APPLICATION OF LOW-COST ALGINATE-BASED BIOSORBENTS FOR EFFECTIVE RECOVERY OF RARE EARTH ELEMENTS

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Abstract

Rare earth elements are used in many high-tech applications but their rarity and availability require the development of methods for their recovery from low-quality sources and recycling from waste materials. Sorption processes, including biosorbents, are an interesting method for their recovery from dilute solutions. This work investigates the sorption of lanthanum(III) ions using cheap, renewable biosorbents: calcium alginate and biochar (considered as reference materials) and an alginate-based biosorbent named alginate-biochar composite (ALG-BC). Sorption properties of these materials were compared using batch-adsorption techniques, under various sorption conditions. The obtained sorption results show the applicability of the biosorbents for rare earth elements recovery.

Keywords: alginate, biochar, biosorbents, rare earth elements, adsorption abilities

Introduction

In recent years rare earth elements (REEs) have gained increasing importance due to their special functionality in many fields, including electronics, glass, ceramics, catalysis, optics, magnets and superconductors. REEs are important strategic elements. Their largest deposits are located in China, which is the main exporter of these raw materials. However, China has recently changed its policy significantly and limited the export of these raw materials, due to the depletion of their natural resources (Anastopoulos et al. 2016, Maksymowicz 2019). The constantly growing demand for these elements all over the world necessitates finding alternative sources. The commonly used methods for preconcentration and recovery of metal ions from different solutions include adsorption, ion exchange, solvent extraction, precipitation, electrochemical or membrane processes (Gupta et al. 2019). Among these methods a very promising one is biosorption using low-cost natural materials, such as alginate, chitosan, zeolite, cellulose, lignin, and solid wastes, such as biochar, fly ash or activated carbon (Galhoum et al. 2017, Gładysz-Płaska et al. 2003, Kołodyńska et al. 2018, Xiaoqi et al. 2016, Zhang et al. 2011). For example Galhoum et al. (2017) studied the sorption of La(III), Nd(III) and Er(III)) using cellulose and the maximum sorption capacities for rare earth metal ions were in the range of 31-53 mg/g. Unfortunately, very often adsorption capacities of natural adsorbents are not as efficient as expected. Therefore, the aim is to improve their adsorption properties through the synthesis of hybrid biosorbents by doping various organic or inorganic materials.

Alginate salts, for example calcium alginate, are some of the carriers for the immobilization of microorganisms or biocatalysts (Pankhurst et al. 2003). They can be also used as a matrix for immobilization of some sorbent materials with very small particle size. This fact is influenced by factors such as the presence of carboxyl groups (Figure 1), natural origin, hydrophilicity, relatively good mechanical strength, and a very cheap and easy procedure to obtain a gel that is non-toxic and benign to the immobilized material.

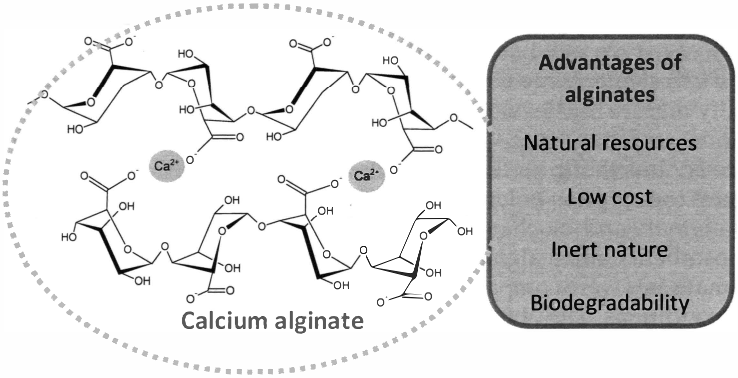

Figure 1. Egg-box structure of calcium alginate and alginate advantages.

Immobilization of biomass on a granular or polymeric matrix can increase the efficiency and adsorption capacity of the biosorbent towards metal ions and facilitates separation of biomass from solution. Wu et al. (2011) prepared magnetic alginate-chitosan gel beads by incorporating iron oxide nanoparticles onto a mixed alginate and chitosan adsorbent. Glutaraldehyde was used as a crosslinking agent. The obtained composite was used for La(III) ions sorption from aqueous solutions. Sorption equilibrium was achieved after 10 hours and the obtained maximum capacity was 97.1 mg/g.

The overall aim of the paper was to study the sorption properties of calcium alginate and biochar as reference materials and to explore the potential of alginate-based biosorbents prepared using sodium alginate as a matrix, different amounts of biochar as an additive, and calcium chloride as a crosslinking agent for the removal and recovery of REEs.

Materials and Methods

To synthetize alginate based composites, sodium alginate purchased from Carl Roth (Germany), calcium chloride purchased from Chempur (Poland), and biochar derived from animal manure combustion were used. The procedure for the synthesis was as follows: a 1% solution of sodium alginate (ALG) was prepared to which various amounts of biochar (BC) were added to obtain ALG:BC ratios of 5:1, 2:1, 1:1, 1:2, 1:5. The whole mixture was stirred using a magnetic stirrer (ES 21, Wigo, Poland). Then this mixture was dripped with 1% calcium chloride solution using a peristaltic pump (BT100S-1, Lead Fluid Technology Co., Ltd. China). After 24 h, the obtained beads were washed several times with distilled water and were allowed to dry. Additionally, calcium alginate beads without additives were prepared and their sorption properties towards rare earth ions were compared.

Sorption studies were performed using the batch sorption method. Nitrate salts of rare earth elements purchased from Sigma Aldrich (Germany) were used for sorption studies. The influence of several operating parameters i.e. solution pH (1-7), contact time (1-1440 minutes), and initial REE concentration (25-500 mg/dm^3) was tested and presented. The metal ions concentration after sorption experiments was analyzed using an ICP-OES spectrometer (720-ES Varian Inc., USA).

Results and Discussion

The ALG-BC composite with different amounts of ALG and BC was prepared and used for adsorption tests. The prepared composite beads were named: ALG (1:0, ALG:BC), BC (0:1 ALG:BC), ALG_5BC_1 (5:1, ALG:BC), ALG_2BC_1 (2:1, ALG:BC), ALG_1BC_1 (1:1, ALG:BC), ALG_1BC_2 (1:2, ALG:BC), and ALG_1BC_5 (1:5, ALG:BC), respectively.

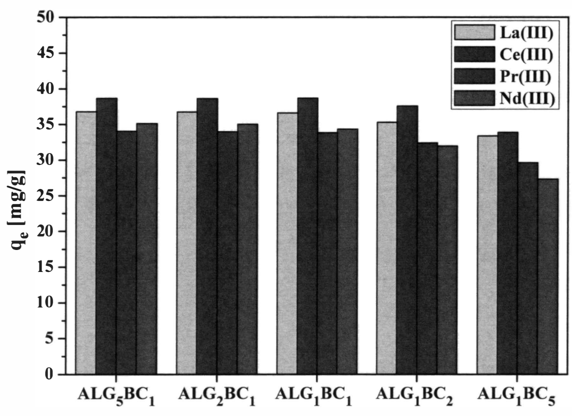

Figure 2. Effect of different amount of ALG and BC on REE sorption process (m= 0.05 g, V= 20 cm^3, C_0= 100 mg/dm^3, t= 480 min, T= 293 K).

ALG_5BC_1, ALG_2BC_1, and ALG_1BC_1 composites had the highest values of q_e (Figure 2) and %S equal to about 100% towards La(III), Ce(III), Pr(III), and

Nd(III) ions sorption, hence one of them, i.e. ALG_5BC_1 composite was chosen in subsequent adsorption experiments (i.e. for effect of solution pH, effect of phase contact time, and effect of initial metal concentration).

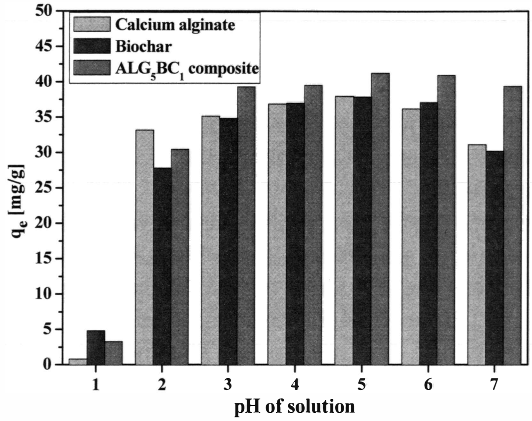

Figure 3. Effect of La(III) solution pH on sorption (m= 0.05 g, V= 20 cm^3, C_0= 100 mg/dm^3, t= 480 min, T= 293 K).

The influence of solution pH value on REE sorption efficiencies was noted. Figure 3 shows the obtained equilibrium adsorption capacities for different solution pH values on the example of La(III) ions for calcium alginate, biochar and their composite. When pH increased from 1 to 5, the equilibrium adsorption of lanthanum(III) ions enhanced. The optimum pH value for REE ions sorption on the biosorbents was 5.

In the next step, the effect of phase contact time on the amount of adsorbed La(III) ions on calcium alginate, biochar, and ALG_5BC_1 composite was investigated.

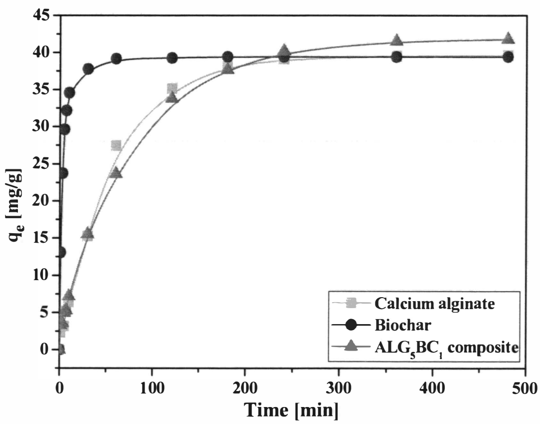

Figure 4. Effect of phase contact time on La(III) sorption effectiveness (m= 0.05 g, V= 20 cm^3, C_0= 100mg/dm^3, pH= 5, t= 480 min, T= 293 K).

As shown in Figure 4, with time increasing, the amount of La(III) ions adsorbed increased until sorption equilibrium was established. For biochar the sorption equilibrium state was achieved after 60 minutes, but for calcium alginate and ALG_5BC_1 composite after 240 minutes, so the biosorbents are characterized by good kinetic properties.

Effect of initial concentration of La(III) ions on the sorption process was investigated (Figure 5). The results showed that the equilibrium sorption capacity of La(III) ions increased with the increase of initial metal concentration. The maximum q_e values were obtained for 500 mg/dm^3 and were: 100.46 mg/g for calcium alginate, 68.42 mg/g for biochar, and 110.28 mg/g for ALG_5BC_1 composite. The synthesized ALG_5BC_1 composite showed better removal efficiency of La(III) ions than the reference materials i.e. calcium alginate and biochar.

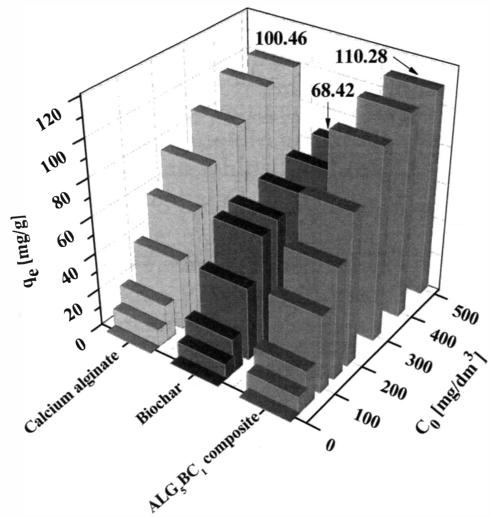

Figure 5. Effect of initial concentration on La(III) ions sorption (m= 0.05 g, V= 20 cm^3, C_0= 100 mg/dm^3, t= 480 min, T= 293 K).

The effectiveness of the La(IIII) ions sorption process on the used biosorbents followed the order: ALG_5BC_1 composite > calcium alginate > biochar.

Conclusions

In this study, it was confirmed that alginate can be used to synthesize alginate-biochar composite. The obtained ALG_5BC_1 composite demonstrated effective sorption of La(III) ions from aqueous solutions and proved to be a very promising biosorbent for REE ions sorption and recovery.

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