Granulation of Fe–Al–Ce nano-adsorbent for fluoride removal from drinking water by spray coating on sand in a fluidized bed

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ABSTRACT

A technology for the granulation of Fe–Al–Ce nano-adsorbent (Fe–Al–Ce) in a fluidized bed was developed. The coating reagent, a mixture of Fe–Al–Ce and a polymer latex, was sprayed onto sand in a fluidized bed. The granule morphology, coating layer thickness, granule stability in water and adsorption capacity for fluoride was investigated by analyzing samples for different coating time. The coating amount was from 3% to 36%. With increasing coating amount, granule stability decreased and adsorption capacity increased. FTIR analysis showed that the latex can react with active hydroxyl on the Fe–Al–Ce adsorbent, which led to a decrease of the adsorption capacity. Coated granules with a coating amount of 27.5% had a fluoride adsorption capacity of 2.22 mg/g (coated granules) at pH 7 and initial fluoride concentration of 0.001 M. A column test showed that 300 bed volumes can be treated with the effluent under 1.0 mg/L at an initial fluoride concentration of 5.5 mg/L, space velocity of 5 h^{-1} and pH of 5.8. The coating granulation of the Fe–Al–Ce adsorbent can produce granules that can be used in a packed bed for the removal of fluoride from drinking water.

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1. Introduction

Excess fluoride in drinking water causes harmful effects such as dental and skeletal fluorosis [1]. The guideline values for fluoride in drinking water are 1.5 mg/L by the World Health Organization and 1.0 mg/L by China [2]. Adsorption is considered a more efficient technology for fluoride removal from drinking water when compared with other technologies like reverse osmosis, nanofiltration, electro-dialysis and Donnan dialysis [2].

Activated alumina is the most widely used adsorbent because it is readily available and inexpensive. However, the need for frequent regeneration due to its low adsorption capacity at neutral pH results in complex operations [3], and the easy dissolution of aluminum in treated water leads to a secondary pollution. Bone char also can be used as a fluoride adsorbent, but it has a lower mechanical strength than activated alumina and it shows a weaker resistance to hydraulic shock in a packed bed [4].

A newly synthesized Fe–Al–Ce trimetal hydroxide adsorbent (Fe–Al–Ce) was reported to have a high adsorption capacity [2]. However, the Fe–Al–Ce adsorbent is available only as a fine powder or

prepared in aqueous suspension as a hydroxide floc. In such forms, the adsorbent is limited to use in reactor configurations with large sedimentation basins or a filtration unit. Under such condition, the solid/liquid separation is fairly difficult. Besides, the Fe–Al–Ce adsorbent alone is not suitable as a filter medium because of its low hydraulic conductivity [5]. Therefore, its powder granulation to give granules of high strength is necessary so that it can be used in a packed bed.

Recently, researchers have developed the technique of coating an adsorbent onto sand to overcome the problem of using adsorbent powders in water treatment processes. Iron oxide-coated sand (IOCS) has been tested for removing cations and anions from synthetic and actual wastes [5]. The IOCS was prepared by the impregnation of sand in a mixed solution of salt and precipitator and subsequent drying [6,7]. However, the thickness of the coated layer was only several micrometers, which resulted in a low adsorption capacity. Furthermore, the coated layer can be easily shed off, which left the coated sand with little adsorption capacity, and caused secondary pollution in drinking water.

In this paper, a Fe–Al–Ce adsorbent with an acrylic-styrene copolymer latex as a binder was spray-coated onto sand in a fluidized bed. The introduction of latex increased the stability of the coated layer [8]. The relationship between the coating properties and the adsorption properties, and the interaction between latex and Fe–Al–Ce adsorbent was investigated. A new type of granule adsorbent with

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

high stability and adsorption capacity that is suitable for use in a packed bed was prepared.

2. Experimental

2.1. Materials

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ and $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ used were analytical grade (Chemical Engineering Company of Beijing, China). The other chemicals used were analytical reagents (AR) grade.

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ and $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ were dissolved in deionized water to form a mixed solution with concentrations of 0.1 M, 0.2 M and 0.1 M, respectively. 6 M NaOH solution was slowly added into the mixed solution until the pH was 9.5. The solution was stirred at 200 rpm during the whole process [2]. The precipitates obtained were centrifuged and washed with deionized water until the pH of the filtrate was 6.5 ± 0.2 . The product, Fe–Al–Ce trivalent hydroxide adsorbent (Fe–Al–Ce) with a diameter of 40 nm, was kept in deionized water.

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

The sand (Gaoyuan Stone Company, Beijing, China) was sieved to give the 1–2 mm fraction, soaked in 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 sand obtained was kept in capped bottles.

2.2. Coating method

A suspension of Fe–Al–Ce mixed with acrylic-styrene copolymer latex was used as the coating reagent. The mass ratio of Fe–Al–Ce to latex was 1:1 [8]. The latex was employed as a binder in the coating layer. The experimental apparatus for coating granulation is shown in Fig. 1. The reagent was agitated in a reactor to prevent the sedimentation of Fe–Al–Ce. The feed rate of the reagent was controlled by a peristaltic pump.

The sand was put into a fluidized bed with a diameter of 55 mm and a height of 500 mm. The sand was fluidized by controlling the gas velocity. The coating reagent was atomized and sprayed onto the sand, and the water in the coating reagent was dried by controlling the temperature of the fluidizing gas at 35 °C. After the spray coating was completed, the coated sand was kept in capped bottles.

2.3. Characterization

The coating amount was characterized by the mass ratio of Fe–Al–Ce to sand. The acrylic-styrene copolymer latex decomposed at 390 °C and burned at 450 °C according to the TG analysis. Thus, the coating amount can be determined by burning the granules in a muffle furnace and using an acid treatment. A known mass of granules was burned in a muffle furnace at 550 °C till the latex was burned off, to give burned sand (m_1). Then the burned sand was soaked in 1 M HCl solution for 3 h with agitation at 160 rpm until the coated layer was

Fig. 2. Images of the granules during the coating process. Coating amount, %: a, 0; b, 3.55; c, 9.55; d, 18.40; e, 27.50; f, 36.20.

dissolved in the solution. The granules were washed, filtered, dried at 105 °C for 3 h, and then weighed (m_2).

Since the Fe–Al–Ce adsorbent is a metal hydrate, Fe–Al–Ce remaining on the burned sand would be the oxide. From the mole ratios in the Fe–Al–Ce synthesis, i.e. Fe:Al:Ce is 1:4:1, the coating amount R can be defined as:

$$R = \frac{(m_1 - m_2)}{m_2} \times \frac{627.02}{455.89} \times 100\%$$

For the characterization of the stability of the granules, a known mass of granules (m_0) was added into 100 mL deionized water in a shaker at 160 rpm for examining weight loss. After 12 h agitation, the granules were filtered and dried at 50 °C for 12 h, and weighed (m_3). The stability of the granules S was defined as:

$$S = \frac{m_3}{m_0} \times 100\%$$

High resolution scanning electron microscopy (HRSEM, JSM 7401, JEOL Co., Japan) was used to inspect the morphology of the granules and structure of the coated layer. A Fourier transform IR spectrometer (NICOLET 5DX, USA) was used to examine the spectrum change of the samples and to determine the interaction between Fe–Al–Ce and latex. KBr was used as background in FTIR analysis. All IR measurements were carried out at room temperature.

2.4. Fluoride adsorption test [2]

A 1000 mg/L fluoride solution was prepared by dissolving 1.1050 g NaF in 500 ml deionized water. Fluoride bearing solutions were prepared by diluting the solution to specified concentrations with deionized water. Known volumes of fluoride solution were added separately into conical flasks, with NaClO₄ as the background

electrolyte in a concentration of 0.1 M. The adsorbent was dosed to give 5 g/L, and the final volume was increased to 100 ml with deionized water. The pH of the test solution was kept at 6.5–7.5 by titrating with 0.05 M HClO₄ or 0.05 M NaOH solution. The test solution was shaken at 180 rpm and 25 °C for 36 h during the adsorption test. The fluoride ions remaining in the test solution were measured with a fluoride ion meter.

2.5. Column test [2]

A column test was performed in a perspex column with a diameter of 8 mm. The volume of the granules was 5 ml, and the bed height was 100 mm. The influent solution was prepared by dissolving NaF in deionized water. The pH of the influent solution was 5.8, the fluoride concentration was 5.5 mg/L, and the space velocity (SV) was 5 h^{−1}. The effluent was collected from the column end at regular intervals of time and the fluoride concentration was measured.

3. Results and discussion

3.1. Analysis of coating process

Experiments showed that sand can be coated in a fluidized bed. The granules were sampled during the coating process for analysis. Fig. 2 shows the images of the granules with size about 2–3 mm. The images in Fig. 2(a)–(f) corresponds to the coating amounts of 0%, 3.55%, 9.55%, 18.40%, 27.50%, 36.20%, respectively. Fig. 2(a) shows the surface image of uncoated sand. The sharp edges on the surface are clearly shown. After a few minutes coating, the edges were covered with discrete patches of Fe–Al–Ce adsorbent, as shown in Fig. 2(b) and (c). With further coating, more Fe–Al–Ce adsorbent was coated, which formed a thicker layer, and the sand surface was smoothly covered, as shown in Fig. 2(d) and (e). As the coating amount increased, some pieces of coated layer were shedded off, as shown in Fig. 2(f).

Fig. 3. Coated layer on the granules. Coating amount, %: a, 9.55; b, 18.40; c, 27.50; d, 36.20.

Fig. 4. Granule surface morphology for different coating amounts. Coating amount, %: a, 0; b, 3.55; c, 9.55; d, 18.40; e, 27.50; f, 36.20.

Fig. 3 shows the cross-section images of the coated sand. For coating amounts of 9.55%, 18.40%, 27.50%, 36.20%, the thickness of the coated layer were 70 μm , 100 μm , 140 μm and 200 μm , which were much thicker than previously reported thicknesses (less than 10 μm) [5].

Fig. 4 shows the morphology of the sand coated with different amounts of Fe–Al–Ce. With increasing coating amount, the edges and roughness of the sand surface decreased and a smooth surface appeared gradually, as shown in Fig. 4(a)–(c). However, with a further increase of the coating amount, some cracks occurred on the surface as shown in Fig. 4(d)–(f).

It was analyzed that stress existed in the coated layer due to water evaporation, which resulted in the formation of cracks and defects. As Fe–Al–Ce oxide is rigid and the latex is elastic, when the latex was introduced into the coated layer, stress can be released. However, with the increasing of the coating amount, the stress cannot be completely released due to the limited amount of latex introduced, and this caused crack formation in the coated layer.

3.2. Stability of the granules

Fig. 5 gives the stability of the granules for different coating amounts. When the coating amount increased from 0% to 36.20%, the

Fig. 5. Stability of granules with different coating amounts.

stability of granules changed from 99.6% to 98.1% after the 12 h shaking test. When the coating amount increased, stress accumulated and more cracks appeared on the layer. The cracks made the coated layer fragile, and it was easily shedded off, leading to a decrease in the stability of the granules. If the stability of granules is too low, it will cause secondary pollution in drinking water. It was inferred that there is an optimum coating amount for acceptable stability. However, the stability of 98.1% of the granules is high enough for practical adsorption in a packed bed.

3.3. Interaction between latex and adsorbent

Acrylic-styrene copolymer latex was employed as the binder in the layer coating process because of its promising properties: tough, soft, nontoxic, and curable at ambient temperature, etc. When the latex was introduced into the coating reagent, the cracks were less and the stability was increased.

The active site for fluoride adsorption is from the hydroxyl groups on the Fe–Al–Ce surface [4]. The FTIR spectra of the Fe–Al–Ce adsorbent before and after adsorption are shown in Fig. 6. Before adsorption, the FTIR spectra had the absorbance peaks of (1) HOH stretching (3500–3200 cm^{-1}) and bending (near 1600 cm^{-1})

Fig. 6. FTIR spectra of Fe–Al–Ce adsorbent before and after adsorption.

Fig. 7. FTIR spectra of Fe-Al-Ce adsorbent, latex and coated layer.

vibrations of water [9] and (2) MOH stretching ($3600\text{--}3500\text{ cm}^{-1}$) and bending (near 1125 cm^{-1}) vibrations of the hydroxyl group [10]. After adsorption, the MOH bending band near 1125 cm^{-1} almost disappeared, while the peaks assigned to H_2O remained unchanged. This showed that the adsorption of fluoride on the Fe-Al-Ce adsorbent surface resulted in a decrease in the intensity of the MOH band near 1125 cm^{-1} or its complete disappearance due to fluoride adsorption. It was inferred that the hydroxyl group MOH with bending vibration at 1125 cm^{-1} had reacted with the fluoride ions in the adsorption process.

The FTIR spectra of latex, Fe-Al-Ce adsorbent and coated layer on the granules are shown in Fig. 7. The FTIR spectra of latex had the HOH stretching ($3500\text{--}3200\text{ cm}^{-1}$) and bending (near 1600 cm^{-1}) vibration of water and a characteristic peak at 1640 cm^{-1} . A clear blue shift of the latex characteristic peak from 1640 cm^{-1} to 1740 cm^{-1} was observed from the coated layer on the granules, which indicated that a chemical bond had been formed between the latex and Fe-Al-Ce adsorbent. In the spectrum of the coated layer on the granules, the MOH stretching vibration near 3500 cm^{-1} had almost disappeared, while the MOH bending vibration near 1125 cm^{-1} was reduced. As discussed above, it is the reaction between the latex and Fe-Al-Ce surface that caused the reduction of the bending vibration of the hydroxyl group, i.e. 1125 cm^{-1} , and that led to the decrease of the adsorption capacity.

Therefore, the ratio of latex and Fe-Al-Ce adsorbent requires to be further optimized for getting both a high stability and adsorption capacity of the granules.

Fig. 8. Fluoride adsorption capacity of the granules (adsorbent dose: 5 g/L ; initial fluoride concentration: 0.001 M and equilibrium time: 36 h).

Fig. 9. Breakthrough curve for fluoride adsorption of the granules.

3.4. Fluoride adsorption examination

The fluoride adsorption capacity of coated sand with different coated amounts is shown in Fig. 8. Curve (a) shows that the adsorption capacity increased with the coating amount, while the stability of the granules decreased, cf. Fig. 5. Curve (b) shows that the fluoride adsorption capacity per Fe-Al-Ce adsorbent decreased with increasing coating amount, and the rate of decrease decreased gradually. For the optimal stability and adsorption capacity, a coating amount of 27.5% is suggested. Using this coated adsorbent, the fluoride adsorption capacity was 2.22 mg/g (coated sand) at pH 7 and initial fluoride concentration of 0.001 M .

3.5. Column test

The coated granules with coating amount 27.5% were packed into a column to evaluate the adsorption performance with fluoride bearing water. The breakthrough curve is shown in Fig. 9. With an influent fluoride concentration of 5.5 mg/L , pH of 5.8, and SV of 5 h^{-1} , the effluent fluoride was below 1 mg/L until 300 bed volumes (BV) were treated, and reached 1.5 mg/L at 500 bed volumes. This showed that the coated granules can be used in a packed bed for the removal of fluoride from drinking water, especially in a rapid recycle and coupled process of adsorption and regeneration, due to the simple preparation, cheap cost and high stability of the coated granules.

4. Conclusion

The granulation of Fe-Al-Ce adsorbent was achieved by spray coating it on sand in a fluidized bed. The granules had spherical shape and high stability with size about $2\text{--}3\text{ mm}$ and coating thickness up to $200\text{ }\mu\text{m}$. The latex introduced can react with the active hydroxyl on the Fe-Al-Ce adsorbent, which led to a decrease of the adsorption capacity. To balance a high stability and adsorption capacity, the ratio of latex to the adsorbent needs to be optimized.

With increasing coating amount, adsorption capacity increased while the stability of the granules decreased. For an acceptable adsorption capacity and stability, the coating amount of 27.5% is suggested. Using the coated granules as adsorbent, the fluoride adsorption capacity was 2.22 mg/g (coated granules) at pH 7 and initial fluoride concentration of 0.001 M . 300 bed volumes can be treated with the effluent fluoride below 1 mg/L for an influent fluoride concentration of 5.5 mg/L , pH of 5.8, and SV of 5 h^{-1} .

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