



Facile defluoridation of drinking water by forming shell@fluorapatite nanoarray during boiling egg shell



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ABSTRACT

High fluoride water is one of the major problems against drinking water and are affecting millions of people all over the world. Refined adsorbents and water treatment plants aim at massive water supply but can't meet scattered household requirements, especially in the developing areas. Here, we developed a facile defluoridation method in which F^- can be removed by boiling eggs or shell assisted by phosphate. 0.4 L of high fluoride water (10 mg/L) can be transformed to safe drinking water with F^- concentration lower than 1.5 mg/L by boiling one egg at 80 °C for 10 min with the addition of 0.3 g/L of NaH_2PO_4 and 0.05 v% acetic acid. The mechanism study shows that F^- is adsorbed onto the egg shell outer surface forming nanorod arrays of fluorapatite and/or F^- substituted hydroxyapatite. Higher F^- adsorption capacity can be obtained (Langmuir adsorption capacity, 47.9 mg/g) if using egg shell powder instead of whole eggs. Pilot scale defluoridation (2.5 L, 10 times) was successfully realized by boiling egg shell in the presence of phosphate and acetic acid. The boiling shell defluoridation technology has potential household applications by common people with little professional backgrounds.

1. Introduction

Drinking high fluoride water may lead to fluorosis, which is a major health threat in many nations, especially in developing countries such as China, India and eastern Africa [1]. There are more than 200 million people suffering from high fluoride groundwater according to the 1.5 mg/L drinking water F^- threshold value set by the World Health Organization (WHO) [2]. A facile and cost-effective defluoridation method is needed [3]. A lot of defluoridation methods have been developed, mostly depending on reverse osmosis, electro dialysis, and adsorption [4]. Reverse osmosis and electro dialysis can effectively remove F^- and other small molecule pollutants from drinking water, but not cost-effective and generally designed for big water treatment plants [5,6]. Adsorption methods are based on ion exchange resins [7], and inorganic adsorbents such as calcium phosphate [8], hydroxyapatite [9], aluminum oxide [10,11], hydrated aluminum oxide [12], ferric oxide [13], ferric hydroxide [14], hydrated lanthanum oxide [15], layered double hydroxides [16], hydrated zirconium oxide [17], natural clay materials [18,19], metal organic framework [20], biogenic material [21], and their hybrids [16,22–24]. They are typically preferred for defluoridation application because adsorption defluoridation

technologies are simple, easy to operate, and cost-effective [25].

One of the cheap adsorbents is hydroxyapatite ($Ca_5(PO_4)_3OH$, HA) which can remove F^- from water through adsorption and form more thermodynamically stable fluorapatite ($Ca_5(PO_4)_3F$, FA), or a mixed F^- partial substituted HA ($Ca_5(PO_4)_3(OH,F)$) [26,27]. Smaller particles usually have bigger specific surface area, higher uptake capacities and adsorption speed [28–32]. Thus, using HA nanoparticles can be an effective way to improve its defluoridation performance [27,33]. However, clustering and aggregation of nanoclusters often result in undesirable filter properties such as low permeability and reduced reaction efficiency. A potential alternative solution is to generate HA nanoclusters on bulk calcite or limestone, which can provide an ideal substrate as it is easy to obtain and economically cheap as Ca source for HA production. Myneni et al. firstly developed this concept by generating nano-micro-crystalline hydroxyapatite-coated-limestone for defluoridation [34]. The adsorption capacity can reach 8.835 mg/g at conditions of initial concentration of 50 mg/L, contact time of 72 h, and room temperature. Although, limestone supported HA adsorbent has great potential for massive water treatment plants. Yet, it still has to face the relative high costs of raw material and the need of professional skill to run an adsorption plant, which may be potential problems in

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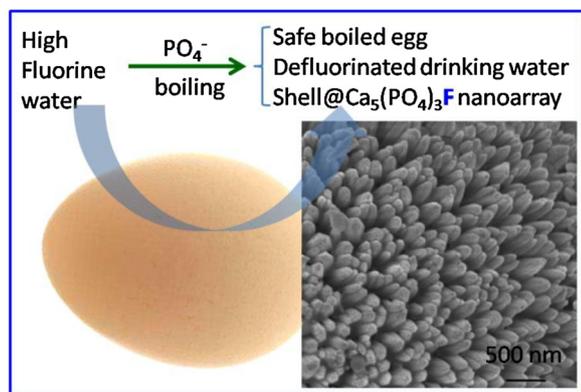


Fig. 1. Schematic illustration of the defluoridation process by boiling eggs.

most of the developing areas. A more cost-effective and facile method, especially for household application, is still a challenge.

Egg shell, a byproduct when we eat eggs, is composed of over 90% calcite CaCO_3 . And more importantly, egg shell is a kind of environmental benign biogenic green material that can be used as calcium supplement in food industry. Some interesting works have studied their potential applications to remove multi-pollutants from water, such as heavy metals (Pb, Cu, As, Cr(VI)) [35–38], phosphate [39,40], and organic dyes [41,42]. Regarding to defluoridation by forming FA nanomaterials using egg shell as calcium source, the precipitation speed can be increased at higher temperatures and thus promoting the precipitation of smaller HA nanoclusters. We propose that egg shell can substitute limestone in high temperature defluoridation process such as when we boiling eggs or egg shell. Thus, we can obtain defluorinated water, safe egg, and discardable fluorinated shell by boiling eggs with no need of buying refined adsorbents or expensive filter plant (Fig. 1).

2. Experimental

2.1. Materials

All solutions were prepared with deionized water. F^- solution was prepared by dissolving NaF. The concentration of F^- was 10 mg/L unless otherwise noted. Phosphate solution was prepared using sodium dihydrogen phosphate. The pH of the fluoride water was adjusted by 5% acetic acid solution. Eggs were purchased from a local market in Guangzhou, China. Commercial hydroxyapatite was purchased from Aladdin Reagent (China). The weight of the used eggs were controlled between 49 g and 51 g. Egg shell membrane (the membrane-like organic matter on the outer surface and the shell membrane in the inner surface of the shell) was removed by washing with 5% acetic acid and artificial peeling off before being used. Egg shell powder was prepared by grinding egg shell into powder and sifted through 100 mesh sifter.

2.2. Defluoridation experiments by boiling egg

0.12 g of sodium dihydrogen phosphate and/or 200 μL of acetic acid were added into 400 mL of fluoride water (10 mg/L) to prepare solution for boiling eggs. Fresh eggs were washed with water, immersed into 5.0 v% acetic acid solution for 5 min, and washed again by water to remove the organic film on the outer surface of eggs. Regarding to the testing of the F^- concentration in the shell, the F^- containing shell was dissolved into HNO_3 (1 M) solution and neutralized with NaOH (1 M) to prepare a solution. Then, its F^- concentration was tested by using the same fluoride electrode analyzer. Regarding to the F^- concentration in the egg white and yolk, the dried sample was immersed into NaOH (1 M) solution for 24 h and the filtrate was neutralized by HNO_3 (1 M) and tested by using the same fluoride electrode analyzer.

2.3. Defluoridation experiments by using egg shell powers

Egg shell powder was used when studying the defluoridation influence factors and the adsorption isotherms during boiling eggs. Certain volume of phosphate and/or acetic acid solutions was added into 100 mL of fluoride water to prepare the solution. 0.2 g egg shell was added into the solution at certain temperatures and a timer was started. The influence of temperatures on defluoridation efficiency was performed at conditions of $C(\text{egg shell}) = 2 \text{ g/L}$, $C(\text{F}) = 10 \text{ mg/L}$, $C(\text{NaH}_2\text{PO}_4) = 0.3 \text{ g/L}$, $C(\text{acetic acid}) = 0.05 \text{ v\%}$. Influence of NaH_2PO_4 concentration was performed at conditions of $C(\text{egg shell}) = 2 \text{ g/L}$, $C_0(\text{F}) = 10 \text{ mg/L}$, $C(\text{acetic acid}) = 0.05 \text{ v\%}$, temperature = 80 °C. The influence of pH was performed at conditions of $C(\text{egg shell}) = 2 \text{ g/L}$, $C_0(\text{F}) = 10 \text{ mg/L}$, $C(\text{NaH}_2\text{PO}_4) = 0.2 \text{ g/L}$, temperature = 80 °C. The influence of egg shell concentration was performed at conditions of $C_0(\text{F}) = 10 \text{ mg/L}$, $C(\text{NaH}_2\text{PO}_4) = 0.2 \text{ g/L}$, initial pH = 4.8, temperature is 80 °C. The reaction was maintained at certain temperatures for 30 min in the study of influence factors. All experiments were conducted in triplicate to obtain mean values.

2.4. Fitting of the adsorption kinetics and isotherms

Pseudo-second-order kinetic fitting was performed according to equation (1):

$$\frac{t}{Q} = \frac{1}{kQ_e^2} + \frac{1}{Q_e}t \quad (1)$$

t (min) is the adsorption time; Q (mg) is the mass of the adsorbed F^- on one egg; k is the adsorption rate constant (calculated from the linear fitting of t/Q vs. t); Q_e is the equilibrium adsorption capacity of one egg.

The adsorption isotherms were fitted by using Langmuir adsorption equation (2):

$$\frac{C}{Q} = \frac{1}{K_L Q_m} + \frac{1}{Q_m}C \quad (2)$$

Q is the adsorption capacity; Q_m is the Langmuir maximum adsorption capacity (calculated from the linear fitting of C/Q vs. C); K_L is a constant; C is the equilibrium concentration of F^- .

The Freundlich equation (3):

$$\ln Q = \ln K_F + \frac{1}{n} \ln C \quad (3)$$

K_F is the Freundlich adsorption constant, n is also a constant.

2.5. Pilot scale defluoridation by boiling egg shell

Egg shell, without grinding, was washed with 5% acetic acid (5 min) and boiled in water for 10 min to remove residue egg taste. Shell (35 g, from 10 eggs), NaH_2PO_4 (0.50 g), acetic acid (1.25 mL) were added into 2.5 L of simulated fluoride water (10 mg/L) in a steel pot (diameter 26 cm, depth 8.5 cm). Natural gas was used as fuel to boil the water for 10 min or 20 min. As the shell was at the bottom, defluorinated water was obtained by simply pouring out.

2.6. Leaching of fluoride from the spent shell

For checking the leaching of fluoride from the spent shell, the fluoride-containing shell was tested as per the protocol of California Waste Extraction Test (WET) [43,44]. 5 g of F^- containing shell after 10 boiling defluoridation cycles (20 min of boiling) was agitated with 50 mL WET extraction solution for 48 h in incubator at room temperature. The WET extraction solution consisting 0.2 M sodium citrate at 5 pH was prepared by titrating A.R. grade citric acid in pure water with 4 M NaOH. The released fluoride in WET solution was detected by using a fluoride electrode. The fluoride content in the shell was tested by the same method in 2.2. The leaching experiment was conducted in

triplicate and mean value is reported.

2.7. Characterization

The concentration of F^- was detected by using a fluoride-electrode analyzer (PXSJ-216, LEICI, China). The concentration of phosphate (calculated as NaH_2PO_4) was determined by molybdenum blue method with a UV/VIS spectrophotometer (UV-1780, SHIMADZU, China). The x-ray diffraction pattern was acquired by using a powder diffractometer with $Cu K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) (D2 PHASER, AXS, Germany). The microstructures of the shell were observed by using a field emission scanning electron microscope with an accelerating voltage of 5 kV (S-4800, Hitachi, Japan). The taste of the water from the pilot scale treatment was tested by 10 volunteers (20 years old, 5 male, 5 female).

3. Results and discussion

We attempt to use bio- $CaCO_3$ as calcium source to remove fluoride from water by forming FA. In order to let it happen, fresh bio- $CaCO_3$ need to be exposed to fluoride water. It should be noted that there is a thin layer of organic matter coating on the egg shell outer surface, which will hinder the FA formation reaction. We find that this membrane-like organic coating can be removed by a simple acid treatment procedure. Briefly, we immersed eggs in 5 v% acetic acid, a concentration used in most of commercial vinegar products. We can see some bubbles formed on the egg shell, probably CO_2 from the dissolution of a part of the bio- $CaCO_3$ on the shell surface. After 2 min of acetic acid treatment, a fragile thin membrane can be removed by washing, as shown in Fig. 2. Acid washed eggs or egg shell powder are used hereafter.

At first, we simply boiled an egg in fluoride water at $80^\circ C$, expecting the possible formation of CaF_2 . The adsorption kinetic results indicate that fluoride can hardly be removed if the egg is only exposed to fluoride water without the assistance of phosphate (Fig. 3). One of the possible reasons is that the initial F^- concentration is not high enough to form CaF_2 on the shell because of its relatively high solubility. In fact, exposure to fluorite is one of the most important reasons forming fluoride contaminated water. Existing publications also indicate that using calcite or limestone alone usually leads to low fluoride removal efficiency, slow adsorption rate and seems not an efficient method for drinking water defluoridation application. For example, the initial F- concentration was 37 mmol (703 mg/L) in Brett's results using calcite alone for fluoride removal [43]. In another paper using calcite for defluoridation, Charcosset's group found that the defluoridation efficiency could only reach 17.4% when treated 5 mg/L fluoride water

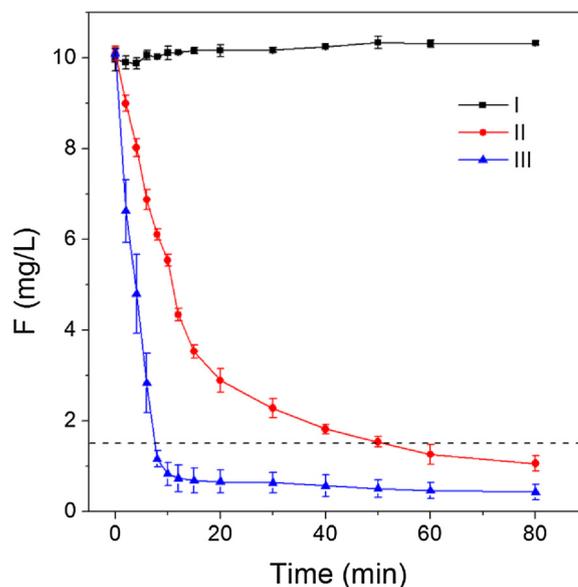


Fig. 3. Defluoridation kinetic curves during boiling eggs in fluoride water (10 mg/L, 400 mL) with (I) an egg, (II) an egg and NaH_2PO_4 (0.3 g/L), (III) an egg, NaH_2PO_4 (0.3 g/L), and acetic acid 0.05 v%.

by calcite. The removal efficiency was improved to 30.4% (3.48 mg/L left in the treated water) even assisted by 0.1 M acetic acid [44]. Larsen et al. found that the fluoride concentration was decreased from 10 mg/L to 0.95 mg/L by boiling fluoride water with brushite and calcite for 90 min [45]. The adsorption rate was slow, possibly because the used minerals were bulk materials and didn't take advantages of nanomaterials. Thus, using egg shell alone seems not an effective method for drinking water defluoridation in which one needs to control the F-concentration lower than 1.5 mg/L. After the addition of phosphate, NaH_2PO_4 (0.3 g/L), the F- concentration decreases quickly in the first 20 min from 10 mg/L to 2.9 mg/L with a defluoridation efficiency of 71%. However, the fluoride removal rate becomes slow hereafter. And, it needs another 1 h to reach a concentration below the 1.5 mg/L threshold. As the boiling egg defluoridation process is actually an interface reaction, the formation of FA may be impeded by the limited surface area of the egg shell. In the third boiling egg experiment, we added acetic acid to tune the initial pH of the fluoride water to weak acid. Therefore, a part of the shell-calcium can be dissolved into water phase to facilitate the interface reaction. Interestingly, the results indicate that F- concentration drops sharply once after the addition of an

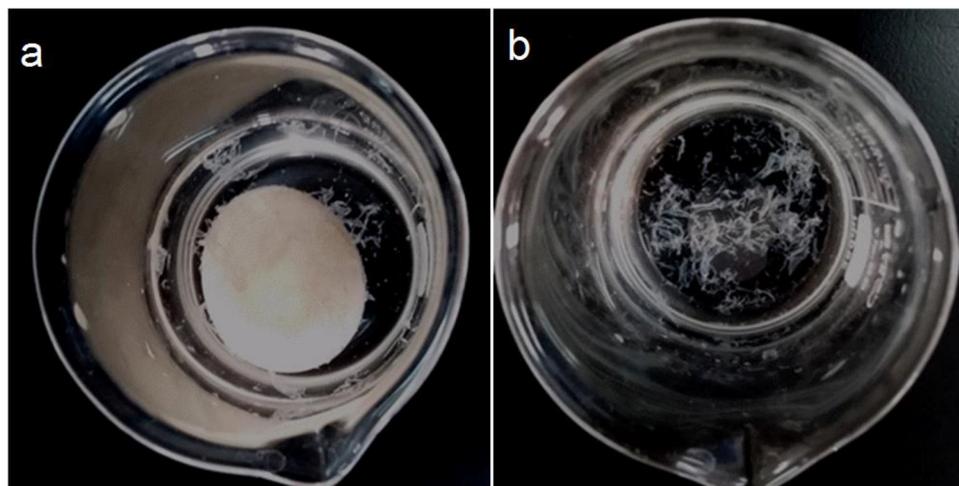


Fig. 2. Acid washing of the eggs using 5 v.% acetic acid for 2 min. (a) an egg in 5 v.% acetic acid, (b) membrane-like matter peeled off from the acid treated eggs.

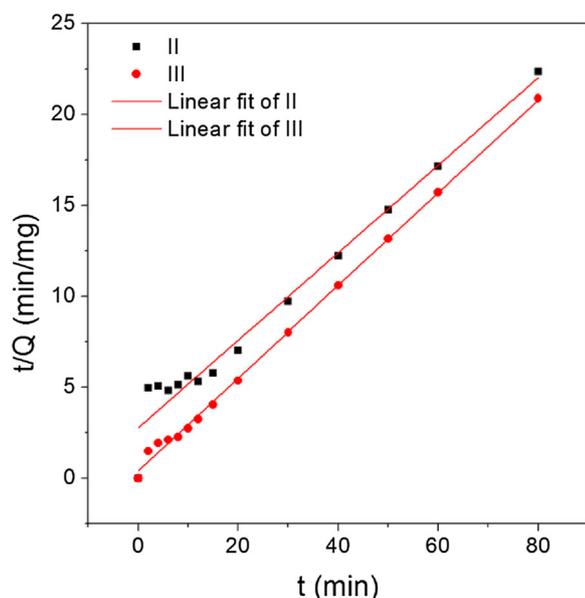


Fig. 4. Pseudo second-order fitting of the defluoridation kinetics.

egg. It only needs ~10 min to reach a defluoridation efficiency of over 90%. The pH was time-dependent (Fig. S1). A pH of 9.5 was obtained when the boiling time is 80 min. After 10 min of boiling, the pH is about 6.1. When the boiling time turned to 20 min, the pH increased to 7.4. The final pH of the boiled water is weakly alkaline (9.6) because excess bio- CaCO_3 exists which can hydrolyze to release bicarbonate and hydroxide ions. Considering proper pH of water, the boiling time should be between 10–20 min. As defluoridation can be realized quickly within 10 min using eggs, simple phosphate and acetic acid, this boiling egg defluoridation process may be conducted in one's kitchen and may have great potential for fluoride containing drinking water treatment without the need of refined adsorbents and expensive water treatment plants.

To understand the mechanism of the enhanced defluoridation efficiency, we fitted the experimental data to pseudo-first-order and pseudo-second-order kinetic models. The results indicate that pseudo-first-order kinetics is not suitable to simulate the defluoridation process (Fig. S2) while pseudo-second-order kinetics can simulate the process well with high correlation coefficients (Fig. 4). These results are consistent with existing reports using synthesized HA for defluoridation, indicating the same chemistry mechanism and thermodynamics [46]. The rate constant k and equilibrium adsorption capacity Q_e were obtained from the linear fitting of the pseudo-second-order kinetic equation.

$$\frac{t}{q} = \frac{1}{kq_e^2} + \frac{t}{q} \quad (4)$$

The results show that the use of acetic acid did not induce significant influence on Q_e . However, the adsorption rate constant using acetic acid and phosphate for defluoridation (III) is greatly increased up to ~8 times in comparison with the defluoridation process (II) using phosphate only (Table 1). Therefore, the defluoridation process by boiling eggs or egg shell with the addition of phosphate and acetic acid doesn't

Table 1

Pseudo second-order fitting parameters of the defluoridation kinetics. k is the adsorption rate constant, Q_e is the equilibrium adsorption capacity of one egg.

experiment	k ($\text{mg}^{-1} \text{min}^{-1}$)	Q_e (mg)	R^2
II	0.0210	4.15	0.968
III	0.166	3.92	0.998

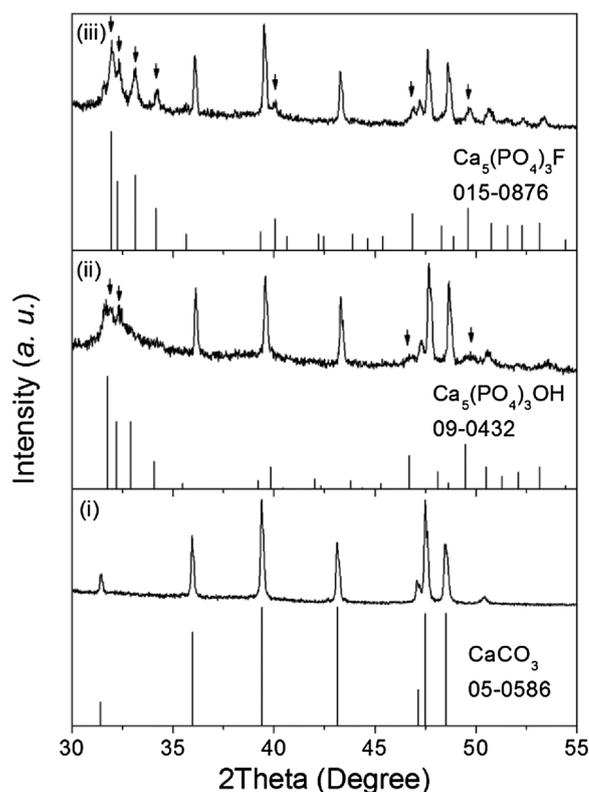


Fig. 5. XRD patterns the egg shell after different boiling treatments at 80 °C with (i) an egg in fluoride water, (ii) an egg and NaH_2PO_4 (0.3 g/L) in deionized water, (iii) an egg, NaH_2PO_4 (0.3 g/L), and acetic acid 0.05 v% in fluoride water. The boiling solution volume is 400 mL, the F^- concentration is 10 mg/L if used.

change the adsorption thermodynamics. The main reason of the enhanced defluoridation efficiency when using acetic acid together with NaH_2PO_4 may be assigned to the increased adsorption rate rather than adsorption capacity.

In order to identify the successful formation of FA or F^- substituted HA on the shell surface, X-ray diffraction patterns were acquired for the boiled egg shell. As shown in Fig. 5, the results confirm that the egg shell is mainly composed of calcite (JCPDS No. 05-0586). No fluorite phase is formed when boiling an egg in fluoride water. After boiling an egg in the presence of phosphate, HA is formed on the egg shell with characteristic diffraction peaks at 31.8° (2 1 1), 32.2° (1 1 2), 46.7° (2 2 2), and 49.7° (2 1 3), corresponding to hexagonal hydroxylapatite (JCPDS No. 09-0432). The diffraction pattern of the shell sample boiled in the presence of both phosphate and acetic acid shows that FA has been successfully formed on the egg shell with characteristic diffraction peaks at 31.9° (2 1 1), 32.3° (1 1 2), 33.1° (3 0 0), 34.1° (2 0 2), 40.0° (3 1 0), 46.9° (2 2 2), and 49.6° (2 1 3), corresponding to hexagonal fluorapatite (JCPDS No. 015-0876). Therefore, the defluoridation during the boiling egg process is mainly realized by the reaction of shell- CaCO_3 , F^- , and phosphate ions, forming FA and/or F^- substituted HA on the egg shell.

We further studied the morphology of the egg shell, as shown in Fig. 6. The results indicate that the shell of the acid washed eggs has a smooth surface with some fine cracks probably caused by the acid corrosion of shell- CaCO_3 during washing off the organic membrane on the shell outer surface (Fig. 6a, b). After the defluoridation process, the smooth egg shell surface becomes coarse. An enlarged SEM picture shows that the coarse shell is mainly composed of dense array of nanorods which is consistent with the micro-morphologies of hydrothermally synthesized HA or FA nanorods, as shown in Fig. 6c and d. Together with the XRD results, our results prove that F^- transformed

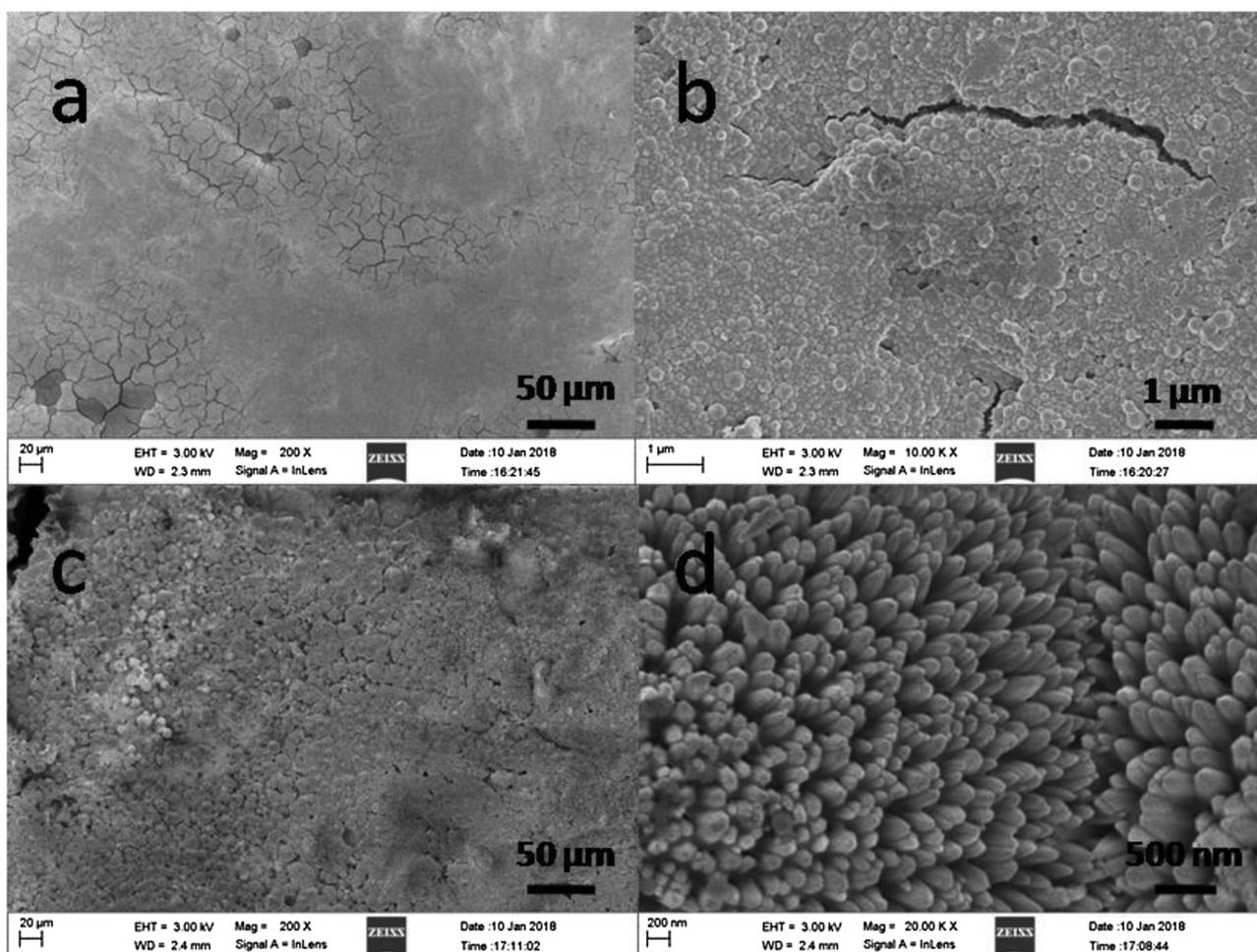


Fig. 6. Scanning electron microscopy images of the egg shell before (a, b) and after the boiling egg defluoridation process in the presence of phosphate and acetic acid.

Table 2

F^- concentration in shell and egg (white and yolk) before and after the boiling defluoridation process.

Treatments	F^- (shell)	F^- (egg white and yolk)
before	0.425 mg/kg	0.331 mg/kg
after	779 mg/kg	0.518 mg/kg

from water phase to shell surface by forming FA nanorod array. Therefore, safe defluorinated water can be obtained as FA-containing egg shell can be easily separated from water by manual operation. An analysis of the fluoride content in the boiled egg shell shows that nearly all of the removed F^- (~95%) is enriched on the shell surface with F^- concentration increasing from 0.425 mg/kg to 779 mg/kg, while the F^- concentration of the egg (egg white and yolk) increases from 0.331 mg/kg to 0.518 mg/kg, as shown in Table 2.

Possible influence factors, including temperature, phosphate concentration, pH, egg shell mass were studied to obtain optimized defluoridation procedures for potential massive water treatment applications. Egg shell powder was used here to avoid individual variation between different eggs. Fig. 7a indicates that ~60% defluoridation efficiency can be obtained at 30 °C. The defluoridation efficiency increases along with the increasing temperatures and reaches an optimum at 80 °C which is consistent with a relative report.³⁶ However, the efficiency drops a little when the temperature increases higher. A possible reason might be increased solubility of FA in hot water. Generally, the below 1.5 mg/L F^- threshold can be reached at temperatures from

60 °C to 90 °C. The results on the influence of phosphate indicate that the use of phosphate is one of the key factors for fluoride removal (Fig. 7b). Nearly no F^- can be adsorbed if no phosphate is used. A concentration of 0.1 g/L can afford a defluoridation efficiency of ~83%. Over 90% efficiency can be reached when phosphate concentration is higher than 0.2 g/L. Further increasing phosphate concentration over 0.3 g/L can't improve the defluoridation effect significantly. Therefore, the suggested phosphate concentration is 0.2–0.3 g/L. Weak acid pH can dissolve a part of the egg shell and help the release calcium ions for the reaction of forming FA. Regarding to higher fluoride removal efficiency, lower initial pH is preferred, as shown in Fig. 7c. However, initial pH of 3.7 will be suggested to ensure satisfying fluoride removal efficiency (over 90%) without acidizing the boiled water too much and influencing its taste to drink (excess Ca^{2+} tastes bitter). Lower pH (2.8) lead to cloudy of the treated water even after filtration, which might be caused by the formation of suspended HA nanoparticles. With regard to the amount of egg shell, generally, the defluoridation efficiency can be increased at higher shell dosages (Fig. 7d). The suggested shell mass will be 2.0 g/L considering the high defluoridation efficiency at this dosage.

Adsorption isotherm was conducted to study the adsorption thermodynamics during the boiling egg defluoridation process, as shown in Fig. 8, Fig. S3 and Table 3. The resulted isotherm can be fitted better with Freundlich model (R^2 , 0.992) than using Langmuir model (R^2 , 0.973), indicating that the defluoridation process is dominated by multi-layer chemical adsorption. The adsorption capacity calculated from Langmuir fitting reaches 47.9 mg/g. Although it is obtained at

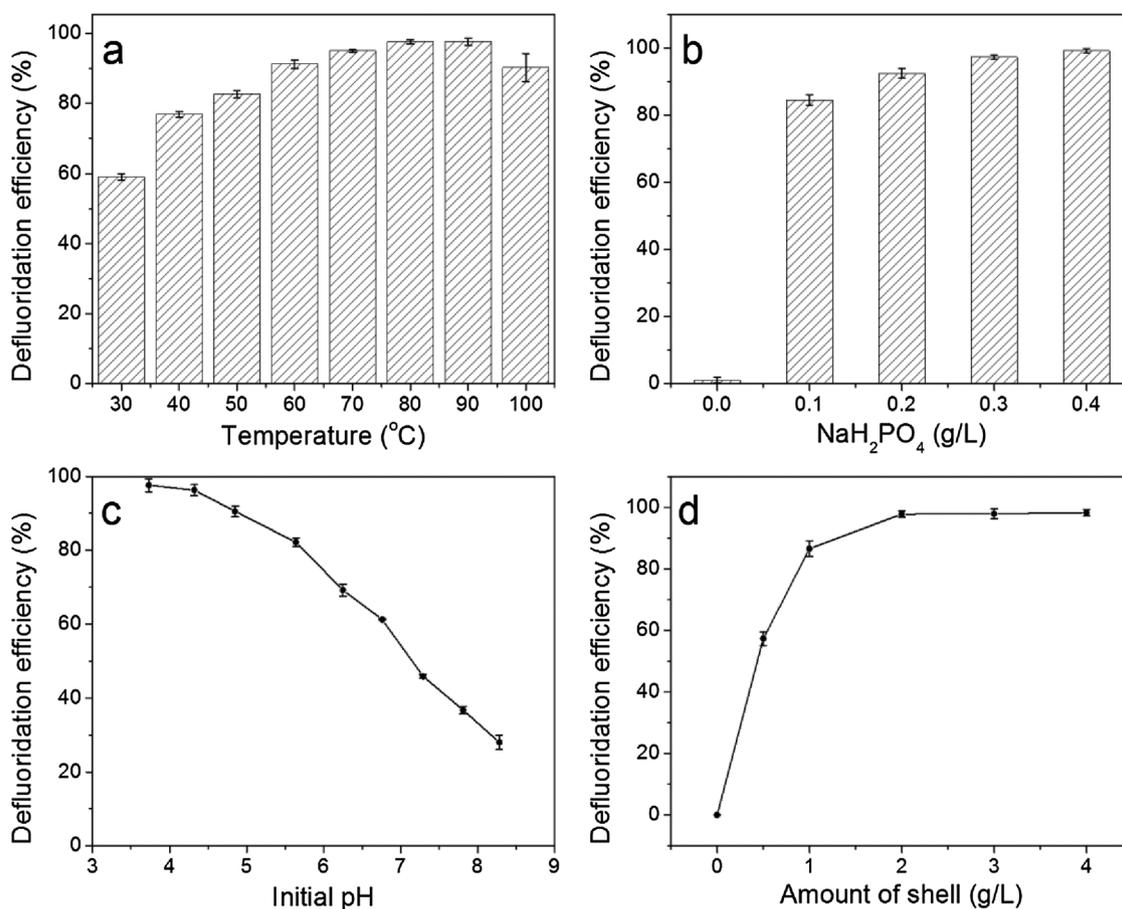


Fig. 7. Influence of (a) temperature, (b) NaH₂PO₄ concentration, (c) pH, and (d) egg shell concentration on defluoridation efficiency.

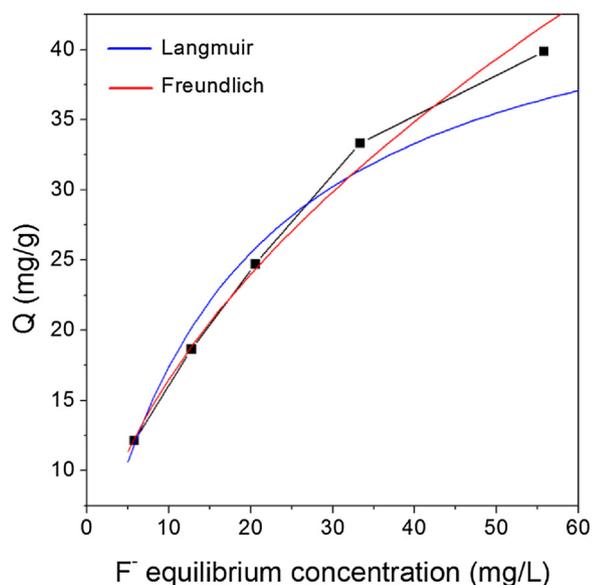


Fig. 8. Adsorption isotherm of egg shell at 80 °C. C(egg shell) = 2 g/L, C(NaH₂PO₄) = 0.2 g/L, initial pH = 4.8 (adjusted by acetic acid), reaction time is 30 min.

high temperature, this adsorption capacity is much bigger than most of other reported HA nano-adsorbents [9,26,27,33–35]. A comparison study was performed by using commercial HA. Same conditions were applied except that no phosphate was added. The Langmuir adsorption capacity of commercial HA is 32.2 mg/g (Fig. S4). Our boiling shell adsorption capacity is 48.3% higher than that of commercial HA. One

Table 3
Langmuir and Freundlich fitting of the adsorption isotherms.

Langmuir			Freundlich		
Q _m (mg/g)	K _L (L/mg)	R ²	1/n	K _F (L/mg)	R ²
47.9	0.0571	0.973	0.539	4.78	0.992

possible reason may be that F⁻ can only be adsorbed onto the HA/water interface when pre-prepared HA adsorbents are used. Regarding to our boiling egg defluoridation process, F⁻ is adsorbed by the formation of FA nanorod array on the egg shell together with its crystal growth. Therefore, there will always be fresh HA interface for the adsorption of extra F⁻ unless phosphate and shell-CaCO₃ are exhausted. Its big adsorption capacity and rapid adsorption speed reveal great potential for household defluoridation applications. Moreover, commercial HA powder is hard to precipitate (Fig. S5). In our experiment, HA nanorods are anchored onto bulk shells, so that the HA nanorods, together with egg shells, will always stay at the bottom of treated water. Treated water and spent shells can be easily separated by pouring.

A possible mechanism is proposed for the boiling egg defluoridation process, as shown in Fig. 9. At first, acetic acid dissolves a part of the shell-CaCO₃ to release free Ca²⁺ ions. Then, the released Ca²⁺ encounters phosphate and F⁻ at shell/water interface, forming FA nanocrystal nucleus on the shell. The FA nucleus keeps growing by absorbing Ca²⁺ from the shell while PO₄⁻ and F⁻ taken up from the treated water. Thus, shell@FA nanorod arrays are obtained in the end while F⁻ be removed from water. The acidic pH in the beginning is helpful for the formation of FA nuclei which are the seed of FA nanorods. This may be the reason why the defluoridation speed can be accelerated a lot by

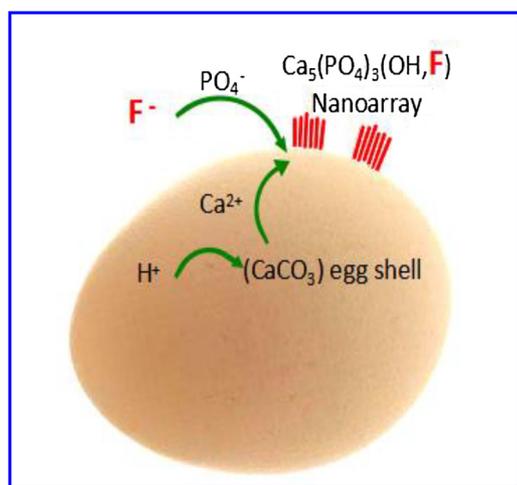


Fig. 9. Possible defluoridation mechanism during boiling egg in water containing phosphate and F^- .

the addition of a little acetic acid.

Directly boiling eggs may lead to a kind of egg taste to the treated water and a waste of egg shell resource. As the actual functional material is the egg shell in our experiment, we suggest a modified boiling shell defluoridation application. A pilot scale defluoridation process was conducted by using 35 g of shell to treat 2.5 L of fluoride water (10 mg/L). The boiling process was performed in a steel pot (Fig. S6) fueled by natural gas. The concentration of acetic acid and NaH_2PO_4 was 0.05% and 0.3 g/L. Successful defluoridation can be realized for 7 cycles without changing shell when the boiling time is 10 min and 10 cycles with 20 min of boiling. When the boiling time was set to 10 min, the final pH of the treated water was 6.6 after the first cycle and gradually decreased to 4.9 after 10 cycles (Fig. S7). If extending the boiling time to 20 min, the pH of the treated water gradually varied from 7.2 to 5.6 after 10 boiling shell defluoridation cycles. Residue phosphate varied from 65.4 mg/L to 82.1 mg/L (Fig. S8). Considering the pH, water yield, and the fully utilization of the egg shell, 20 min of boiling is suggested. We found 10 volunteers (20 years old, 5 male, 5 female) to taste the treated water and untreated water. 5 volunteers couldn't tell the difference, 3 of them felt weak astringent, 2 of them had a weak vinegar taste. None of them felt uncomfortable. Cost analysis was performed according to the local price in Guangzhou, China (Table S1). The necessary material cost (acetic acid and NaH_2PO_4) is only 0.00233 USD/L or 6.8% of the total cost. The cost in eggs and fuel can be cut down. In many places, egg shell is considered as useless waste and are not fully utilized. We proposed a modified boiling shell defluoridation application instead of boiling eggs, so that the egg purchase cost can be decreased greatly or even ignored. Other calcium resource, such as synthetic food-grade calcium carbonate or natural calcium mineral, may be possible alternatives for egg shell, so that the cost may be further decreased and the defluoridation process may be possibly accepted by broader population. Regarding to fuel, one can do the boiling shell defluoridation along with cooking in which water has to be boiled, so that no extra fuel will be needed specially for defluoridation. The pilot scale defluoridation was also successfully realized by using household vinegar (acidity, 5%) and fertilizer-grade KH_2PO_4 (> 99%), as shown in Fig. S9. Our boiling shell method may be a necessary complementation to community-scale defluoridation. People live in a variety of environments. There is not a single technology that can meet all or most of the defluoridation requirements. There is a need to develop different methods so that people can choose the most suitable one according to their own situations (Fig. 10).

In order to check the leaching of fluoride from the spent shell, the fluoride-containing shell was tested as per the protocol of California Waste Extraction Test (WET) [47,48]. 5 g of F^- containing spent shell

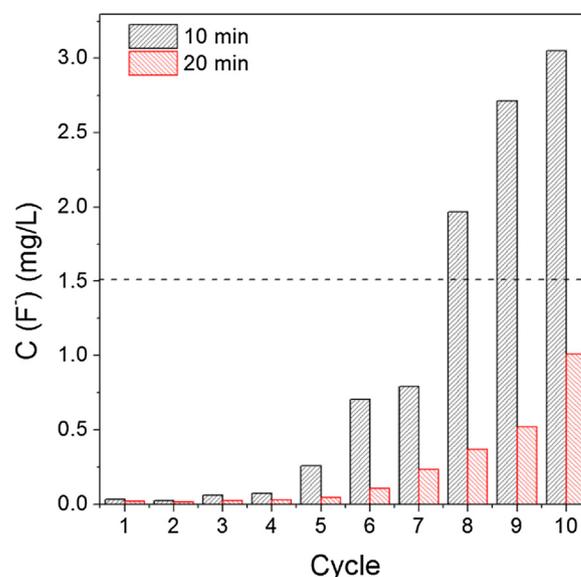


Fig. 10. Pilot scale defluoridation by boiling shell. 2.5 L of fluoride water (10 mg/L) was treated in each cycle.

was agitated with 50 mL of WET extraction solution for 48 h in incubator at room temperature. The results indicated that the equilibrium F^- concentration of the extraction solution is 1.12 mg/L (95% confidence limit, from 0.88 to 1.36 mg/L), which means that only 0.16% of the adsorbed F^- can be released under the standard leaching conditions. Possible reason about the low leaching rate may be as follows. The defluoridation process is dominated by multi-layer chemical adsorption according to the Freundlich fitting result of the adsorption isotherm in Fig. 8. F^- is removed during the growth of HA nanocrystal. Most of F^- will be located inside of the HA crystal. Excess phosphate may form HA layer covering the F-HA and thus will hinder the release of F^- . In addition, proper amount of fluoride is helpful for human health. Fluoride is only toxic when its concentration become higher than 1.5 mg/L. Slow and scattered release of fluoride into the environment may not likely lead to severe environmental risk.

4. Conclusion

A facile defluoridation method is realized for household drinking water treatment by boiling eggs in fluoride water assisted by phosphate. 0.4 L of high fluoride water (10 mg/L) can be transformed to safe drinking water with F^- concentration lower than 1.5 mg/L by boiling one egg at 80 °C for 10 min with the addition of 0.3 g/L of NaH_2PO_4 and 0.05 v% acetic acid. F^- is adsorbed onto the egg shell outer surface forming nanorod arrays of fluorapatite and/or F^- substituted hydroxyapatite. Higher defluoridation efficiency can be realized if using egg shell powder instead of whole eggs. The Langmuir adsorption capacity reaches 47.9 mg/g. Although many other finely designed high quality adsorbents have been developed with good defluoridation capacity and adsorption speed, they are relatively expensive, and/or not easy to obtain. Further, they are usually designed for big water treatment plant which one will need professional skills to operate. Regarding to our boiling egg defluoridation technology, people only need eggs, phosphate, and acetic acid for defluorinated drinking water. Therefore, this technology has great potential applications for household drinking water treatment by common people with little professional backgrounds, especially for families in less developing areas.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jhazmat.2018.09.007>.

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