



Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

A simple approach to fabricate granular adsorbent for adsorption of rare elements

Yongfeng Zhu^{a,b}, Yian Zheng^a, Aiqin Wang^{a,*}^a Center of Xuyi Attapulgite Applied Technology, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China^b University of Chinese Academy of Sciences, Beijing 100049, PR China

ARTICLE INFO

Article history:

Received 4 July 2014

Received in revised form 7 August 2014

Accepted 10 August 2014

Available online xxx

Keywords:

Granular hybrid hydrogel

Hydroxypropyl cellulose

Attapulgite

Adsorption

Rare earth

ABSTRACT

A kind of granular hybrid hydrogel was prepared under an ambient temperature in air atmosphere using Fenton reagent as the redox initiator, and its three-dimensional structured polymeric network can be formed by the grafting reaction of acrylic acid (AA) onto hydroxypropyl cellulose (HPC) with attapulgite (APT) as the inorganic component. The resulting granular hybrid hydrogel was marked as HPC-g-PAA/APT and used as the adsorbent to remove the rare earth elements, La(III) and Ce(III). The effects of pH and APT content on the adsorption capacity, as well as the adsorption isotherms and kinetics, were systematically investigated. Finally, the reusability of HPC-g-PAA/APT for La(III) and Ce(III) were evaluated. The results indicate that the adsorption process is pH-independent at $\text{pH} \geq 4.0$ and can be described using the pseudo-second-order kinetic model. The equilibrium isotherm matches well with the Langmuir model. The adsorbed La(III) and Ce(III) can be desorbed by 0.5 mol/L HCl, with the desorption percentage of 80% for La(III) and Ce(III). After five adsorption–desorption cycles, the adsorption capacity shows a slight decrease (about 15%), implying that the granular hybrid hydrogel can be used as an effective adsorbent for the removal and recovery of La(III) and Ce(III) from aqueous solution.

© 2014 Published by Elsevier B.V.

1. Introduction

Rare earth elements (REEs), including the lanthanide series from the atomic number 57 to 71 and the other two elements Sc and Y, have a similar atomic structure and chemical and physical properties [1]. Rely upon their chemical, catalytic, electrical, magnetic, and optical properties, REEs have been applied in many high-tech fields, such as chemical engineering, information storage, energy conservation and nuclear energy [2–8]. In recent years, with the ever-increasing demand for high-purity rare earths and their compounds, the separation and purification of REEs have gained considerable attention. Up to now, many methods have been used to separation, purification and preconcentration of REEs, such as coprecipitation [9], solvent extraction [10,11], and ion-exchange [12]. However, these traditional methods have some disadvantages, such as high consumption of reagent and energy, low selectivity, high operational cost and generation of secondary metabolites [13]. In comparison with conventional technologies, adsorption is one of the most attractive methods and has been used for the concentration and recovery of metal ion [14–17].

Recently, the adsorbents based on natural polymers have drawn wide attention, because of the features of rich material sources, low cost, non-toxicity and biodegradability, such as alginate [18], chitin [19], chitosan [20], β -cyclodextrin [21], cellulose [22], starch [23], and gum acacia [24]. Hydroxypropyl cellulose (HPC) is an ether of cellulose in which some of the hydroxyl groups in the repeating glucose units have been hydroxypropylated forming $-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_3$ groups using propylene oxide. It has been widely used in the tissue engineering [25] and drug release [26,27]. The HPC has ether bond ($-\text{C}-\text{O}-\text{C}-$) and hydroxyl ($-\text{OH}$) groups, which can serve as the coordination sites to form complexes with various heavy metal ions, so HPC can be used as a potential adsorbent material.

In this paper, HPC was used as the backbone to graft poly (acrylic acid) to form a granular hybrid hydrogel via a facile fabrication at room temperature using Fenton reagent as the redox initiator. In order to lower the cost of water treatment and improve the gel strength, attapulgite, a crystalline hydrated magnesium silicate with a fibrous morphology, large specific surface area and moderate cation exchange capacity, was introduced in the hydrogel matrix. The resulting hybrid hydrogel was evaluated the adsorption ability for two common rare earth elements La(III) and Ce(III), which advanced new materials such as super alloys, catalysts, special ceramics and organic synthesis [28,29]. The effects of pH and

* Corresponding author. Tel.: +86 9314968118.
E-mail addresses: aqwang@lzb.ac.cn, aqwang@licp.cas.cn (A. Wang).

65 APT content on the adsorption capacity were studied. The adsorption
66 isotherms and adsorption kinetics of HPC-g-PAA/APT for La(III)
67 and Ce(III) were investigated. Furthermore, the reusability of HPC-
68 g-PAA/APT for adsorption of La(III) and Ce(III) were also evaluated.

69 2. Experimental

70 2.1. Materials

71 Acrylic acid (AA, chemically pure) was purchased from Shanghai
72 Shanpu Chemical Factory, China, and used without further treat-
73 ment. Hydroxypropyl cellulose (HPC, the average molecular weight
74 is 1.0×10^4) was received from Amatek Chemical Technology
75 Co., Ltd., China. *N,N*-methylenebisacrylamide (MBA, chemically
76 pure) was received from Shanghai Yuanfan additives plant, China.
77 Ammonium iron (II) sulfate hexahydrate ($(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$,
78 analytical grade), hydrogen peroxide solution (H_2O_2 , analytical
79 grade), cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, analytical
80 grade) and lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, ana-
81 lytical grade) were all supplied by Sinopharm Chemical Reagent
82 Co., Ltd., China. Natural attapulgite (APT, industrial grade, the R&D
83 Center of Xuyi Attapulgite Applied Technology, Lanzhou Institute of
84 Chemical Physics, CAS) was milled and sieved through a 200-mesh
85 screen prior to use. Other reagents used were all analytical grade
86 and all solutions were prepared with distilled water.

87 2.2. Preparation of the granular adsorbent

88 A series of granular hydrogels was prepared according to fol-
89 lowing procedure: 3.6 g AA, 0.15 g MBA and 45 mL distilled water
90 were added in a 250 mL three-neck flask. The mixture was stirred
91 at 500 rpm for 0.5 h. Afterward, 0.3 g HPC was added in the flask
92 and kept stirring for 4 h until HPC was completely dissolved. After-
93 ward, a certain amount of APT (0.18 g for 1:20 to AA, 0.36 g for
94 1:10 to AA, 0.6 g for 1:6 to AA, 1.2 g for 1:3 to AA and 1.8 g for 1:2
95 to AA) was added and stirred for 60 min. Later, a given mass of
96 $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and H_2O_2 (3%) were all added. In just a few
97 minutes, the reaction solution changed the color from colorless to
98 brown, hereafter, the granular hydrogel was observed. And then
99 the reaction was kept for another 1 h at room temperature. When
100 the reaction was finished, the granular hydrogel was sieved and
101 immersed in 2.0 mol/L NaOH solution to neutral pH (approximately
102 60% neutralization degree according to the amount of AA), then the
103 industrial alcohol was added to dehydrate. The resulting granular
104 hydrogel was dried at room temperature. The blank sample without
105 APT was named as HPC-g-PAA/APT (AA/APT = 1/0), and the other
106 adsorbent was denoted as HPC-g-PAA/APT (AA/APT = $a/1$) ($a = 20$,
107 10, 6, 3, 2). All hydrogel samples used in the adsorption experiment
108 was ground and had a particle size in the range of 40–80 mesh.

109 2.3. Characterization

110 The conformation of granular hydrogel was analyzed by FTIR
111 spectra, which were determined by a Nicolet NEXUS FTIR spectrom-
112 eter in the wave number region of 4000–400 cm^{-1} using KBr pellets.
113 The morphologies of the samples were observed using a JSM-6701F
114 Field Emission Scanning Electron Microscope (JEOL) after coating
115 the sample with gold film.

116 2.4. Batch adsorption studies

117 The stock La(III) and Ce(III) solution with a concentration of
118 1000 mg/L was prepared by dissolving an appropriate amount of
119 $\text{La}(\text{NO}_3)_3$ or $\text{Ce}(\text{NO}_3)_3$ in distilled water. The different concentra-
120 tions of La(III) and Ce(III) for adsorption study were all prepared by
121 dilution of the stock solution.

All the adsorption experiments were preformed with 25 mg of
adsorbent and 25 mL La(III) or Ce(III) solution at desired concen-
tration. The mixture was shaken with a constant speed (120 rpm)
and constant temperature (30 °C) in a thermostatic orbital shaker
(THZ-98A) for a given time, and then the adsorbents were filtrated.
Afterward, the concentration of La(III) or Ce(III) in the solution was
determined by UV-visible spectrophotometer (UV-3010, HITACHI),
using Chlorophosphonazo mA (CPA-mA) as the complexing agent.
The La(III) or Ce(III) uptake was calculated from the following equa-
tion:

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where Q_e is the removal amount of La(III) or Ce(III) at any time
(mg/g), C_0 and C_e are the initial and final concentration of La(III) or
Ce(III) (mg/L), V is the volume of solution (mL) and m is the weight
of adsorbent (mg).

The influence of pH on the adsorption performance was stud-
ied in a wide pH range from 3 to 7. The initial pH of 300 mg/L
La(III) and Ce(III) solution was adjusted by 0.1 mol/L NaOH or
HCl solutions. The mixtures were all shaken for 2 h. The kinetics
study was performed with 300 mg/L La(III) or Ce(III) solution by
varying the adsorption time from 5 to 120 min. To evaluate the
control factors of the adsorption process, the adsorption kinet-
ics was evaluated based on the pseudo-first-order equation and
pseudo-second-order equation. The adsorption isotherms for La(III)
or Ce(III) were conducted with concentrations from 50 to 500 mg/L.
The optimum pH for La(III) and Ce(III) adsorption was fixed at
pH 5. To evaluate the control factors of the adsorption process,
the Langmuir isotherm model, Freundlich isotherm model and
Dubinin–Radoskevich (D-R) isotherm model were used.

151 2.5. Desorption and regeneration studies

152 In order to find the optimum condition using HCl solution as the
153 desorbing reagent for La(III) or Ce(III)-loaded composite, different
154 HCl concentration on the desorption efficiency was firstly studied.
155 The HPC-g-PAA/APT (20/1) was immersed in La(III) or Ce(III) solu-
156 tion for reaching adsorption saturation. Then, the adsorbent loaded
157 the rare earth was filtrate, put into 25 mL HCl solution with differ-
158 ent concentrations from 0.10 to 2 mol/L and shaken for 2 h. After
159 this adsorption–desorption process, the adsorption capacity and
160 desorption capacity can be calculated, upon which the desorption
161 ratios were expressed by the mass ratio of the eluted ions to the
162 adsorbed ions.

The reusability of the adsorbent was evaluated according to the
following procedures: 25 mg adsorbent was immersed in La(III)
or Ce(III) solution until adsorption saturation was reached, then
the adsorbent was separated from the solution by filtration and
regenerated using 0.1 mol/L NaOH solution. The recovered adsor-
bent was washed with distilled water for three times and then used
in next adsorption process. The consecutive adsorption–desorption
process was performed for five times, and the adsorption capacity
and recovery ratio of the adsorbent regenerated for different times
were obtained. The solution concentration of adsorption process
and desorption process were all determined and used to calculate
the adsorption rate and the desorption rate.

175 3. Results and discussion

176 For the graft polymerization, persulfate, benzoyl peroxide and
177 azoisobutyronitrile are the frequently used initiators. However, the
178 grafting efficiency is low than redox initiator [30]. This is because
179 that the hydroxyl radical ($\cdot\text{OH}$) is the most reactive radical among
180 the reactive oxygen species. In this study, the hydroxyl radical
181 ($\cdot\text{OH}$) was firstly produced through the decomposition of H_2O_2

Download English Version:

<https://daneshyari.com/en/article/8332458>

Download Persian Version:

<https://daneshyari.com/article/8332458>

[Daneshyari.com](https://daneshyari.com)