Heat regeneration of hydroxyapatite/attapulgite composite beads for defluoridation of drinking water

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ABSTRACT

Regeneration is one of the key factors in evaluating an adsorbent. A novel heat regeneration method for hydroxyapatite/attapulgite (HAP/ATT) composite beads was studied. The investigation included heat regeneration temperature, regeneration time, and regeneration effects. A possible mechanism for the heat regeneration is described that explains the results of XPS, and SEM with EDAX. Exhausted HAP/ATT composite beads can be regenerated for more than 10 cycles using boiling water or steam. The total capacity increases by 10 times compared to a single defluoridation cycle. The regeneration process involves F⁻ ions adsorbed on the surface of the beads to move quickly into the bulk of the HAP through the effect of heating this composite material. The surface active sites are thus re-exposed and the beads recover their fluoride sequestration properties. HAP/ATT composite beads were successfully used for the removal of fluoride from field water taken from a nearby village where fluoride contamination is endemic. Defluoridation and regeneration cycles performed in the same container provide a high efficient and simple operation. No chemical agents are used and no waste products are produced during the heat regeneration process, so this is a nearly zero emission process. This method can easily be up-scaled to a large throughput application.

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1. Introduction

Fluorine is an important micro-element needed for the maintenance of healthy human bones and teeth. Drinking water is the major contributor of fluoride (75–90% of daily intake) but other sources include food, cosmetics and drugs [1]. The maximum fluorine level for good health in drinking water suggested by the World Health Organization is 1.5 mg/l. Concentrations higher than this could lead to fluorosis, which is a serious chronic disease affecting many millions of people worldwide [2,3].

Various treatment technologies based on adsorption [4–9], ion-exchange [10,11], precipitation [12], membrane osmosis [13–15], or electrochemical technology [16,17] have been studied as ways to remove fluoride from water. Among these existing techniques adsorption is regarded as an important, cost effective technique appropriate for use in developing countries [18]. A wide variety of adsorbents, such as activated alumina, activated carbon, bone charcoal, or other low cost materials, have been used [1,19]. The adsorption process can lower fluoride concentrations to a safe level, however the reuse of the adsorbent is necessary for the

application to be economically feasible [20]. Evaluating an adsorbent for practical use requires consideration of the effects from regeneration. Some adsorbents are appropriate for traditional chemical regeneration, namely an alkaline or acid solution treatment used as the regenerant followed by an acid or alkaline solution neutralizer [20,21]. For example, activated alumina can be regenerated by flushing with a solution of 4% sodium hydroxide. This procedure is followed by flushing with acid to re-establish a positive charge on the alumina surface [22]. This process is complicated and will release harmful chemicals into the environment. Moreover the efficiency of regeneration is very low. So this type of adsorbent has not been used for fluoride removal in engineering in China [1,19,23,24].

Hydroxyapatite (HAP; $Ca_{10}(PO_4)_6(OH)_2$) has been found to be a better sorbent because of its low cost, ready availability, and higher defluoridation capacity [5–7,25]. Sundaram et al. [25] reported that nano-HAP possessed a maximum defluoridation capacity of 1845 mg F⁻/kg starting from a 10 mg/L initial fluoride concentration. Poinern et al. [6] reported that nano-structured hydroxyapatite, synthesized through a combined ultrasonic and microwave method, possessed a maximum monolayer adsorption capacity of 5500 mg/kg at 298 K. The adsorption capacity increased from 500 mg/kg to 4300 mg/kg as the equilibrium fluoride concentration increased from 0.75 mg/L to 30.6 mg/L. Gao et al. [5] have

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observed that the defluoridation capacity increases with increasing initial fluoride concentrations. Observed experimental defluoridation capacities were in the range from 702 to 6161 mg/kg with initial fluoride concentration from 2 to 80 mg/L. However, HAP in powder form cannot be used in either in fixed bed columns or in any other flow-through system because it would cause excessive pressure drop during filtration [7]. To overcome this limitation, we studied the preparation of hydroxyapatite/attapulgite (HAP/ATT) composite beads as a possible alternative method.

ATT is a fiber-like hydrated magnesium aluminum silicate clay mineral, which has good plasticity and strong bonding ability [26]. In composite beads, ATT acts mainly as a bonding agent for granulation of ceramic powdered HAP. HAP cannot be formed into beads itself without ATT. Of course, the defluoridation capacity of the composite beads decreases with increasing amounts of added ATT. The capacity is also affected by the decrease in specific surface area. By increasing the ratio of HAP in the beads from 60% to 70% through improved technology, these problems can be mitigated. Interestingly, the exhausted composite beads can be regenerated many times through heating. The total defluoridation capacity and effective utilization efficiency of these composite beads are both greatly improved after regeneration. The number of filter changes required decreases and the labor needed to change the materials is reduced.

Thermal regeneration is a well-established technique that has been widely used in processes such as activated carbon regeneration. In that case heating the activated carbon under a purge gas flow removes the desorbed adsorbate and affects regeneration cycles [27,28]. The heat regeneration mechanism in the present case differs from thermal regeneration of activated carbon. The heat regeneration method described herein presents many advantages, such as high efficiency, more regeneration cycles, simple operation, and being environmental friendly. More importantly, no chemical agents are used and no wastes are produced during the heat regeneration process, so it is nearly a zero emission process.

A novel, non-polluting heat regeneration method for hydroxyapatite/attapulgite (HAP/ATT) composite beads is reported here. The heat regeneration temperature, regeneration time, and regeneration effects are discussed. A possible mechanism of the heat regeneration was also investigated by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX).

2. Materials and methods

2.1. Materials

HAP/ATT composite beads were supplied by the Jiangsu Yongguan Water Supply and Drainage Equipment Co. Ltd., Xuzhou, Jiangsu, China. Composite beads appeared brown, granular and ranged in size from 1 to 2 mm. The static defluoridation capacity (DC) was 284 mg/kg and the dynamic defluoridation capacity (DC*) was 340 mg/kg starting from 3 mg/L as the initial fluoride concentration (this was raw water collected from Feng county). The HAP:ATT ratio is 60:40 in these beads. At a HAP:ATT ratio of 70:30 the DC is 477 mg/kg and the DC* is 740 mg/kg with the same 3 mg/L initial fluoride concentration. The DC is 524 mg/kg and the DC* is 1490 mg/kg with a 5 mg/L initial fluoride concentration and the DC is 1087.9 mg/kg with a 10 mg/L initial fluoride concentration. The DC for a pure HAP powder is 3460 mg/kg with a 5 mg/L initial fluoride concentration or 4640 mg/kg with a 10 mg/L initial fluoride concentration. The composite beads used in the following experiments consisted of 60% HAP.

NaF and all other reagents used were of analytical grade purchased from Shanghai Chemical Corporation, China. For the field study, fluoride-containing water was collected from a nearby village in Feng county, Xuzhou, Jiangsu Province where fluoride levels are endemic.

2.2. Characterization

X-ray powder diffraction (XRD) patterns were obtained using a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation, a nickel filter, and a LynxEye detector. The X-ray photoelectron spectroscopy (XPS) data were obtained using an ESCALab250 electron spectrometer from Thermo Scientific Corporation and monochromatic, 150 W Al Kα radiation. The base pressure was about 6.5×10^{-10} mbar. The binding energies were referenced to the C1s line at 284.8 eV associated with alkyl carbon. Examination of samples with a scanning electron microscope (SEM) (FEI Quanta TM 250 model) fitted with an energy dispersive X-ray analyzer (EDAX) allowed a qualitative detection and localization of elements within the samples. These observations were obtained from the surface of the beads.

2.3. Preparation of the fluoride solution

A fluoride standard stock solution (100 mg/L) was prepared by drying 5 g of NaF at 105 °C for 2 h, weighing 0.2210 g of NaF, dissolving it in distilled water, and making up to a volume of 1000 ml.

A 5 mg/L fluoride solution was prepared by diluting 50 ml of the stock solution to 1000 ml. This was used as the fluoride containing water sample.

2.4. The static saturation of HAP/ATT composite beads

The saturation of composite beads was obtained by putting HAP/ATT composite beads (10 g) into 1 L of fluoride containing water (5 mg/L), allowing the mixture to stand for 24 h, and then filtering. The residual fluoride ion concentration in the water sample was measured using an ion analyzer (EA940) with a fluoride ion selective electrode, pF-1 (made in China). The static defluoridation capacity (DC) was then calculated as:

$$DC = \frac{(C_0 - C) \times V}{m} \tag{1}$$

where DC (mg/kg) is the static defluoridation capacity, C_0 (mg/L) is the initial F$^-$ concentration in the raw water sample, and C (mg/L) is the residual F$^-$ concentration in the water sample after adsorption by the composite beads. V (L) is the volume of the solution and m (kg) is the mass of the composite beads.

2.5. The dynamic saturation of HAP/ATT composite beads

The F$^-$ adsorbing performance of the composite beads was evaluated in a flow-through system. A 1.5 cm diameter, 50 cm long open-ended glass column was packed with 30 g of composite beads. The feed water was a 3 mg/L fluoride ion solution collected from a nearby village. The feed water flow rate was restricted by a clamp to 4.5 ml/min to ensure adequate time for sorption reaction to take place. When the F$^-$ concentration in the effluent reached 1 mg/L the penetration point was considered to have been reached. This is when the composite beads are saturated. The flow volume and F$^-$ concentration were monitored during the trials and the dynamic defluoridation capacity (DC*) was calculated as:

$$DC^* = \frac{(C_0 - C) \times V}{m} \tag{2}$$

where DC* (mg/kg) is the dynamic defluoridation capacity at the defined penetration point, C_0 (mg/L) is the initial F$^-$ concentration in the raw water sample, and C (mg/L) is the F$^-$ concentration in the water sample after passing through the composite beads. V (L)

is the total volume of the raw solution used and m (kg) is the mass of composite beads.

For a comparison, a 5 mg/L fluoride ion pre-prepared solution was used as the feed water in a dynamic filter trial and the DC* value was also obtained.

2.6. Determining heat regeneration temperature and time

A 10 g portion of the static, saturated HAP/ATT composite beads were put into a temperature controlled oven. After heating for 2 h at different temperatures ranging from 40 to 110 °C, spaced at 10 °C increments, the static regeneration capacity of the composite beads was determined. A 10 g portion of the saturated HAP/ATT composite beads were heated for times from 20 to 180 min at 80 °C and the static regeneration capacity was again determined.

2.7. Heat regeneration using boiling water

A 10 g portion of the statically, or dynamically, saturated HAP/ATT composite beads and 100 ml distilled water were combined in a temperature controlled mechanical shaker. After heating for 2 h in boiling water the composite beads were leached, collected, and tested for adsorption capacity again. The static and dynamic regeneration capacities were determined. The fluoride ion content of the water in the flask was also determined after regeneration.

2.8. The regenerated capacity of the heat-regenerated beads

After heat regeneration by either oven or boiling water the beads were put into a fluoride containing water sample (5 mg/L) and allowed to reach the saturated adsorption condition. Then the fluoride ion concentration in the water sample was measured using the fluoride ion selective electrode. The static regenerated capacity (RC) was calculated as:

$$RC = \frac{(C_0 - C) \times V}{m} \tag{3}$$

where RC (mg/kg) is the static regenerated capacity, C_0 (mg/L) is the initial F$^-$ concentration in the raw water sample, and C (mg/L) is the residual F$^-$ concentration in the water after adsorption by the composite beads. V (L) is the volume of the solution and m (kg) is the mass of the beads.

The determination method of the dynamic regenerated capacity (RC*) is similar to the method of testing the dynamic defluoridation capacity (DC*). The only difference is that the beads were heat regenerated before the defluoridation test.

2.9. Field trials

Field trials were performed in a village in Feng county, Xuzhou, Jiangsu Province, where fluoride ion concentrations in the water are consistently about 3 mg/L and the pH value is about 8.4. Steam was used for heat regeneration. Following adsorption with the composite beads, a regeneration step was performed. This procedure was repeated. After the beads reached the saturation point the heat regeneration process using steam was allowed to work for 2 h. The dynamic regeneration capacity was determined after each heat regeneration step. Meanwhile, condensed steam and water samples in the container were collected and the respective fluoride ion contents were determined.

2.10. Determination of fluoride content in the beads

The saturated beads were ground into powder. The elemental composition and fluoride content in the beads were determined using XPS.
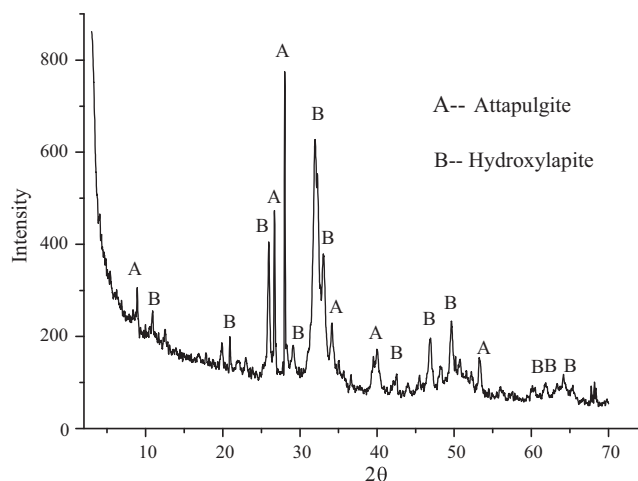

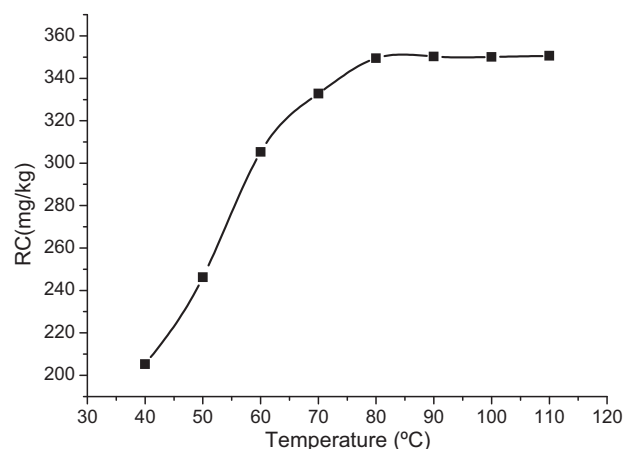**Fig. 1.** XRD pattern of the HAP/ATT composite beads.

Fig. 2. The effect of regeneration temperature on regenerated capacity.

3. Results and discussion

3.1. Characterization of the beads

The XRD pattern of a HAP/ATT sample (Fig. 1) confirmed that HAP and ATT were in the typical crystalline phases compared to the standard JCPDS–ICDD cards. No other peaks appeared in the pattern indicating that no other chemical was in this HAP/ATT sample.

3.2. The effect of regeneration temperature on regenerated capacity

The change in regenerated capacity (RC) with temperature was studied and the results are shown in Fig. 2. In this graph it is evident that the RC of the beads rises quickly with increasing temperature from 40 to 80 °C but plateaus at temperatures above 80 °C. The regenerated capacity is highly dependent on the regeneration temperature at the lower temperatures. The defluoridation properties are recovered to a greater extent with rising temperatures because more energy is available to activate the surface [29,30]. When the temperature is high enough (80 °C) the RC of beads reach to 350 mg/kg and ceases to increase, which indicates that the bead surface approaches to saturated adsorption. A more detailed discussion will be presented in Section 3.6.
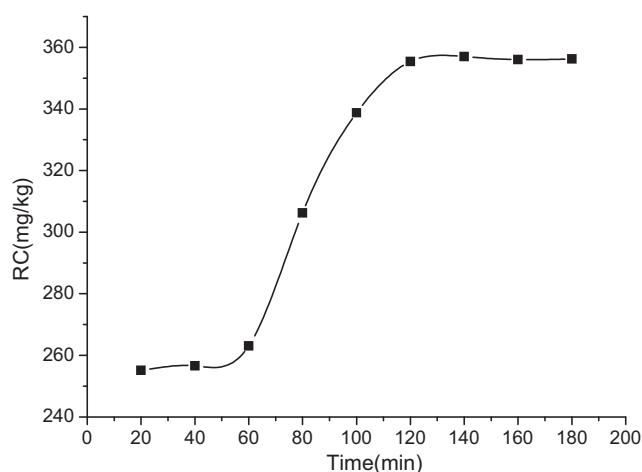
Fig. 3. The effect of regeneration time on regenerated capacity.

3.3. The effect of regeneration time on regenerated capacity

The change of regenerated capacity with time was studied. The results are shown in Fig. 3. In this graph the RC of the beads is seen to change little when the time varies from 20 min to 60 min but it then rises quickly from 60 min to 120 min. The RC becomes constant for times exceeding 120 min. When the regeneration time is less than 60 min insufficient energy for activation of the bead surface is present and the defluoridation properties do not recover. Longer regeneration times allow the beads to adsorb enough energy to activate the surfaces [20,30] and the RC of the beads increases. For regeneration times greater than 120 min the saturated adsorption point has been reached and the RC approaches to a maximum. A more detailed discussion appears in Section 3.6.

3.4. Heat regeneration using boiling water

From an industrial point of view, the process of defluoridization and regeneration being performed in the same container is indeed an advantageous step as it reduces processing time. Heat regeneration using boiling water is easily realized. The exhausted beads were regenerated 10 cycles using boiling water and the results

are listed in Table 1. Though the exhausted beads were regenerated 10 cycles the value of each new RC varied around 300 mg/kg, which indicates that the exhausted beads have recovered the same adsorption properties as new beads and that the surface of the recovered beads has the same number of active fluoride adsorbing sites after a sufficiently long period of regeneration. The 3270 mg/kg total RC approaches the DC of HAP powder, itself (3460 mg/kg).

RC* decreased gradually with an increasing number of regenerations because the rapid flow rate of the water sample caused incomplete adsorption on the beads. So the regeneration capacity in this case did not reach the maximum defluoridation capacity. RC* increased with a rise in the fluoride concentration of the feed water. The RC* in the first cycle was 260 mg/kg and the total capacity was 1400 mg/kg for a feed water having a 3 mg/L fluoride ion level. This was a solution collected from the nearby village. The RC* in the first cycle was 560 mg/kg and the total capacity was 2970 mg/kg when the feed water consisted of a prepared 5 mg/L fluoride ion solution. It is more meaningful to use a field water sample as the feed water because this reflects actual running conditions. Free F^- was not found in the water sample after regeneration, which indicates that the F^- did not desorb from the beads during regeneration.

The mobility of F^- ions was confirmed by measuring the fluorine content of three samples by XPS. Sample 1 was the powder from new beads. Sample 2 was the ground powder from beads saturated after the 10th static saturation/regeneration cycle. Sample 3 was the ground powder from regenerated beads after the 10th static saturation/regeneration cycle. The elemental composition and fluorine content obtained are listed in Table 2. Fluorine is not found in new beads. Sample 2 has undergone one more saturated adsorption cycle than sample 3 and the difference in fluorine content between it and sample 3 is 297 mg/kg, which is approximately consistent with the RC tested using the fluoride ion selective electrode. These results show that the surface of the beads after regeneration was not occupied by fluoride and that the regenerated adsorption capacity can reach the maximum static adsorption capacity. Further confirmation of this point was done by sampling thin surface layers of different batches of HAP/ATT composite beads both before and after regeneration. This was done by adhering adhesive tape to the surface and stripping it off. The fluorine content in the thin surface layers was then tested by EDAX. Fig. 4(1(b), (d)) and 2(b), (d) is EDAX spectra of random points of random samples so prepared. The EDAX spectra of the beads before regeneration confirm the

Table 1
The results of heat regeneration using boiling water.

Regeneration cycle	RC (mg/kg)	RC* (mg/kg) Field water sample	RC* (mg/kg) Prepared water sample	F-contents in the water sample after regeneration
0	284	340	1490	
1	293	260	560	0
2	293	160	210	0
3	247	160	300	0
4	300	130	140	0
5	354	130	90	0
6	281	120	130	0
7	310	100	50	0
8	310	Not tested	Not tested	0
9	320	Not tested	Not tested	0
10	271	Not tested	Not tested	0
Total capacity	3263	1400	2970	0

Table 2
The elemental composition (at.%) and the fluorine content (mg/kg) of powdered beads.

Samples	C1s	O1s	Si2p	Ca2p	P2p	N1s	Fe2p	F1s	F-content
1	49.89	32.77	5.75	5.84	4.52	1.04	0.21	0	0
2	53.84	30.35	4.02	5.8	4.44	1.1	0.2	0.25	2906
3	45.25	35.37	5.25	7.21	5.54	0.88	0.27	0.24	2609

(a) SEM image   (b) EDAX spectrum

(c) SEM image   (d) EDAX spectrum

(1) Before regeneration

(a) SEM image   (b) EDAX spectrum

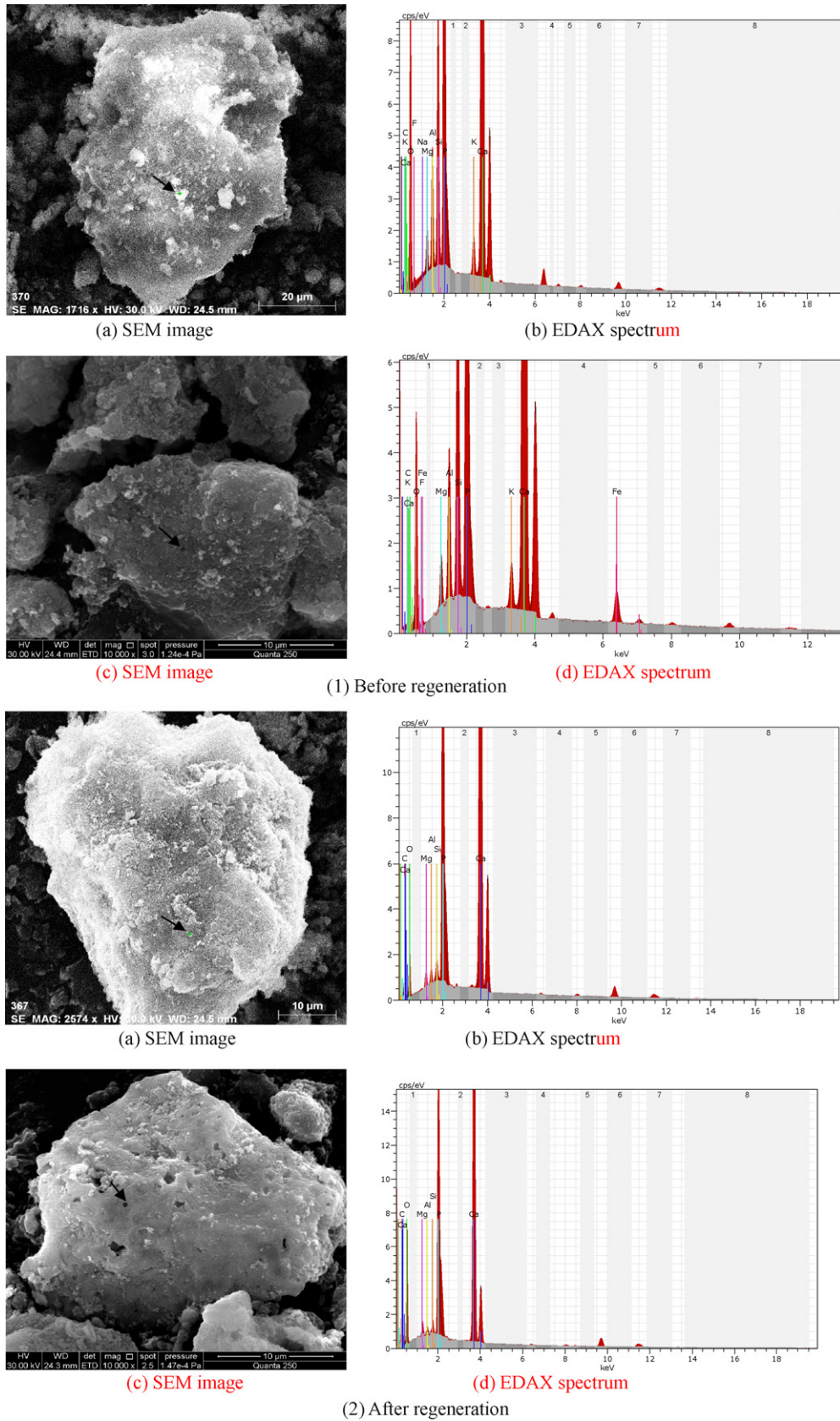(c) SEM image   (d) EDAX spectrum

(2) After regeneration

Fig. 4. SEM images and EDAX spectra of thin surface layers on HAP/ATT beads before and after regeneration.

Table 3
The results of heat regeneration: field trials.
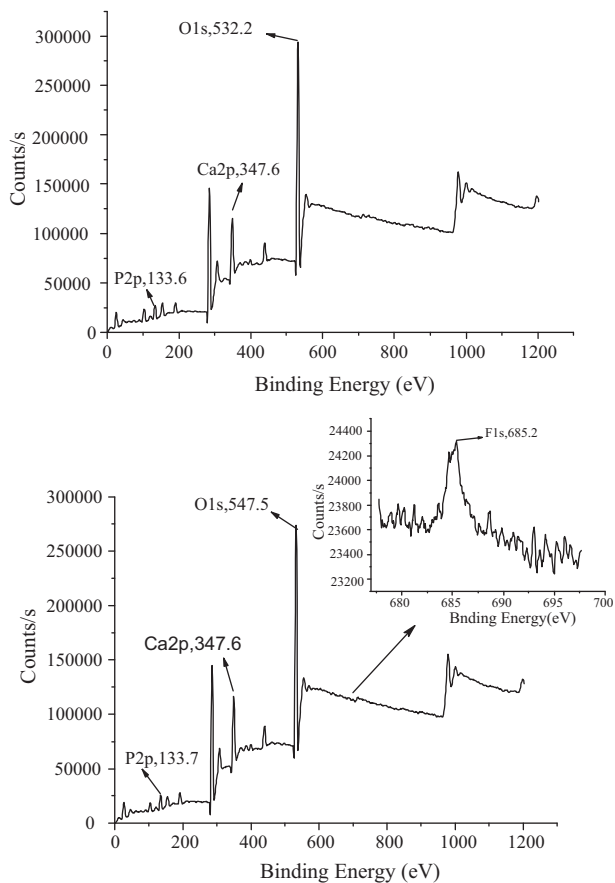
Regeneration cycle	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
RC* (mg/kg)	380	380	310	300	180	160	210	130	140	100	100	80	80	70	60
F-content in steam	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table 4
Elemental composition of bead powder (at.%).

Sample	C1s	K2p	O1s	Si2p	Fe2p3	Ca2p	Na1s	P2p	Mg2p	F1s
1	12.21	0.61	55.99	8.19	0.37	11.97	0.58	8.60	1.39	0.09
2	14.19	0.18	52.48	8.18	0.39	13.24	0.36	8.13	2.04	0.80
3	12.20	0.30	53.95	9.33	0.40	13.17	0.42	8.37	1.08	0.80

Fig. 5. XPS spectra of three bead samples.

presence of elemental fluorine on the surface, while there is no fluorine on the bead surface after regeneration [31,32].

Fig. 5 illustrates the XPS spectra of these three samples. The F1s binding energy is about 685 eV, appropriate for of F⁻ existing as M–F (M: metal). This is fluorine chemically bonded and confirms that the defluoridation process of the HAP/ATT composite beads is not a simple physisorption process.

3.5. Field trials

The HAP/ATT composite beads were applied to the removal of excess fluoride from drinking water in Feng county in Jiangsu Province. The application results show that the composite beads have good operability, environmental characteristics, and provide an economic advantage.

The exhausted beads were regenerated 15 cycles and the results are listed in Table 3. The dynamic regeneration capacity for the first and second cycle reached 380 mg/kg. This value is more than the RC* of new beads (340 mg/kg), which indicates that the surface of the HAP/ATT composite beads was activated by the heat treatment and that active sites for adsorbing have reached or exceeded the value for new beads. The RC* decreased gradually after each regeneration process, which indicates that the maximum defluoridation capacity will not be reached for each cycle. This may be caused by the rapid flow of the water samples that prevents adsorbents from contacting beads for enough time thus resulting in incomplete adsorption of fluoride. Free F⁻ was not found in the regeneration steam, which indicates that the exhaust gas did not contain desorbed F⁻ from the beads.

To confirm the mobility of the F⁻ ions the fluorine content of three samples was tested by XPS. Sample 1 was a powder of a blank sample. Sample 2 was the ground powder of beads re-saturated after the 15th dynamic saturation/regeneration cycle. Sample 3 was the ground powder of regenerated beads after the 16th dynamic saturation/regeneration cycle. The elemental composition is listed in Table 4. Sample 3 has one more regeneration cycle than sample 2 but they have nearly the same fluorine content, which indicates that the fluorine is in the beads and did not escape from them during the heat regeneration process.

Fig. 6 illustrates the XPS spectra of the three samples. The binding energy of F1s is about 685 eV, which represents F⁻ in a chemically bonded combination. This also confirms that the defluoridation process by the HAP/ATT composite beads is a chemical process, not a simple physisorption process.

3.6. A possible mechanism for heat regeneration

During the heat generation process beads were soaked in boiling water or steamed. The experimental results show that the fluoride ion was neither in the boiling water nor in the steam. This indicates that the fluoride is retained in the beads. So the following possible mechanism of heat regeneration is proposed.

In HAP/ATT composite beads, the HAP plays the main role in defluoridation [25]. After the adsorption reaction reaches saturation, the intra-particle diffusion of F⁻ ions is very slow within the HAP/ATT composite beads: Only a few F⁻ ions diffuse into the internal lattice of the HAP crystal. The surface of HAP may recover part of the active sites for adsorption of F⁻ ions. When the diffusion rate to the interior is less than the surface reaction rate, active OH⁻ on the HAP surface is quickly replaced by F⁻, so HAP loses the ability for defluoridation.

Heating provides additional energy for the F⁻ ions to diffuse into the internal HAP lattice, which accelerates the movement of fluoride ions. When the temperatures are high enough and the heating time is long enough the surface of the beads can be reactivated.
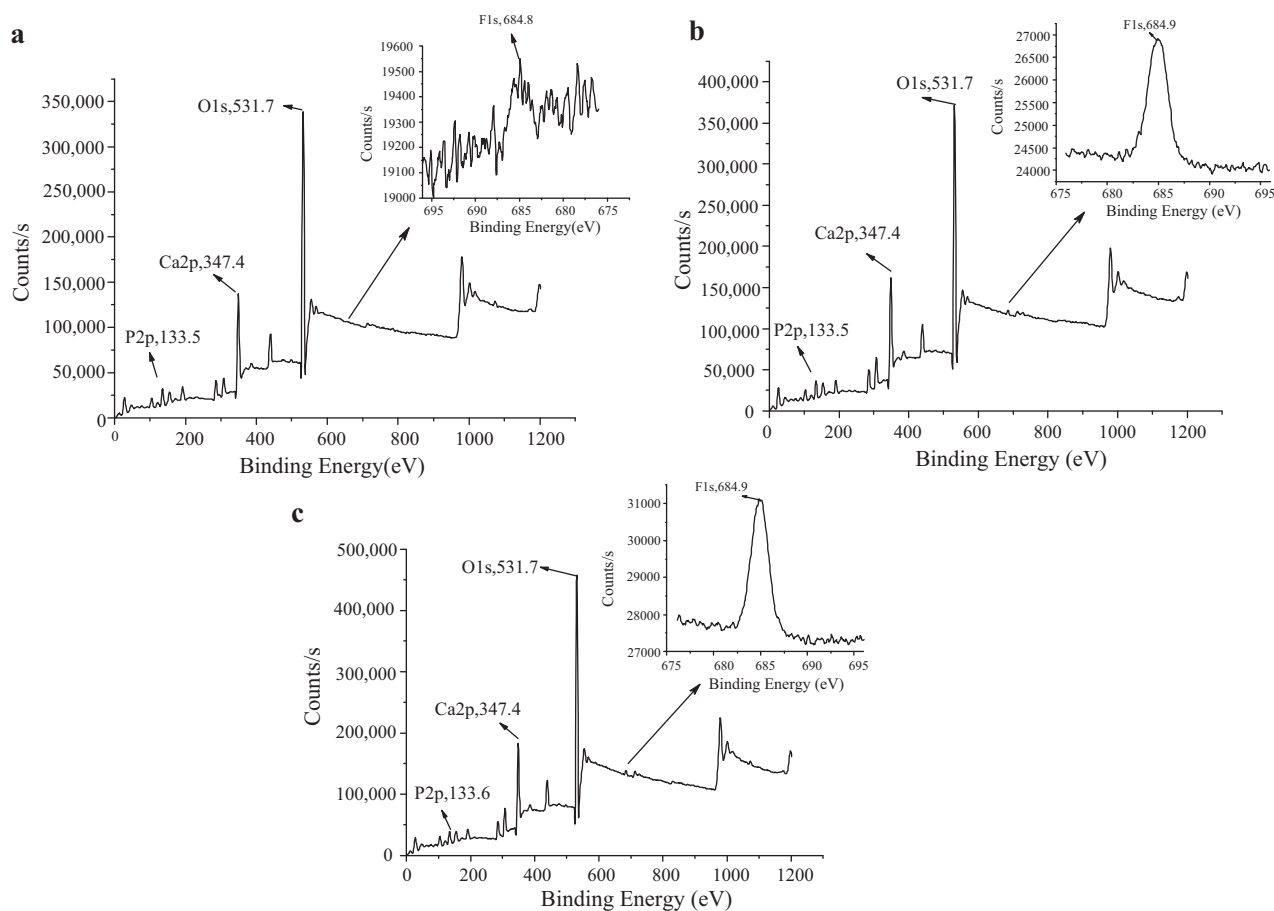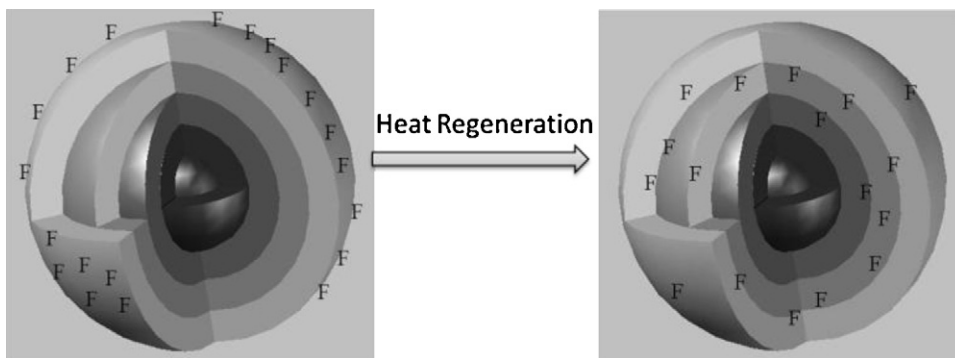
Fig. 6. XPS spectra of three powdered samples, field trials.

Scheme 1. Schematic showing the heat regeneration process.

When the rate of diffusion to the interior exceeds the rate of surface adsorption the active sites on the surface of HAP are exposed and the defluoridation properties are recovered, which explains why the regenerated capacity can reach 100% again.

The fluoride content of the interior of the beads increases with the number of regeneration cycles. When the rate of F^- diffusion to the interior from the surface is slower than the adsorption rate, parts of the surface will be occupied by F^- ions and the defluoridation capacity will decrease.

The regeneration process is illustrated here as Scheme 1. F^- ions adsorbed on the surface of the beads move quickly into the bulk of the HAP through the effect of heating. As the surface active sites are exposed the beads recover their defluoridation capacity.

The effects of heat regeneration are corroborated by the SEM and EDAX data of the thin surface layers before and after regeneration, see Fig. 4(1(a)–(d)) and (2(a)–(d)). Changes on the bead surface before and after regeneration were observed by taking thin surface samples from the different batches by using adhesive tape. Fig. 4 is the SEM images and EDAX spectra from random points in these thin surface layers. Random samples from different batches of composite beads were taken for these tests. Comparing Fig. 4(1) and (2), note that there are changes to the surface morphology and composition. The EDAX spectra before regeneration confirm the presence of elemental fluorine on the surface. Yet, there is no elemental fluorine on the bead surface after the regeneration cycle. The hypothesis that fluoride ions, first adsorbed on the surface of the beads,

subsequently moves toward the interior after regeneration is consistent with the experimental results shown in Tables 1 and 3.

4. Conclusion

(1) Exhausted HAP/ATT composite beads can be regenerated more than 10 times using boiling water or steam. Defluoridation and regeneration cycles performed in the same container show the characteristics of high efficiency and simple operation.

(2) The HAP component of the HAP/ATT composite beads plays the central role in fluoride sequestration. During regeneration, fluoride ions that are adsorbed to the surface move into the interior of the bead thereby exposing more adsorbing sites on the surface. Hence, the beads are regenerated.

(3) No chemical agents are used and no waste products are produced during the heat regeneration process, so this provides a nearly zero emission process.

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