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Optimization of a Fe–Al–Ce nano-adsorbent granulation process that used spray coating in a fluidized bed for fluoride removal from drinking water

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ABSTRACT

A coating granulation technology comprising the spraying of a Fe–Al–Ce nano-adsorbent suspension onto glass beads in a fluidized bed was developed. An acrylic-styrene copolymer latex was used as a binder. The granulated adsorbent was used in a packed bed for fluoride removal from drinking water. The effects of coating temperature, latex/Fe–Al–Ce ratio, and coating amount on granule compressive strength and adsorption capacity were investigated. With increased coating temperature, cross linking in the polymer in the coated layer increased, which resulted in increased granule strength but decreased adsorption capacity. With increased latex/Fe–Al–Ce ratio, more active sites were covered by the polymer, which also resulted in increased granule strength but decreased adsorption capacity. The optimal parameters for making high performance adsorbent granules were for the granules to be coated at 65 °C using a latex/Fe–Al–Ce ratio of 0.5:1 and a coating amount of 27.8%. These granules had a fluoride adsorption capacity of 2.77 mg/g (coated granules) for water with an initial fluoride concentration of 0.001 M that was treated at pH 7.

1. Introduction

Although the fluoride present in drinking water is essential for health, an excessive intake of fluoride causes severe dental or skeletal fluorosis [1]. Therefore, it is necessary to treat fluoride-contaminated water and control the fluoride concentration to a permissible limit, which is 1.5 mg/L in the WHO guidelines [2]. Adsorption is considered one of the most efficient technologies for fluoride removal from drinking water, and is more efficient than many other technologies including reverse osmosis, nanofiltration, electrodialysis and Donnan dialysis [3]. Activated alumina and bone char that are 1–2 mm in diameter are the most widely used adsorbent because they are low cost and can be packed into columns with acceptable hydraulic conductivity. However, they have low compressive strength, which results in a lack of resistance to hydraulic shock and leads to the fracturing of the adsorbent in a packed bed [4].

Many adsorbents are synthesized as fine powders or as hydroxide floc [5] with sizes from nanometers to micrometers. Recently, a newly synthesized Fe–Al–Ce trimetal hydroxide adsorbent (Fe–Al–Ce) with a high adsorption capacity was reported [3]. However, the use of this adsorbent was limited by its low hydraulic conductivity in a packed bed [6]. This work focuses on producing granules of the above material that have a sufficiently high compressive strength, so that they can be used for adsorption in a packed bed.

Recently, an approach was proposed that used the immobilizing of a powder adsorbent on an inert support to overcome the large pressure drop when small powder particles are used in a water treatment process. Iron oxide-coated sand was prepared by the impregnation of sand with a mixed solution of salts, titration of the precipitator, and subsequent drying [7,8]. However, the thickness of the coated layer was only several micrometers and the coated layer shedded easily, which resulted in a low adsorption capacity and secondary pollution in the drinking water.

To overcome the above problems, Ake et al. [9,10] developed a new granulation method in which clay minerals were coated on silica surfaces using mucilage and carboxymethylcellulose as binders. These granules were used as a wastewater filter to remove contaminant ions such as Ni^{2+}. In the reported procedure, the polymers were first mixed with the solid support (either silica sand or glass beads), and then the clay minerals were added into the mixture. After calcining at a high temperature and rinsing with water, a composite adsorbent of a clay-silica material was obtained. However, the calcining resulted in a low adsorption capacity for the granules because most of the active sites on the adsorbent were destroyed by the high temperature [3].

Other polymers, such as polyacrylamide (PAM) and polyvinyl alcohol (PVA), were also promising binders for the binding of the clay by hydrogen bonding and ion exchanger [11]. Wu et al. [12] reported the use of an acrylic-styrene copolymer latex as binder for coating a nano-adsorbent on an inert carrier that did not use calcining at a high

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temperature. The latex can crosslink and be cured at room temperature. The use of the latex increased the compressive strength of the coated layer but the latex covered some active sites on the adsorbent surface. Therefore, the latex/Fe–Al–Ce adsorbent ratio has to be optimized for the optimum compressive strength and adsorption capacity of the granules [13].

In this work, a Fe–Al–Ce nano-adsorbent was coated onto glass beads using an acrylic-styrene copolymer latex as a binder in a fluidized bed. To optimize the coating granulation, the effects of the coating temperature, latex/Fe–Al–Ce ratio, and coating amount on granule adsorption capacity and compressive strength were investigated. The aim was to prepare a high performance adsorbent granule that can be used in a packed bed for fluoride removal from drinking water.

2. Experimental

2.1. Materials

$FeSO_4 \cdot 7H_2O$, $Al_2(SO_4)_3 \cdot 12H_2O$ and $Ce(SO_4)_2 \cdot 4H_2O$ used were of analytical grade (Chemical Engineering Company of Beijing, China). The other chemicals used were of analytical reagent (AR) grade.

$FeSO_4 \cdot 7H_2O$, $Al_2(SO_4)_3 \cdot 12H_2O$ and $Ce(SO_4)_2 \cdot 4H_2O$ were dissolved in deionized water to form a mixed solution with concentrations of 0.1 M, 0.2 M and 0.1 M, respectively. A 6 M NaOH solution was slowly titrated into the mixed solution until the pH reached 9.5. The solution was stirred at 200 rpm during the whole process [3]. The precipitate obtained were centrifuged and washed with deionized water until the pH of the filtrate was 6.5 ± 0.2. The product was Fe–Al–Ce trimetal hydroxide adsorbent (Fe–Al–Ce), which has a high specific surface area of 90 m^2/g and diameter of 40 nm. This was kept in deionized water.

The glass beads (Technology Development Center of China Paint Association, Beijing, China) were sieved to give a 2–3 mm fraction. These were soaked in the HCl solution ($pH = 1$) for 4 h, rinsed with deionized water until the pH reached 6 ± 0.2, and dried at 105 °C for 24 h. The glass beads obtained were kept in a capped bottle.

An acrylic-styrene copolymer latex that can crosslink and cure at room temperature was supplied by the Institute of Polymer Science and Technology (Dept. of Chem. Eng., Tsinghua University, China). The latex had a solid fraction of 40% and dynamic viscosity of 20 cP at 20 °C. The glass transformation temperature of the latex was 22.8 °C.

2.2. Coating granulation procedure

A fluidized bed in a Perspex column with an inner diameter of 55 mm and height of 500 mm was used for the coating granulation of the Fe–Al–Ce nano-adsorbent. The glass beads were fluidized by compressed air. A suspension of Fe–Al–Ce mixed with the acrylic-styrene copolymer latex at a set concentration was used as the coating reagent. The coating reagent was atomized and sprayed onto the glass beads. The particles in the fluidized bed were dried by controlling the temperature of the fluidizing gas.

The procedure for the coating granulation followed that reported by Chen et al. [13]. The experimental apparatus is shown in Fig. 1. The coating reagent was agitated in a vessel to prevent the sedimentation of the Fe–Al–Ce adsorbent. The feed rate of the reagent was controlled by a peristaltic pump. After the spray coating of a fixed amount of the coating reagent, the granules were sampled for analysis.

2.3. Characterization

A high resolution scanning electron microscope (HRSEM, JSM 7401, JEOL Co., Japan), was used to examine the morphology of the granules and microstructure of the coated layer. A particle strength meter (0–200 N, KQ-2, Jiangyan, China) was used to measure the compressive strength of the granules. The pressure at which a crack first appeared in the coated layer was recorded. For each sample, an average value from the measurements of 10 particles was used.

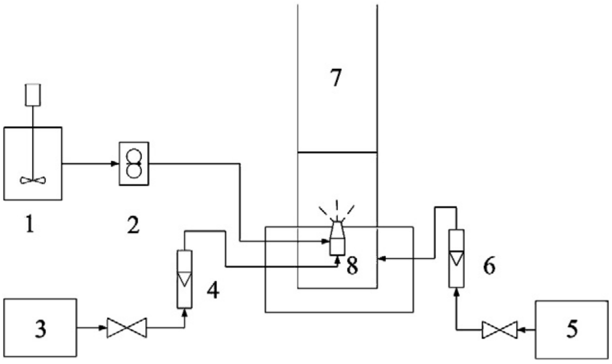

Fig. 1. Coating granulation apparatus. 1. Coating reagent vessel; 2. Peristaltic pump; 3. Atomized gas; 4. Flow meter; 5. Compressed gas; 6. Flow meter; 7. Fluidized bed; and 8. Nozzle.

The coating amount was characterized by the mass ratio of Fe–Al–Ce trimetal hydroxide to glass bead in the granules. A TG analysis showed that the acrylic-styrene copolymer latex decomposed at 390 °C and was completely burnt off at 450 °C. Thus, the coating amount was determined by the following procedure. A known mass of granules was heated in a muffle furnace at 550 °C until the acrylic-styrene copolymer was burnt off to leave the glass beads (m_1). Then the glass beads were soaked in a 1 M HCl solution for 3 h with agitation at 160 rpm until the Fe–Al–Ce trimetal oxide on the glass bead surface was completely dissolved in the acid solution. The remaining granules were washed, filtered, dried at 105 °C for 3 h, and then weighed (m_2).

From the TG analysis of the Fe–Al–Ce nano-adsorbent powder, the weight of the remaining solid became constant at 72% of the initial weight for temperatures higher than 550 °C. Therefore, the coating amount R can be calculated by

$$R = \frac{(m_1 - m_2)}{m_2 \times 72\%} \times 100\%. \tag{1}$$

2.4. Fluoride adsorption capacity determination [3]

A 1000 mg/L fluoride solution was prepared by dissolving 1.1050 g NaF in 500 mL deionized water. Fluoride containing solutions were prepared by diluting the above solution to specified concentrations with deionized water. Known volumes of these fluoride solutions were added separately into conical flasks. A 0.5 g adsorbent was dosed into 100 mL of fluoride containing solution. The pH of the test solution was kept at 6.5–7.5 by titration with either 0.05 M $HClO_4$ or 0.05 M NaOH solution. The test solution was shaken at 180 rpm and kept at 25 °C for 36 h during the adsorption. After adsorption, the granules were filtered and the filtrate was analyzed. KNO_3 solution was added to the filtrate as the background electrolyte at a concentration of 0.2 M. The fluoride ion concentration remaining in the filtrate was measured with a fluoride selective electrode connected to an ion meter (PXS-450, Shanghai Kang-Yi Instruments Co., LTD, China).

The adsorption capacity, q_e (mg/g), was calculated using

$$q_e = \frac{C_0 - C_f}{m} \times V \tag{2}$$

where C_0 (mg/L) is the initial fluoride concentration and C_f (mg/L) is the final fluoride concentration after adsorption, V is the volume of the solution containing fluoride ions, i.e. 100 mL in text, and m is the adsorbent granules dose of 0.5 g.