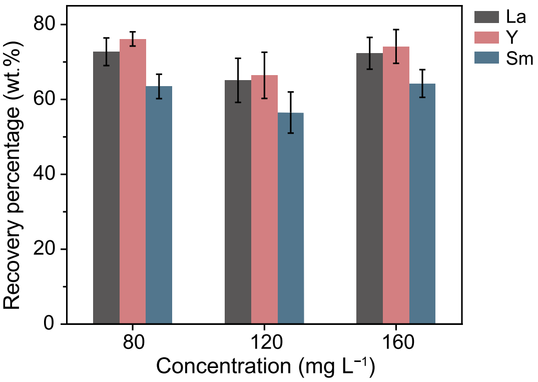

Fig. 7. Recovery percentages of REEs from GS-BDs-15 after treatment of REE wastewater under 80, 120, and 160 mg L^{-1} La, Y, and Sm with 200 mg L^{-1} NH_4^+.

of cultivation of GS-BDs with initial ammonium concentrations of 150, 200, and 250 mg L^{-1}, proving that adsorption equilibrium of ammonium is reached with alginate-based immobilization. Although the ammonium removal efficiencies after 5 days with initial concentrations of 150, 200, and 250 mg L^{-1} are lower for GS-BDs than free *G. sulphuraria*, the adsorption of REEs by GS-BDs offsets the extra cost for immobilization of microalgae and reduced ammonium removal efficiency.

Unlike the adsorption of REEs, the removal of ammonium is primarily attributed to the metabolism of algal cells. Thus, the effect of the size of GS-BDs, which determines the mass transfer resistance of NH_4^+ from wastewater to algae cells, on the ammonium removal rate was also investigated. GS-BDs with diameters of 1.5, 3 and 6 mm, named GS-BDs-1.5, GS-BDs-3.0, and GS-BDs-6.0, were used to remove ammonium from acidic mining wastewater. According to Fig. 9, 58.6, 74.6, and 112.0 mg L^{-1} ammonium is observed after the treatment of REE wastewater by GS-BDs-1.5, GS-BDs-3.0, and GS-BDs-6.0, respectively. Obviously, reducing the size of GS-BDs from 6.0 mm to 1.5 mm is more favorable to ammonium removal owing to both increased surface area and lower mass transfer resistance at smaller diameters. However, a continuous decrease might lead to larger mass transfer resistance because of both the formation of tightly bound BDs caused by enhanced ion exchange and self-shading of GS-BDs, subsequently leading to a decrease in ammonium removal efficiency [46].

4. Conclusions

In this work, simultaneous removal of both REEs and ammonium from acidic rare earth mining wastewater is achieved by calcium alginate-immobilized *Galdieria sulphuraria* beads (GS-BDs). Four major conclusions are reached as follows:

First, 95.47%, 94.15%, and 96.72% of La, Y, and Sm, respectively, are removed from REE wastewater by BDs, while slightly higher amounts of La, Y, and Sm can be removed by GS-BDs owing to the REE bioaccumulation capacity of microalgae.

Second, the adsorption of REEs by BDs and GS-BDs is well fitted by PFO and PSO kinetic models because they are a combination of both physical adsorption due to the affinity of functional groups and ion exchange of Ca^{2+} with REEs. The removal efficiencies of

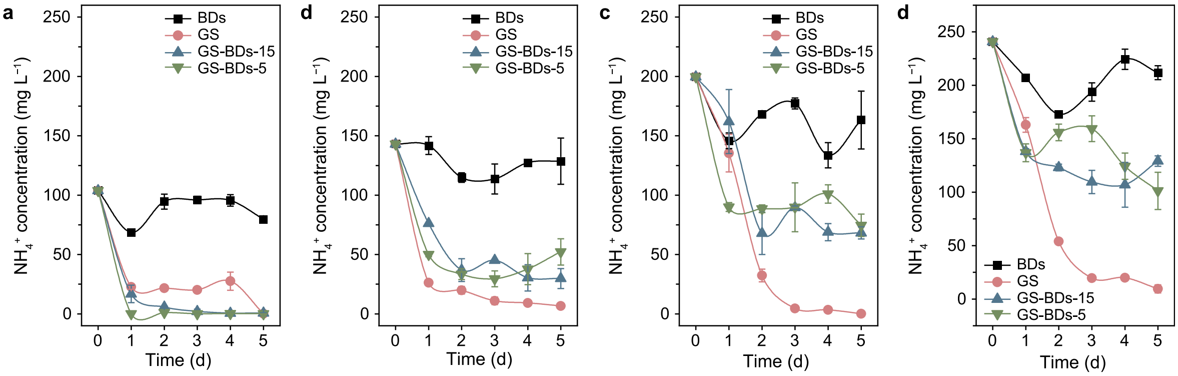

Fig. 8. Removal of ammonium by BDs, free *G. sulphuraria* cells (GS), GS-BDs-15, and GS-BDs-5 with a mixture of coexisting REEs (40 mg L^{-1} La, 40 mg L^{-1} Y, and 40 mg L^{-1} Sm) under the following initial concentrations: **a**, 100 mg L^{-1}; **b**, 150 mg L^{-1}; **c**, 200 mg L^{-1}; **d**, 250 mg L^{-1}.

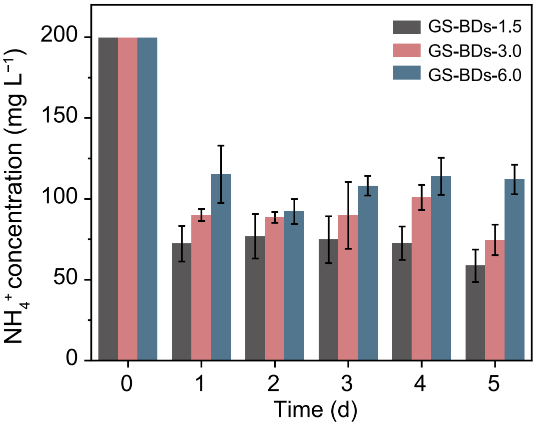

Fig. 9. Ammonia nitrogen removal by GS-BDs (5 g L^{-1}) with particle sizes of 1.5, 3, and 6 mm.

REEs at 80–160 mg L^{-1} are ranked as Sm > La > Y, with maximum removal efficiencies of 99.1%, 97.9%, and 96.6%, respectively.

Third, the recovery efficiencies of La, Y, and Sm with initial concentrations ranging from 80 to 160 mg L^{-1} by GS-BDs are contrary to their removal efficiencies since the affinity of BDs for REEs is positively related to their REE adsorption capacity.

Fourth, the ammonium removal efficiencies of both GS-BDs-15 and GS-BDs-5 are higher than the ammonium removal efficiency of free *G. sulphuraria* at an initial concentration of 100 mg L^{-1} but are lower when the initial ammonium concentration is higher than 150 mg L^{-1} because electrostatic repulsion hinders the further adsorption of ammonium by algae cells. Additionally, reducing the size of GS-BDs from 6.0 mm to 1.5 mm favors ammonium removal owing to both the increased surface area and lower mass transfer resistance at smaller diameters.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ese.2022.100204.

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