Preparation of hollow Fe-Al binary metal oxyhydroxide for efficient aqueous fluoride removal

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**HIGHLIGHTS**

• Hollow Fe-Al binary metal oxyhydroxide (FeAl-OOH) was fabricated by sacrificial template method.
• Protonation abilities of the oxygen binding sites were intensified by Al incorporation.
• Adsorption capacity of $F^-$ by FeAl-OOH outperformed comparable metal sorbents.
• Only 15 min was needed for decreasing $F^-$ below 1 mg L$^{-1}$ by FeAl-OOH adsorption.

**GRAPHICAL ABSTRACT**

**ABSTRACT**

Fluoride contamination of drinking water, which causes fluorosis and neurological damage, is an exigent worldwide problem. Adsorption by metal oxyhydroxides is an attractive technology for water defluorination, although the removal efficiency is restricted by protonation of the oxygen binding sites (M-OH and M-O-M) for $F^-$. Herein, hollow Fe-Al binary metal oxyhydroxide micro-boxes (FeAl-OOH MB) were prepared by annealing derivatives of Prussian blue analogues (PBA$s$). XRD and $^{27}$Al MAS NMR analyses showed that the hollow structures were composed of Al oxyhydroxides (Al(O)$_6$, Al(O)$_4$) and Al-incorporated ferrihydrite. The surface oxygen was easily protonated in the presence of Al oxyhydroxides; with the introduction of Al into the lattice, the extent of protonation on the surface of the ferrihydrite was intensified via weakening the electronegativity of Fe sites. Therefore the limitation on adsorption efficiency was alleviated through tuning the surface charge. Together with large specific surface area (242 m$^2$ g$^{-1}$) and good mass diffusion, hollow FeAl-OOH MB exhibited outstanding maximum $F^-$ adsorption capacity (146.59 mg g$^{-1}$) and adsorption rate (20 min was needed to reach equilibrium for initial $F^-$ concentration of 10 mg L$^{-1}$), outperforming comparable metal oxyhydroxide/oxide adsorbents. Meanwhile, except for PO$_4^{3-}$, co-existing anions (NO$_3^-$, Cl$^-$, SO$_4^{2-}$ and HCO$_3^-$) showed negligible influence on the adsorption of $F^-$ on FeAl-OOH MB. Furthermore, the $F^-$ adsorbed on FeAl-OOH MB could be effectively

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1. Introduction

Fluoride contamination in drinking water, which arises mainly from dissolution of natural minerals in rocks and soils, is an ongoing global environmental problem, especially in north and northeast China, India, Mexico and Africa [1–3]. Excess intake of fluoride can cause dental and skeletal fluorosis, as well as serious neurological damage [4]. Therefore, water defluorination is of significant urgency. In contrast to other technologies including coagulation and precipitation, capacitive deionization, reverse osmosis and ion exchange, adsorption has been recently considered the most efficient and least costly path for aqueous F− removal [5,6]. Fe or Al oxyhydroxides are the most widely used adsorbents due to their natural abundance, chemical stability, and high binding affinity for F− [7–10].

During the adsorption process, the rate-determining first step involves the protonation of oxygen coordinated to the metals, which is positively correlated with the pHdeq (pH at zero point of charge) on the surfaces of these Al- or Fe-based adsorbents. A high pHdeq facilitates the diffusion of F− from solution to the surface of metal oxyhydroxides/oixides via electrostatic attraction between the positive surface and negative F−. Recently, some researchers reported that Fe-Al binary oxyhydroxides with high surface positive charge exhibited marked enhancement of fluoride removal compared to Fe- or Al- based adsorbents, and this was also attributed to their increased protonation with Al incorporation [11,12]. Thus, development of an alternative synthesis method with particular simplicity for adsorbents with superior activity is of great significance to the application of binary metal oxyhydroxide sorbents.

Hollow hybrid metal oxyhydroxides/oixides, with well-defined interior voids and adjustable components, exhibit great potential in the field of separation and purification [13,14]. Benefiting from their tunable characteristics, hollow hybrid metal oxyhydroxides/oixides with large surface area provide abundant active sites and good mass diffusion internally, thereby achieving superior adsorption efficiency [15,16]. In contrast to the conventional hard templating method [17] or self-assembly method [18], the sacrificial template method has been applied as an effective strategy for achieving uniform hollow metal oxides [19,20]. Recently, Prussian blue (PB) and its analogues (PBAs), with the formula of M3II[MIII(CN)6]n·mH2O (M = Fe, Ni, Mn, Co, etc.), have been proposed as ideal templates to fabricate hollow structures for various applications [21,22]. In addition to serving as the template, PBAs can also supply the metal framework during the process of obtaining the desired hollow hybrid metal hydroxides via template-engaged reactions [23]. This template approach has the potential to offer an alternative route toward large-scale and multi-component synthesis of hollow hybrid metal oxyhydroxides. Notably, Fe-Al oxyhydroxides with various molar ratios of Fe to Al can be achieved via chemical etching of PB with NaAlO2 solutions of different concentrations. Therefore, it is reasonable to speculate that the template-engaged method might be an effective way to prepare the ideal adsorbents for aqueous removal of fluoride.

In this work, hollow Fe-Al oxyhydroxide micro-boxes (FeAl-OOH MB) with optimal molar ratio of Al to Fe were obtained by properly annealing PB derivative Fe-Al hydroxides for highly efficient defluorination of water. Via characterization with X-ray diffraction (XRD), 27Al solid-state nuclear magnetic resonance (27Al NMR), field-emission scanning electron microscopy (FESEM) and scanning transmission electron microscopy (STEM), the formation pathway and structure of the adsorbents were elucidated thoroughly. The defluoridation performance of hollow FeAl-OOH MB was evaluated through isotherm analysis and kinetic studies under various initial F− concentrations and different pH conditions. The effects of co-existing ions, desorption and regeneration cycles on F− removal capacities of the adsorbent were also investigated. Furthermore, the F− adsorption mechanism and protonation ability of surface oxygen were elucidated using X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV) and theoretical calculation.

2. Materials and methods

2.1. Materials

Polyvinylpyrroldione (PVP, K30) was guaranteed reagent grade. Potassium hexacyano-ferrate (II) trihydrate (K3[Fe(CN)6]·3H2O), sodium aluminate (NaAlO2), hydrochloric acid (HCl, 36–38%), sodium hydrate anhydrous (NaOH), sodium fluoride (NaF), sodium nitrate (NaNO3), sodium chloride (NaCl), sodium sulfate anhydrous (Na2SO4), sodium hydrogen carbonate (NaHCO3), and potassium phosphate tribasic anhydrous (K2PO4) were analytical reagent grade. All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). NaF stock solutions were prepared by dissolving NaF into deionized water.

2.2. Synthesis of FeAl-OOH MB

Hollow Fe-Al oxyhydroxide micro-boxes (FeAl-OOH MB) were prepared by appropriately annealing the Fe-Al hydroxide intermediates, which were products of the reaction between Prussian blue (PB) templates and NaAlO2 solutions with different concentrations. Briefly, 3.80 g PVP and 0.11 g K3[Fe(CN)6]·3H2O were dissolved entirely into 50 mL HCl solution (0.1 M) in turn. The mixed solution was placed in an oven at 80 °C for 24 h to form the PB microcube templates [23]. The PB template material was centrifuged and washed by deionized water and ethanol, and then dispersed in 20 mL ethanol for further use. For synthesis of Fe-Al hydroxide intermediates with a range of molar ratios of Al to Fe (Ra:Fe), 20 mL of the above PB template suspension was mixed with 30 mL NaAlO2 solutions with different concentrations (0.03, 0.04, 0.05, 0.06, 0.08, 0.10 and 0.12 M) while stirring rapidly for one hour. Finally, Fe-Al oxyhydroxides were acquired by annealing the Fe-Al hydroxide intermediates at different temperatures, 300, 400, 450 and 500 °C, in air for six hours with a slow heating rate of 0.5 °C min⁻¹.

2.3. Characterization

A Hitachi field-emission scanning electron microscope combined with an energy dispersive spectrometer (FESEM-EDS, CARL ZEISS SIGMA, Germany) and scanning transmission electron microscope combined with energy dispersive X-ray spectroscopy elemental mapping (STEM-EDX, JEOL 2010F, Japan) were employed to further reveal the morphology and structure of the adsorbents.
X-ray diffraction (XRD, XPert PRO MPD, Holland) analysis was carried out on a D/Max-3A diffractometer using Ni-filtered copper Kα1 radiation. The Al species were determined and quantified by 27Al solid-state magic angle spinning Nuclear Magnetic Resonance (27Al MAS NMR, Bruker Avance II 400, Switzerland). The bonding of Al, Fe, O, and F of the adsorbent were explored using a Kratos Axis Ultra X-ray photoelectron spectrometer (XPS, Axis Ultra, Japan) with monochromatic Al Kα radiation (1486.7 eV). The pore size distribution and specific surface area were determined by N2 adsorption–desorption testing with a Micro-Meritics ASAP 2020HD88 instrument (USA).

2.4. Adsorption experiments

The adsorption capacities of Fe-Al oxyhydroxides with varying RAl:Fe and different annealing temperatures, were evaluated at initial F− concentration of 10 mg L−1 and adsorbent dosages of 0.4 g L−1 at 25 °C. The pH value was maintained using 0.1 M HCl and NaOH. The F− solution and adsorbent were magnetically stirred at 160 rpm for 12 h. After adsorption, the adsorbents and solutions were separated using 0.22 μm polytetrafluoroethylene (PTFE) membranes; the F− concentrations in the filtrates were analyzed.

Adsorption kinetics experiments were performed at different initial F− concentrations (5, 10, 30, 50 and 100 mg L−1), with aluminum oxyhydroxide prepared according to a literature method for comparison [24]. The pH value was 7.0, and the adsorbent dose was 0.4 g L−1. During adsorption, solution samples were taken at different time intervals for the determination of F− concentrations.

The adsorption isotherms were determined with F− concentrations ranging from 5 to 250 mg L−1 at various pH values (5, 6, 7 and 8) to investigate the pH effect at the same time. The adsorbent dose was 1.0 g L−1. Other procedures were the same as in the above study.

In experiments to determine the effect of co-existing ions on adsorption, two concentration levels (5 mg L−1 and 20 mg L−1) of NaNO3, NaCl, Na2SO4, NaHCO3, and K23PO4 were respectively added to solutions that had F− concentration of 10 mg L−1. The pH was 7.0, and the adsorbent dose was 0.4 mg L−1.

In the desorption and reuse study, the spent adsorbent was separated using 0.22 μm PTFE membranes and then washed with deionized water five times. 20 mg samples of adsorbents were desorbed using 100 mL of NaOH solution (0.0001, 0.001, 0.01, 0.1 and 1 M) with stirring for 12 h followed by drying at 60 °C in a vacuum drying oven for 24 h. The adsorption abilities of regenerated adsorbents were investigated with 10 mg L−1 initial F− concentration and 0.4 g L−1 adsorbent dose as well. Five regeneration cycles were conducted to evaluate the reusability of the adsorbent.

2.5. Analytical methods

The concentrations of F− were analyzed on a Dionex Ion Chromatography System (ICS) 2000 (USA), equipped with an IonPac AS-19 anion exchange analytical column. 15 mM of KOH was used as the mobile phase eluent, and the flow rate was 1.0 mL min−1. Dissolved Al and Fe were analyzed on a Perkin-Elmer Optima Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, USA). The zeta potentials were measured with a Malvern Zetasizer Nano 2000 instrument (U.K.).

3. Results and discussion

3.1. Synthesis and characterization of FeAl-OOH MB

Hollow Fe-Al binary oxyhydroxide micro-boxes were obtained by annealing the intermediates – hollow Fe-Al binary hydroxides, which were the product of a template-engaged reaction between PB microcubes and NaAlO2 [23]. As Fig. 1 illustrates, during the process of chemical etching by the alkali solution, an ion exchange reaction first took place at the surface of the PB. Meanwhile, the consumption of OH− promoted the hydrolysis of AlO2− in solution near the surface, resulting in the production of Fe-Al(OH)3 at the interface between PB microcubes and the solution, and the reaction process can be depicted as follows:

\[
\text{Fe}_4[\text{Fe}(\text{CN})_{6}]_3\text{SO}_4 + 12\text{AlO}_2^{-2}_{\text{aq}} + 24\text{H}_2\text{O} \rightarrow 3\text{Fe}(\text{CN})_{6}^{4-} + 4\text{Al(OH)}_3 + 3\text{SO}_4^{2-} + 12\text{H}_2\text{O}
\]

(1)

As the reaction proceeded, OH− flowed inward to etch the residual PB, and Fe-Al hydroxides with large interior cavities were finally obtained, followed by an annealing procedure to produce the hollow Fe-Al oxyhydroxides.

The prepared PB microcube templates with 500 nm diameter are shown in Fig. 2a. After the template-engaged reaction with NaAlO2, the microcubes were converted to Fe-Al hydroxide microboxes. It was found that the morphologies and the RAl:Fe in the Fe-Al hydroxides were dependent on the concentration of NaAlO2. In contrast to the incompletely hollow structure obtained when the concentration was lower than 0.05 M, higher concentrations of NaAlO2 (0.12 M) collapsed the structure (Fig. S1). Thus, the optimal concentration range for NaAlO2 was from 0.05 to 0.10 M (Fig. 2b–e), in which the PB cubes were etched into hollow structures surrounded by Fe-Al hydroxide nanosheets with thickness about 62.7 nm (Fig. 2f).

According to the results of acid dissolution experiments, the RAl:Fe of the as-prepared Fe-Al hydroxide was determined to be 1.20, 0.92, 0.65, 0.40 corresponding to 0.05, 0.06, 0.08 and 0.10 M NaAlO2 (Fig. 2g), which was further confirmed by energy dispersive spectrometry (EDS) (Fig. S2).

The pristine hollow Fe-Al hydroxide (RAl:Fe 1.20) with an amorphous structure is depicted in Fig. 3a, while 2-line ferrihydrite crystals were achieved after annealing in air. The 2-line ferrihydrite (Fe3O4·4H2O) is a hydrous ferric oxide phase with poor crystallinity [25, 26]. However, in contrast to the XRD pattern of pure ferrihydrite, the two main peaks at 33° and 61° shifted toward higher angles with increasing annealing temperature in the presence of Al, which resulted from the incorporation of Al into the crystal lattice of ferrihydrite [27, 28]. Meanwhile, the characteristic peak belonging to 2-line ferrihydrite vanished when the annealing temperature increased to 500 °C (Fig. 3a top). Notably, the hollow structures were preserved, while their shells were thinner after annealing (Fig. 3b–c). According to the results of the EDX measure-
Fig. 2. Characterization results for PB template and Fe-Al hydroxide intermediate. (a) FESEM image and XRD pattern of PB microcube template. (b-e) FESEM image of Fe-Al hydroxide microboxes produced from reactions between PB cubes and different concentration NaAlO₂ solutions; (b) 0.05 M NaAlO₂; (c) 0.06 M NaAlO₂; (d) 0.08 M NaAlO₂; (e) 0.10 M NaAlO₂. (f) STEM image and energy dispersive X-ray spectroscopy (EDX) elemental mappings (insets) of Fe-Al hydroxide microboxes. (g) The R_{Al:Fe} values corresponding to different concentration NaAlO₂ solutions, analyzed by acid dissolution experiment.

Fig. 3. Characterization results for Fe-Al oxhydroxide (R_{Al:Fe} 1.20). (a) XRD patterns of Fe-Al oxhydroxide annealed at 300, 400, 450 and 500 °C. (b) FESEM image, (c) STEM image, (insets) EDX-elemental mappings and (d) HRTEM image of the Fe-Al oxhydroxide annealed at 450 °C (FeAl-OOH MB).
ments, the elements of Al, Fe and O were uniformly distributed in the shells (Fig. 3c insets).

Additionally, the porous texture of the hollow Fe-Al oxyhydroxide microboxes (R_{AFA} 1.20, 450 °C, FeAl-OOH MB), with a surface area of 242.12 m² g⁻¹ and small average pore diameter of 12.90 nm, based on BET calculations (Fig. S3), was directly confirmed by High Resolution Transmission Electron Microscopy (HRTEM) imaging (Fig. 3d). These results demonstrate the high potential of FeAl-OOH MB for adsorption provided by their large surface area and porous structure.

In order to analyze the Al species in the FeAl-OOH MB, 27Al MAS NMR was then performed on the hollow structures. The peaks at 64 ppm and 4 ppm with associated spinning sidebands (SSBs) in the FeAl-OOH MB sample (Fig. 4a) were assigned to 6- and 4-fold coordinated Al sites respectively [29]. In contrast to the NMR spectra of Fe-Al hydroxide, some percentage of Al(O)₆ octahedra converted into Al(O)₄ tetrahedra after annealing, thereby exposing many more Al-coordinated sites. Generally, the observed peaks corresponded to the unincorporated Al phase, so that the amounts of Al phases could be further quantified (Section 1 in the Supporting Information) [30]. As shown in Fig. 4b, 19% of the Al content was incorporated into the ferrhydrite crystal lattice, and the remaining 81% was unincorporated Al phases containing the species Al(O)₆ and Al(O)₄ mixed with the 2-line ferrhydrite.

3.2. Adsorption experiments

3.2.1. Effect of annealing temperature and molar ratio of Al to Fe

The annealing temperature of the metal oxyhydroxides played a significant role in their F⁻ adsorption capacity. The F⁻ adsorption capacities for Fe-Al oxyhydroxides with various R_{AFA} annealed at 300, 400, 450, and 500 °C were investigated (Fig. 5). After annealing, the adsorption capacities of the hollow stuctures were greatly promoted; and for every R_{AFA} value, Fe-Al oxyhydroxides annealed at 450 °C exhibited higher F⁻ adsorption percentages than adsorbents annealed at other temperatures. For example, the F⁻ adsorption percentages of Fe-Al oxyhydroxide (R_{AFA} 1.20) increased from 3.57% to 53.65%, 84.26%, 96.12% and 33.17%, corresponding to 300, 400, 450, and 500 °C respectively. During the process of F⁻ adsorption, H₂O or OH⁻ as the ligands of Fe³⁺ and Al³⁺ negatively affected the removal efficiency due to the competition with F⁻ for metal cations. This can be ameliorated by removing the physically adsorbed water or dehydroxylation via an annealing procedure.

However, the replacement of the ligands tends to be difficult in highly crystalline Fe or Al oxides (high annealing temperature), which hampers the adsorption process as well [31].

Meanwhile, the effect of R_{AFA} on F⁻ adsorption efficiencies was investigated. The FeOOH hollow structure was the product of the template-engaged reaction between PB and NaOH (0.20 M) [23]. As shown in Fig. 5, the Fe-Al oxyhydroxides exhibited a considerably high adsorption capacity in contrast to pure hollow FeOOH; and Fe-Al oxyhydroxides annealed at 450 °C with R_{AFA} of 1.20 (FeAl-OOH MB) exhibited the highest F⁻ adsorption efficiency. In contrast to the 34.21% removal percentage of hollow FeOOH, the F⁻ removal percentage of FeAl-OOH MB reached 96.12% for an initial F⁻ concentration of 10 mg L⁻¹ at pH = 7.0 (with the adsorbent dosage of 0.4 g L⁻¹).

3.2.2. Adsorption kinetics

The adsorption kinetics of FeAl-OOH MB at various initial F⁻ concentration were investigated (Fig. 6a). When the initial F⁻ concentration was 5 or 10 mg L⁻¹, adsorption equilibrium was reached in 10 or 20 min, and followed pseudo-first-order kinetics; when the initial F⁻ concentration was at a high level, for example 30, 50 and 100 mg L⁻¹, adsorption equilibrium was achieved in 2 h, following pseudo-second-order kinetics (Table 1). Compared with the equilbrium time of other reported adsorbents [32-34], the F⁻ adsorption by FeAl-OOH MB was very fast. AIOOH, as the state-of-the-art flu- oride adsorbent, was herein selected as the basis for comparison [24]. The AIOOH particles were about 200 nm to 600 nm in size with irregular shape (Fig. S4), the adsorption kinetics of which followed the pseudo-second-order model. As shown in Fig. 6b, 15 min were needed to decrease the F⁻ concentration from 10 mg L⁻¹ to below 1 mg L⁻¹ by FeAl-OOH MB, while the same decrease required about 120 min in the presence of AIOOH under the same experimental conditions. The intra-particle diffusion model has been used to describe the kinetics of F⁻ adsorption on FeAl-OOH MB and AIOOH, and the model parameters obtained are listed in Table 1. The slopes of lines rose with the increase of initial F⁻ concentration, which could be explained by the heightened concentration gradient acting as the driving force of diffusion. The decrease in line slopes along with adsorption time occurred because of the weakened concentration gradient and reduced number of surface sites. The slope of the FeAl-OOH MB line was larger than the slope for AIOOH (Fig. S5), which suggested that the hollow and porous structure of FeAl-OOH MB was favorable for internal diffusion and promoted a faster adsorption rate.
Table 1
Adsorption kinetics parameters of FeAl-OOH MB and AlOOH for $F^-$.

| Adsorbent       | Initial $F^-$ concentration [mg L$^{-1}$] | Pseudo-first-order Model $q_t = q_e \frac{t}{t + \tau}$ | Pseudo-second-order Model $q_t = \frac{K_s q_e^2}{1 + K_s q_e t}$ | Intra-particle diffusion Model $q_t = k_d t^{0.5} + C$ |
|-----------------|------------------------------------------|--------------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
|                 |                                          | $k_1 \times 10^2$ [min$^{-1}$] | $q_e$ [mg g$^{-1}$] | $R^2$ | $k_2 \times 10^3$ [g mg$^{-1}$ min$^{-1}$] | $q_e$ [mg g$^{-1}$] | $R^2$ | $k_3$ [g mg$^{-1}$ min$^{-1}$] | $C$ | $R^2$ | $k_4$ [g mg$^{-1}$ min$^{-1}$] | $R^2$ |
| FeAl-OOH MB     | 5                                        | 29.66 | 11.67 | 0.998 | 34.09 | 12.52 | 0.978 | 5.35 | -2.55 | 0.998 | - | - |
|                 | 10                                       | 17.28 | 24.11 | 0.998 | 8.91 | 26.54 | 0.976 | 7.86 | -4.32 | 0.996 | - | - |
|                 | 30                                       | 5.20  | 55.71 | 0.993 | 0.96 | 67.01 | 0.997 | 8.73 | -4.63 | 0.999 | 2.83 | 0.890 |
|                 | 50                                       | 5.07  | 68.52 | 0.994 | 0.69 | 82.35 | 0.997 | 9.87 | -2.50 | 0.996 | 4.66 | 0.949 |
|                 | 100                                      | 5.52  | 77.99 | 0.978 | 0.72 | 91.99 | 0.993 | 11.01 | -0.36 | 0.991 | 6.10 | 0.952 |
| AlOOH           | 10                                       | 5.29  | 22.42 | 0.977 | 2.54 | 26.19 | 0.992 | 3.92 | -0.31 | 0.986 | - | - |

Note: $q_t$ and $q_e$ are adsorption quantity of $F^-$ at time ($t$) and equilibrium ($e$), k is the equilibrium rate constant, and C is the intercept of the fitting line in the intra-particle diffusion model.

![Fig. 6](image1.png)

(a) $F^-$ adsorption kinetics of FeAl-OOH MB at different initial $F^-$ concentration values at pH 7.0. Adsorbent dose, 0.4 g L$^{-1}$. (b) Comparison of adsorption kinetics between FeAl-OOH MB and AlOOH. The inset exhibits the change of $F^-$ concentration with time.

Fig. 6. $F^-$ adsorption kinetics of FeAl-OOH MB at different initial $F^-$ concentration values at pH 7.0. Adsorbent dose, 0.4 g L$^{-1}$. (b) Comparison of adsorption kinetics between FeAl-OOH MB and AlOOH. The inset exhibits the change of $F^-$ concentration with time. $F^-$ increase, which was related to the mechanism of $F^-$ adsorption by the metal oxyhydroxides. During the process of adsorption, metal oxyhydroxides first bonded with $H^+$, causing the surface of the material to be positively charged (Eqs. (2)–(3)). The $F^-$ anions were then attracted to the external surface via electrostatic attraction between the positive surface and $F^-$ anions [35,36]. Furthermore, low pH is conducive to driving the reaction to the right and accelerating the exchange of $F^-$ with $OH^-$ due to the neutralization effect of $H^+$.

$$MOX(OH)_{3-2x} + H^+ \rightarrow [MOX_{1-1}(OH)_{3-2x}]^+$$  

(2)

$$MOX(OH)_{3-2x} + H^+ \rightarrow [MOX(OH)_{2-2x}(H_2O)]^+$$  

(3)

3.2.4. Effect of coexisting anions

The effects of co-existing anions on $F^-$ adsorption were further investigated, including NO$_3^-$, Cl$^-$, SO$_4^{2-}$, HCO$_3^-$ and PO$_4^{3-}$ (Fig. 8). With the exception of PO$_4^{3-}$, the $F^-$ adsorption efficiencies of FeAl-OOH MB were more than 90.0% over a wide concentration range of ions, including NO$_3^-$, Cl$^-$, SO$_4^{2-}$ and HCO$_3^-$. However, the high negative charge of the phosphate anion led to strong attraction between PO$_4^{3-}$ and the positive surface of FeAl-OOH MB, resulting in a decrease in $F^-$ removal efficiency from 96.12% to 88.0% and 78.1% with the PO$_4^{3-}$ concentrations of 5 mg L$^{-1}$ and 20 mg L$^{-1}$, respectively [37].

3.2.5. Desorption and reuse

The desorption and reuse of FeAl-OOH MB at the initial $F^-$ concentration of 10 mg L$^{-1}$ were evaluated for five regeneration cycles, as presented in Fig. 9. The $F^-$ desorption efficiency, which equals the
Table 2
Comparison of \( F^- \) adsorption capacities of FeAl-OOH MB and reported metal-based materials.

| Adsorbents                      | \( Q_{\text{max}} \) [mg g\(^{-1}\)] | pH  | Temperature [K] | Reference       |
|--------------------------------|--------------------------------------|-----|----------------|----------------|
| FeAl-OOH MB                    | 145.84                               | 5.0 | 298            | This study      |
|                                | 109.59                               | 6.0 | 298            | This study      |
|                                | 85.74                                | 7.0 | 298            | This study      |
| 2 dimensional \( \text{Al}_2\text{O}_3 \) | 41.30                                |     | 298            | [41]           |
| Graphene oxide-incorporated Fe-Al mixed oxide | 22.90                                | 7.0 | 308            | [32]           |
| Al-humic acid-lanthanum        | 50.00                                | 7.0 | 298            | [42]           |
| Microporous Al-based material  | 50.00                                |     | 298            | [43]           |
| Porous polystyrene anion exchanger supported nano-sized hydrous zirconium oxide | 24.20                                | 7.0 | 298            | [44]           |
| Sulfate-doped \( \text{Fe}_2\text{O}_4/\text{Al}_2\text{O}_3 \) nanoparticles | 70.4                                 | 7.0 | 298            | [38]           |
| Basic Al sulfate and graphene hydrogel | 68.90                                | 7.0 | 298            | [45]           |
| Granular Zr-Fe oxide           | 23.33                                | 5.0 | 298            | [46]           |
| Fe(III)-Al (III)-Cr            | 31.89                                | 5.6 | 303            | [47]           |
| (III) ternary mixed oxide      |                                      |     |                |                |

Note: \( Q_c \) (mg g\(^{-1}\)) is the adsorption quantity of \( F^- \) at equilibrium, \( C_e \) (mg L\(^{-1}\)) is the concentration of \( F^- \) at equilibrium, \( Q_{\text{max}} \) (mg g\(^{-1}\)) is the maximum adsorption quantity of the adsorbent, and Langmuir constant \( L \) is indicative of the free energy of adsorption (mg g\(^{-1}\) min\(^{-1}\)). Freundlich constant \( F \) indicates the relative adsorption quantity of the adsorbent (mg g\(^{-1}\)), and \( 1/n \) is the adsorption intensity.

Table 3
Adsorption isotherms parameters of FeAl-OOH MB for \( F^- \).

| pH | \( Q_{\text{max}} \) [mg g\(^{-1}\)] | \( L \) [L mg\(^{-1}\)] | \( R^2 \) | \( F \) [mg g\(^{-1}\)] | \( 1/n \) | \( R^2 \) |
|----|--------------------------------------|--------------------------|----------|--------------------------|---------|----------|
|    | \( Q_c = (L \times C_c \times Q_{\text{max}})/(1 + L \times C_c) \) | \( Q_{\text{max}} \) \( = F \times C_c^1 \)\(n\) |
| 5  | 146.59                               | 0.05                     | 0.96     | 21.44                    | 0.38    | 0.99     |
| 6  | 109.59                               | 0.04                     | 0.97     | 14.74                    | 0.38    | 0.99     |
| 7  | 85.74                                | 0.02                     | 0.99     | 6.68                     | 0.46    | 0.99     |
| 8  | 73.01                                | 0.01                     | 0.99     | 3.61                     | 0.52    | 0.99     |

Fig. 8. Effect of co-existing anions (\( \text{NO}_3^- \), \( \text{Cl}^- \), \( \text{SO}_4^{2-} \), \( \text{HCO}_3^- \) and \( \text{PO}_4^{3-} \)) on \( F^- \) adsorption efficiency. Initial \( F^- \) concentration, 10.0 mg L\(^{-1}\); adsorbent dose, 0.4 g L\(^{-1}\).

3.3. Mechanism of \( F^- \) adsorption on FeAl-OOH MB

In order to uncover the adsorption mechanism on the surface of FeAl-OOH MB, XPS measurements for the adsorbents before and after \( F^- \) adsorption were performed. As shown in Fig. 10a, the appearance of new peaks in the Fe 1s region was attributed to the successful adsorption of \( F^- \) onto the surface of FeAl-OOH MB. Notably, the binding energies of the Al 2p and Fe 2p peaks tended to shift to higher values after adsorption as well, which was mainly due to the strong chemical interactions between F and the metallic sites (Fe or Al) (Fig. 10b) [38]. The peaks at 685.6 eV and 684.4 eV of Fe 1s were assigned to Al-F and Fe-F, and the content was calculated to be 71% and 29% respectively. In addition, as depicted in Table S1, the relative areas of Al-O-H (532.0 eV), Fe-O-H (531.3 eV) and Al-O-Al (530.2 eV) peaks of FeAl-OOH MB exhibited an obvious decrease after adsorption, which was mainly due to the exchange of \( F^- \) with the oxygen ligands (Fig. 10c,d) [39,40]. Thus, we concluded that Al-O-H, Fe-O-H and Al-O-Al were active sites for \( F^- \) adsorption on the surface of FeAl-OOH MB.

The adsorption process of FeAl-OOH MB for \( F^- \) followed a two-step protonation/ligand exchange reaction mechanism, which is demonstrated in Fig. 11a. The first step involved the protonation of \( O^{2-} \), thereby creating a positively charged surface to induce the diffusion of \( F^- \) from solution to the surface. In FeAl-OOH MB, the protonated \( O^{2-} \) sites were mainly Al-O-Al, Al-OH of Al(\( O_6 \)) and Al(OH)\(_4 \), and Fe-O-Fe of ferrihydrite. Next, the \( F^- \) tended to exchange with the OH\(^-\) or H\(_2\)O from coordination sites, and Al-F and Fe-F coordination bonds were finally achieved. Clearly, the first step of protonation was the rate-determining step for \( F^- \) adsorption. A highly positively charged surface could be achieved in the FeAl-OOH MB via the incorporation of Al into the Fe oxyhydroxide. This was related to the difference in relative electronegativity between Al and Fe. The electronegativity of Al is lower than that of Fe, whereby Al exhibits weaker attraction for electrons than Fe.
Thus, the electronegativity of O sites involving Al was higher than that of those involving Fe, and this was confirmed by natural population analysis of the charge of $[\text{Al(OH)}_6]^{3-}$ and $[\text{Fe(OH)}_6]^{3+}$ (Fig. S6). Moreover, cyclic voltammograms (CV) were then measured to evaluate the electronegativity of the Fe-based adsorbents (Fig. S7). Strikingly, the current density of the FeAl-OOH MB was larger than that of the pure ferrhydrite, indicating its low electronegativity due to the presence of Al. Generally, there is a negative correlation between the electronegativity and the extent of protonation (positive charge) on the surface of metal oxyhydroxides. The zeta potential demonstrated that the most positive surface was achieved in the FeAl-OOH MB sample with the $R_{\text{Al:Fe}}$ of 1.20 (Fig. 11b), which corresponded to the highest $F^-$ removal efficiency.

Additionally, the hollow and porous structure of FeAl-OOH MB was the other factor responsible for the high adsorption efficiency. The large specific surface area led FeAl-OOH MB to expose a great deal of reactive sites. The hollow and porous structure was extremely favorable for FeAl-OOH MB to achieve adequate contact with $F^-$, and extremely beneficial for transfer and diffusion of $F^-$ inside the material.

4. Conclusions

A novel hollow Fe-Al binary metal oxyhydroxide micro-box (FeAl-OOH MB) adsorbent for effective $F^-$ removal was successfully developed by annealing PB derivative Fe-Al hydroxides, which can overcome the limitations of fluoride adsorption technology via enhancing the protonation of oxygen on the surface of the material. With 19% of Al incorporated into the ferrhydrite crystal lattice, as well as an Al phase containing Al(O)$_4$ tetrahedra and Al(O)$_6$ octahedra in close proximity, the surface oxygen species were easily protonated, resulting in high surface charge (zeta potential) for hollow FeAl-OOH MB over a wide pH region.

The adsorption kinetics results indicated that the $F^-$ adsorption onto FeAl-OOH MB followed the pseudo-first-order kinetic model at low initial $F^-$ concentrations (5 and 10 mg L$^{-1}$), and followed the...
pseudo-second-order kinetic model at high initial F− concentrations (30, 50, and 100 mg L−1). Only 15 min was needed to decrease 10 mg L−1 of F− to below the standard limit (1 mg L−1), which could be attributed to the porous structure, beneficial for internal diffusion of F−. The optimal pH for F− adsorption was 5.0, and the maximum adsorption capacity was 146.59 mg g−1, outperforming many reported metal-based adsorbents. Co-existing anions (NO3−, Cl−, SO42− and HCO3−) other than PO43− did not inhibit F− adsorption, illustrating that FeAl-OOH MB had a high selectivity for F−. Furthermore, the adsorbed F− could be desorbed by 0.1 M NaOH, and the adsorption capacity achieved 94.38% after regeneration. Therefore the FeAl-OOH MB was demonstrated to be an effective, fast, highly selective adsorbent with stable reusability for practical aqueous defluorination. Moreover, the hollow structures with tunable physicochemical properties obtained by the sacrificial template method promise great potential for various applications, including catalysis and adsorption in water purification.

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Appendix A. Supplementary data
Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.colsurfa.2017.02.017.

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