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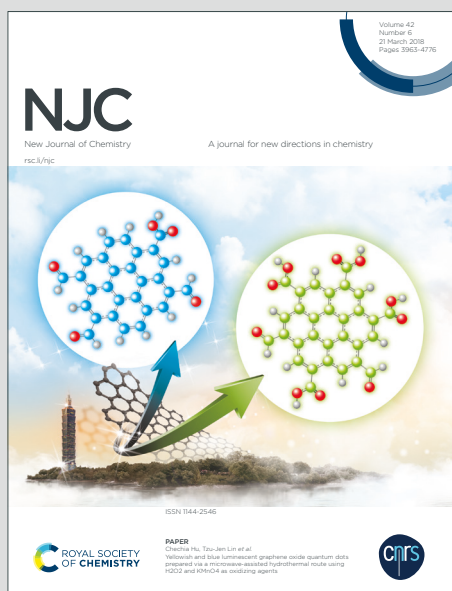
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Fe(III)-Modified Activated Alumina with Enhanced Fluoride Adsorption under Near-Neutral pH Conditions

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Abstract: The development of new adsorbents with improved fluoride adsorption capacities under realistic water conditions remains a major challenge for making groundwater potable. In this study, an Fe(III)-modified activated alumina (FMAA) was prepared via a wet-chemical treatment of commercially available activated alumina (AA), a widely used adsorbent for water defluoridation. Batch adsorption experiments were conducted by varying key parameters such as adsorbent dose, initial fluoride concentration, pH, and contact time to evaluate the performance of FMAA in comparison with AA. At an initial fluoride concentration of 10 mg/L and near-neutral pH, FMAA exhibited a higher fluoride adsorption capacity (2.63 mg/g) than AA (1.8 mg/g) under these conditions. Fluoride uptake on both materials was better described by the pseudo-second-order kinetic model. Isotherm analysis showed that adsorption on AA follows the Freundlich model, whereas FMAA is better described by the Langmuir model, consistent with a more uniform population of fluoride-binding sites after Fe(III) modification. The improved fluoride removal performance of FMAA is attributed to the presence of Fe(III)-containing surface sites and to a shift in the point of zero charge.

Keywords: Defluoridation; Adsorbent; Alumina; Surface modification; Water purification

1. Introduction

Groundwater, a major source of drinking water worldwide, is contaminated with excessive fluoride in many regions. Long-term consumption of fluoride-rich water can lead to dental and skeletal fluorosis [1-3], chronic and often disabling conditions that disproportionately affect low-income communities across the Global South. In India, for instance, fluoride concentrations as high as 48 mg/L have been reported in groundwater, and more than 60 million people are estimated to be at risk of fluorosis, with severe cases documented in Rajasthan, Andhra Pradesh, Bihar, and the Himalayan foothills [4]. Similar situations occur in East Africa, where the geochemistry of the Rift Valley results in extremely elevated groundwater fluoride levels reaching up to 2,800 mg/L in Kenya's Lake Nakuru, with Ethiopia, Kenya, Tanzania, Sudan, and Nigeria reporting widespread dental and skeletal fluorosis affecting millions of people [5]. In Latin America, high fluoride levels have been documented in the semiarid Northeast of Brazil [6], where groundwater concentrations reach 9.3 mg/L, and in low socioeconomic areas of Mexico [7], exposing vulnerable populations to both dental and skeletal fluorosis. Beyond fluoride alone, co-contamination with fluoride and arsenic poses a severe additional health threat in parts of the Bengal Basin in India and Bangladesh, where groundwater extraction from geogenic aquifers has created one of the world's most severe drinking-water crises [8-9]. These environmentally driven conditions remain pervasive, underdiagnosed, and chronically under-addressed due to limited resources and restricted access to safe water and treatment technologies.

Effective and safe treatment methods are therefore essential to reduce fluoride to acceptable levels. Electrocoagulation, ion exchange, adsorption, and reverse osmosis have all been extensively studied for the defluoridation of water [10-17]. Among these, adsorption-based defluoridation remains particularly attractive because of its simplicity, efficiency, and relatively low cost [18]. A

wide range of adsorbents, including activated alumina, activated carbons, zeolites, clays, biochar, and polymers, has been investigated for fluoride removal [19-26]. Activated alumina (AA) is considered one of the most promising adsorbents due to its strong affinity and selectivity toward fluoride, making it suitable for both community-level and household applications [27]. Its chemical stability, mechanical strength, and large-scale availability further support its widespread use [18]. Nonetheless, continued research is needed to improve its adsorption capacity and broaden its applicability.

In particular, chemical modification of AA has been widely explored to enhance fluoride uptake. For example, Kun You et al. reported that manganese oxyhydroxide-supported AA (MnOOH-AA) exhibits improved performance compared to pristine AA, with adsorption capacities reported in the range of ~6–10 mg/g under acidic conditions (pH 4–5) [28]. Similarly, manganese-oxide-coated activated alumina (MOCA) has been shown to enhance fluoride removal performance, with a maximum adsorption capacity of 2.85 mg/g compared to 1.08 mg/g for unmodified AA, and optimum fluoride removal occurring in the pH range of 4–7 [29]. These results demonstrate that surface modification can improve fluoride adsorption; however, the enhanced performance is often observed under mildly acidic conditions or optimized experimental settings, which may differ from typical groundwater conditions where pH is near neutral.

Commercial activated alumina beads are typically produced by partial dehydroxylation of boehmite (γ -AlOOH) or gibbsite ($\text{Al}(\text{OH})_3$), yielding a mixture of γ - Al_2O_3 and residual $\text{Al}(\text{OH})_3$ [30]. In most cases, γ - Al_2O_3 is the dominant phase, although the relative proportions of γ - Al_2O_3 and $\text{Al}(\text{OH})_3$ depend strongly on the calcination temperature and processing conditions [31-32]. The coexistence of these phases is advantageous because it facilitates gelation and structuring during bead formation. The shaped beads are then calcined at relatively low temperatures to

remove organic binders and pore-forming agents, producing the porous activated alumina beads that are commercially available [33]. In pristine AA, the surface is dominated by Al–O(H) groups involved in inner-sphere Al–O coordination. Under typical drinking-water conditions, fluoride adsorption is therefore often controlled by comparatively weaker outer-sphere interactions with these surface sites [34]. The point of zero charge (pH_{pzc}) of AA is generally in the mildly alkaline range, so that under near-neutral to slightly alkaline conditions a substantial fraction of the surface can become negatively charged, which reduces the electrostatic attraction toward fluoride. In this pH range, AA may also undergo partial dissolution, releasing Al^{3+} into solution. The dissolved Al^{3+} ions readily form stable fluoroaluminate complexes (e.g., AlF^{2+} , AlF_2^+ , $\text{AlF}_3(\text{aq})$), which compete with surface sites for fluoride, hinder its readsorption onto AA, and ultimately decrease the effective defluoridation capacity [35].

These limitations motivate the exploration of chemical modification strategies for AA that (i) promote inner-sphere fluoride binding, (ii) shift the point of zero charge toward near-neutral pH, and (iii) reduce Al^{3+} leaching. We hypothesize that modifying AA with $\text{Fe}(\text{OH})_3$ can help address these issues. $\text{Fe}(\text{OH})_3$ can form strong inner-sphere Fe–F bonds through ligand exchange, in which surface –OH groups are replaced by F^- . Unlike Al^{3+} species, Fe^{3+} and Fe–F surface complexes exhibit very low solubility under neutral water conditions [36]. Thus, $\text{Fe}(\text{OH})_3$ -modified AA is anticipated to diminish metal leaching and mitigate the formation of soluble fluoride–metal complexes. This view is consistent with the considerably higher solubility of AlF_3 (0.67 g per 100 mL at 20 °C) compared to FeF_3 (0.091 g per 100 mL), as reported elsewhere [37].

In light of these considerations, this work develops an $\text{Fe}(\text{OH})_3$ -modified activated alumina (FMAA) via a simple wet-chemical treatment and evaluates its defluoridation performance in comparison with pristine AA. Batch adsorption experiments under near-neutral pH conditions

show that FMAA achieves higher fluoride adsorption capacities than AA and suggest improved performance for practical groundwater treatment.

2. Methods

2.1. Preparation and structural characterization of adsorbents

FMAA was prepared from commercial AA beads (1–3 mm, Sorbead India Ltd.) using a wet-chemical treatment. To synthesize FMAA, 50 g of AA were immersed in 100 mL of an aqueous mixture containing 0.05 M iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and polyvinyl alcohol, and the suspension was stirred for 2 h. Before impregnation, the beads were gently washed with 1 M NH_4OH . The treated beads were then heated at 120 °C in a hot-air oven for 6 h. After cooling to room temperature, the beads were repeatedly washed with double-distilled water, dried again at 70 °C for 2 h, and finally allowed to cool naturally to room temperature. The average Fe loading was estimated to be approximately 4–5 wt% by comparing the dry weights of unmodified and modified beads prepared in three independent batches.

Fourier-transform infrared spectroscopy (FTIR; Midac Corporation, Irvine, USA, M2000), X-ray diffraction (XRD; PANalytical X'Pert Pro), scanning electron microscopy (SEM; JEOL JSM-7900F), and energy-dispersive X-ray spectroscopy (EDX) were used to characterize AA and FMAA before and after modification. The pH_{pzc} values of AA and FMAA were determined using the pH-drift method reported elsewhere [38].

2.2. Fluoride adsorption studies using both adsorbents

Batch fluoride adsorption experiments were performed to examine the effects of contact time, initial fluoride concentration, pH, adsorbent dose, and competing ions. All experiments were

conducted in 50 mL centrifuge tubes containing 30 mL of fluoride solution. Approximately 0.025 ± 0.0005 g of adsorbent (AA or FMAA) was added to each tube, and the suspensions were maintained at room temperature (25 °C) for the desired contact time.

To investigate the effect of adsorbent dose, the mass of AA (or FMAA) was varied from 0.025 g to 4 g in solutions with an initial fluoride concentration of 10 mg/L. The influence of pH was studied over the range ~4.0 to 10.01, and initial fluoride concentrations were varied between ~2 and 10 mg/L. Contact times ranged from 15 min to 24 h.

The fluoride adsorption capacity at time t , q_t (mg/g), was calculated using:

$$q_t = \frac{(C_i - C_f)V}{W_s} \quad (1)$$

where C_i and C_f (mg/L) are the initial and final fluoride concentrations, V (L) is the solution volume, and W_s (g) is the mass of adsorbent. Fluoride concentrations were measured using a Thermo Scientific Orion fluoride ion-selective electrode. The electrode was calibrated with standard fluoride solutions of 0.5, 1.0, 5.0, and 10 mg/L, and a total ionic strength adjustment buffer (TISAB III) was used to control pH and maintain a constant background ionic strength during all measurements.

3. Results and discussion

3.1. Characterization of activated alumina and FMAA

Figure 1a shows digital photographs of the AA and FMAA beads. A fractured bead (inset of Figure 1a) suggests that the Fe-containing layer is primarily localized near the outer region of the beads. The FTIR spectra of AA and FMAA are presented in Figure 1b. A broad band in the range 3200–

3600 cm^{-1} is attributed to the stretching vibrations of surface hydroxyl ($-\text{OH}$) groups, while the peak centered at 1647 cm^{-1} corresponds to the bending vibration of $\text{H}-\text{O}-\text{H}$ from adsorbed water molecules. The $\text{Al}-\text{O}-\text{H}$ bending vibration appears at 1359 cm^{-1} , and the band at 1074 cm^{-1} is assigned to $\text{Al}-\text{O}-\text{Al}$ asymmetric stretching. Peaks at 735 and 514 cm^{-1} are associated with $\text{Al}-\text{O}$ stretching in tetrahedral and octahedral sites, respectively [18]. FTIR bands from $\text{Fe}(\text{OH})_3$ often overlap with those of $\gamma\text{-Al}_2\text{O}_3$ because $\text{Fe}-\text{O}$ and $\text{Al}-\text{O}$ bonds have similar vibrational frequencies [39]. In particular, the $\text{Fe}-\text{O}$ stretching band near 520–550 cm^{-1} can coincide with the $\text{Al}-\text{O}$ vibration at $\sim 514 \text{ cm}^{-1}$, and surface hydroxyl groups ($\text{Fe}-\text{OH}$ and $\text{Al}-\text{OH}$) contribute overlapping features in the 1350–1400 cm^{-1} region, making it difficult to distinguish the two phases unambiguously by FTIR alone.

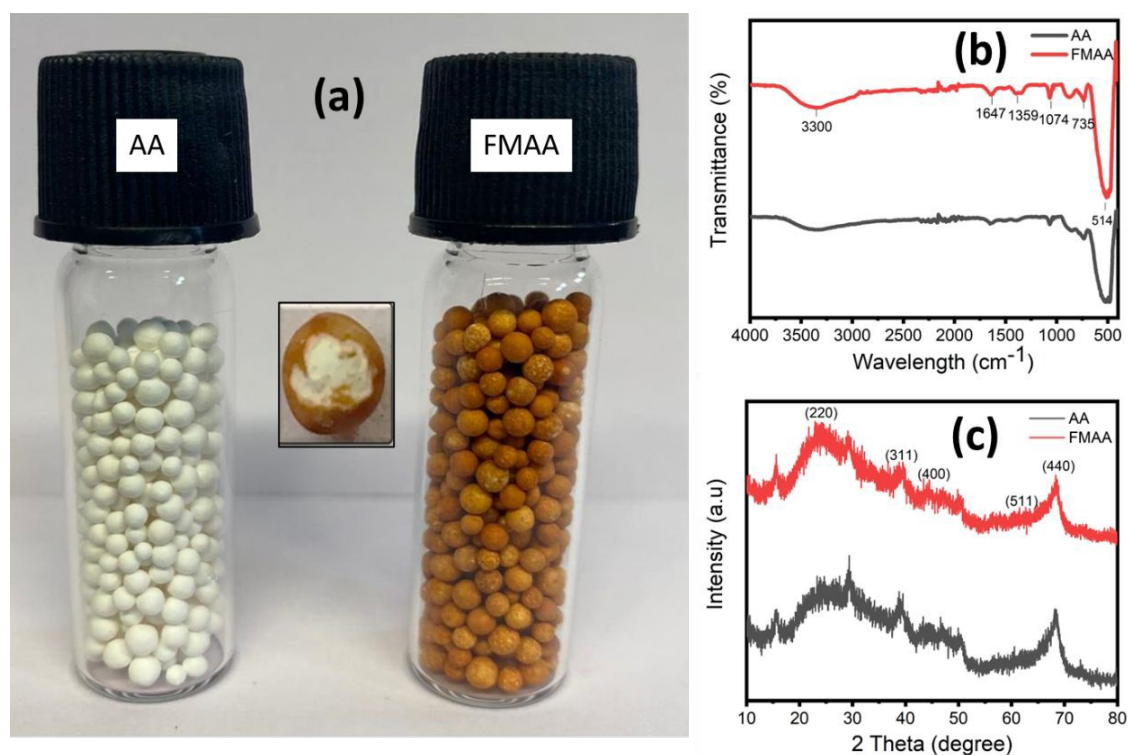


Figure 1. (a) Digital photographs of AA and FMAA beads, with an inset showing a fractured FMAA bead illustrating the surface-localized modification. (b) FTIR spectra of AA and FMAA. (c) XRD patterns of AA and FMAA.

Figure 1c shows the XRD patterns of the AA and FMAA samples. The presence of γ - Al_2O_3 in both adsorbents is confirmed by comparison with the standard JCPDS card 29-0063, with diffraction peaks corresponding to the (220), (311), (400), (511), and (440) planes of γ - Al_2O_3 [40]. Because FMAA was obtained by treating AA with dilute NH_3 , followed by impregnation with Fe(III), thorough washing, and low-temperature heat treatment ($\sim 120^\circ\text{C}$), Fe predominantly remains as a noncrystalline $\text{Fe}(\text{OH})_3$ phase at relatively low loading ($\approx 4\text{--}5\text{ wt}\%$). As a result, no additional crystalline peaks attributable to iron-containing phases are observed, and the overall XRD patterns of AA and FMAA remain similar, aside from a slight decrease in the γ - Al_2O_3 peak intensities for FMAA.

It is important to note that the iron species present in FMAA are not expected to form well-defined crystalline phases under the synthesis conditions employed. The use of aqueous $\text{Fe}(\text{NO}_3)_3$ followed by alkaline treatment promotes hydrolysis of Fe^{3+} ions, leading to the formation of amorphous Fe(III) hydroxide or oxyhydroxide species. The absence of characteristic crystalline iron oxide peaks in the XRD patterns supports this interpretation. Therefore, the iron phase in FMAA is more appropriately described as amorphous Fe(III) hydroxide/oxyhydroxide rather than a crystalline $\text{Fe}(\text{OH})_3$ phase.

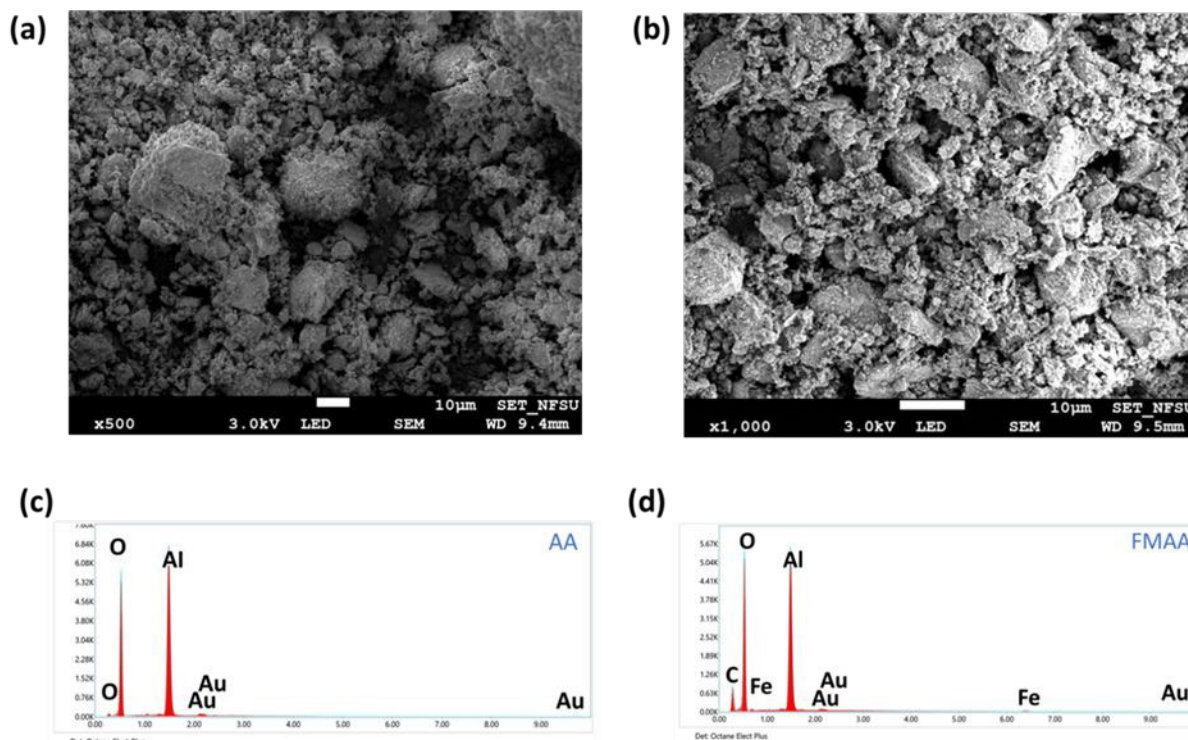


Figure 2. SEM images of (a) AA and (b) FMAA, and EDX spectra of (c) AA and (d) FMAA.

Figures 2a and 2b show SEM images of AA and FMAA powders obtained by crushing the respective beads. No significant differences in surface morphology can be identified between the two samples at this magnification. However, the EDX spectra collected during SEM imaging (Figures 2c and 2d) clearly reveal the presence of Fe in FMAA, confirming successful incorporation of iron species on the activated alumina.

3.2. Fluoride adsorption studies

Effect of pH. The pH_{pzc} values of AA and FMAA were determined to be 8.5 and 8.1, respectively (Figure 3a). The pH_{pzc} plays a critical role in controlling fluoride adsorption, as it determines the

surface charge of the adsorbent as a function of solution pH. When the solution pH is lower than the pH_{pzc} , the surface of the adsorbent becomes positively charged due to protonation of surface hydroxyl groups ($\equiv\text{M}-\text{OH}_2^+$, where $\text{M} = \text{Al}$ or Fe). Under these conditions, electrostatic attraction between the positively charged surface and negatively charged fluoride ions (F^-) enhances adsorption. Conversely, at pH values higher than the pH_{pzc} , the surface becomes negatively charged ($\equiv\text{M}-\text{O}^-$), leading to electrostatic repulsion and a decrease in fluoride uptake. Accordingly, the pH_{pzc} values of 8.5 and 8.1 indicate that both AA and FMAA retain a net positive surface charge under near-neutral conditions, which is favourable for fluoride adsorption. The slightly lower pH_{pzc} of FMAA suggests a modest shift in surface charge toward lower pH due to Fe(III) modification, which may contribute to improved adsorption performance under near-neutral conditions. In addition to electrostatic interactions, ligand exchange between surface hydroxyl groups and fluoride ions also plays an important role, particularly at Fe-OH sites, further enhancing fluoride adsorption. Therefore, the relationship between solution pH and pH_{pzc} is a key factor controlling fluoride adsorption, as it influences both electrostatic interactions and the availability of active surface sites.

To examine the influence of initial pH on fluoride adsorption, AA and FMAA were contacted with 10 mg/L fluoride solutions adjusted to pH 4, 7, or 10 at 25 °C. In each case, 0.025 g of adsorbent was added to 30 mL of solution, and the residual fluoride concentration was measured after 24 h. As shown in Figure 3b, the adsorption capacity of both materials decreases as the initial pH increases from 4 to 10. At pH 4.0, AA and FMAA exhibit maximum adsorption capacities of 1.90 mg/g and 2.70 mg/g, respectively. When the pH is increased to 7.0, these values decrease slightly to 1.80 mg/g for AA and 2.63 mg/g for FMAA, and at pH 10.0 the capacities reach their lowest values, 1.76 mg/g for AA and 2.52 mg/g for FMAA.

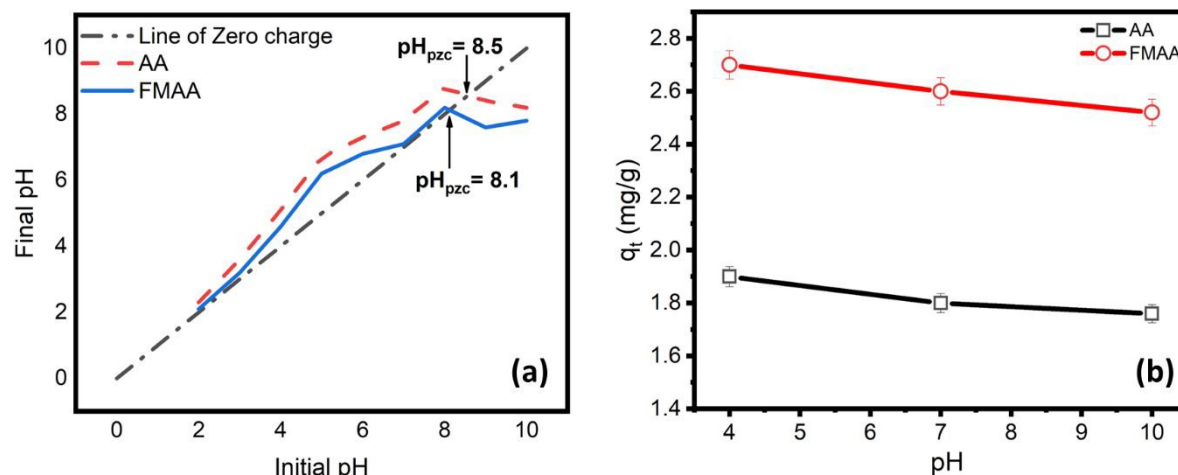


Figure 3. (a) pH_{pzc} of AA and FMAA. **(b)** Effect of initial pH on fluoride adsorption capacity of AA and FMAA (initial fluoride concentration = 10 mg/L, 25 °C, contact time = 24 h).

The adsorption capacity of activated alumina reported in the literature varies significantly (≈ 1 –25 mg/g), depending strongly on pH, initial fluoride concentration, and particle size. Under near-neutral pH and low fluoride concentration (around 10 mg/L), AA typically exhibits capacities on the order of 1–3 mg/g, consistent with the value observed in this study (1.8 mg/g) and with reports such as Mondal et al. [41], who measured 1.2 mg/g under comparable conditions. This agreement indicates that the performance of the AA used here is representative of commercial materials operating under realistic groundwater conditions and provides a reliable baseline for assessing the improvement achieved with FMAA.

Effect of adsorbent dose. The effect of adsorbent dosage (0.025–4 g per 30 mL) on the adsorption capacities of AA and FMAA at an initial fluoride concentration of 10 mg/L, initial pH 7, a contact time of 24 h, and 25 °C is shown in Figure 4. As the adsorbent dose increases, the fluoride adsorption capacity (mg/g) of both materials decreases. This decrease, which reflects the amount of fluoride adsorbed per unit mass of adsorbent, arises from the lower ratio of fluoride ions to

available surface sites at higher dosages and the consequent underutilization of the adsorbent. Although higher dosages generally lead to greater overall fluoride removal, they require more material to achieve a comparable treatment effect and are therefore less mass-efficient and less attractive from a cost and sustainability standpoint.

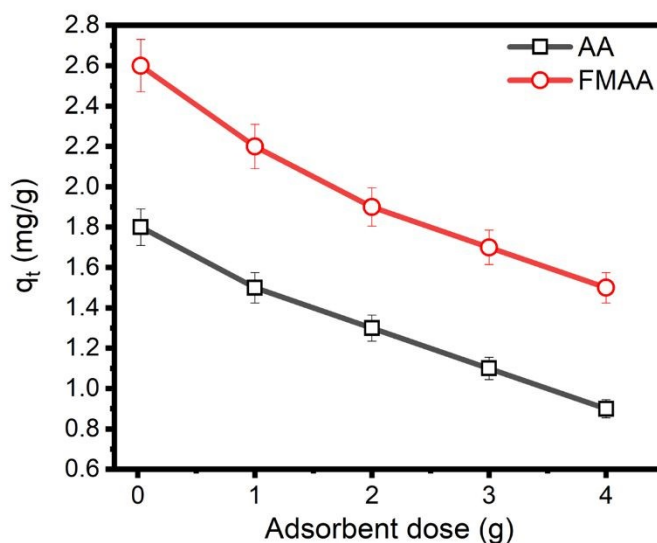


Figure 4. Effect of adsorbent dose (0.025–4 g per 30 mL) on the fluoride adsorption capacity of AA and FMAA (initial fluoride concentration = 10 mg/L, pH 7, contact time = 24 h, 25 °C).

Effect of fluoride concentration and contact time. Figures 5a and 5b show the influence of contact time on the fluoride adsorption capacity of AA and FMAA at different initial fluoride concentrations. For both adsorbents, the adsorption capacity increases with contact time, with a rapid uptake during the first 60 min when a large number of surface sites are still available to accommodate F^- ions. At all concentrations studied, FMAA exhibits higher capacities than AA. The adsorption capacity also increases with increasing initial fluoride concentration, reflecting the stronger driving force for mass transfer at higher F^- levels. A direct comparison of the equilibrium capacities of AA and FMAA at different initial concentrations is presented in Figure 5c. At an

initial fluoride concentration of 10 mg/L, the maximum equilibrium adsorption capacities are 1.8 mg/g for AA and 2.63 mg/g for FMAA.

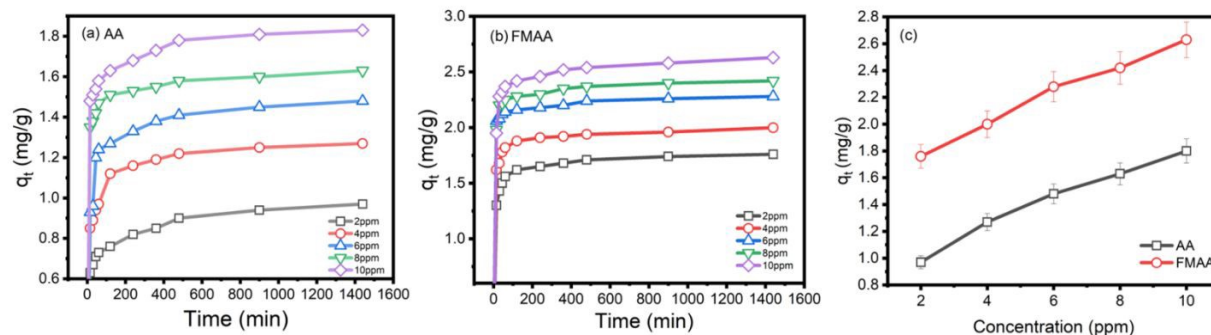


Figure 5. Effect of contact time and initial fluoride concentration (2–10 mg/L) on adsorption capacity for (a) AA and (b) FMAA (contact time up to 1440 min = 24 h). (c) Comparison of equilibrium fluoride adsorption capacities of AA and FMAA as a function of initial fluoride concentration.

Effect of co-existing ions on fluoride adsorption. In most natural waters, fluoride is accompanied by other anions that can potentially interfere with adsorption-based defluoridation. To assess these effects, a separate set of batch experiments was performed to examine how common coexisting anions (Cl^- , NO_3^- , SO_4^{2-} , HCO_3^- , and PO_4^{3-}) influence fluoride uptake by AA and FMAA. As shown in Figures 6a and 6b, the equilibrium fluoride adsorption capacities of AA and FMAA were measured in the presence of each anion at concentrations between 10 and 500 mg/L (10, 20, 50, 100, 250, and 500 mg/L), while the initial fluoride concentration was kept constant at 10 mg/L. The temperature (25 °C) and contact time (24 h) were held constant for all experiments. For both adsorbents, Cl^- , NO_3^- , and PO_4^{3-} exert only a minor influence on fluoride adsorption over the entire concentration range tested. In contrast, HCO_3^- and SO_4^{2-} significantly reduce the fluoride adsorption capacity when present at high concentrations (>100 mg/L). This decrease in fluoride

removal may arise from pH changes induced by these anions and/or direct competition with fluoride for active adsorption sites [42].

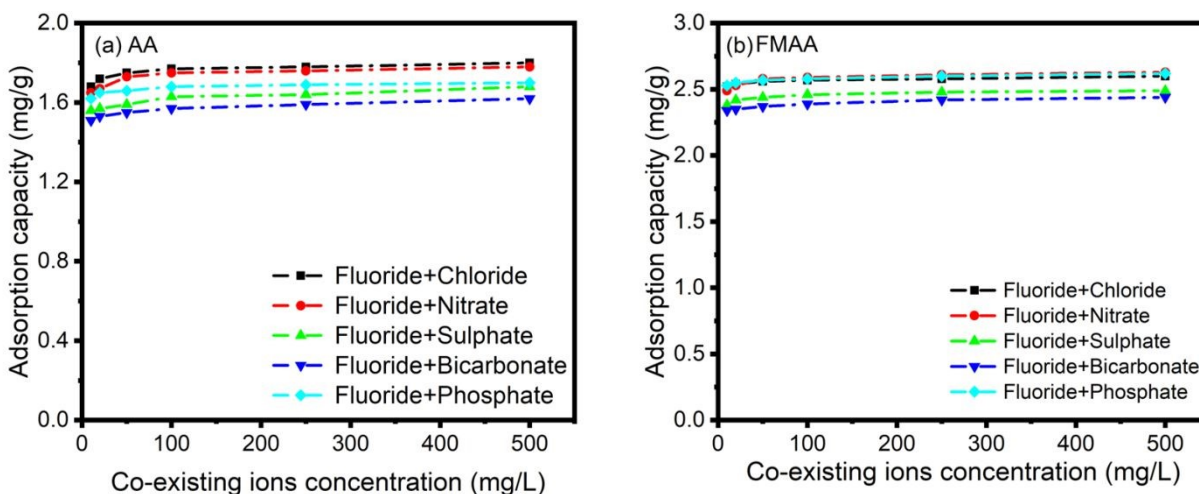


Figure 6. Effects of coexisting anions on fluoride adsorption by (a) AA and (b) FMAA. Initial fluoride concentration = 10 mg/L; co-ion concentrations = 10–500 mg/L; contact time = 24 h; temperature = 25 °C.

The results discussed above show that FMAA adsorbs fluoride more efficiently than AA under the conditions studied. A schematic representation of the proposed mechanism is provided in Figure 7. As illustrated there, the modification of AA is envisaged to produce an $\text{Fe}(\text{OH})_3$ -rich coating on the bead surface, which can offer several advantages for fluoride removal. First, $\text{Fe}(\text{III})$ -containing sites can form strong inner-sphere complexes with fluoride ions. Second, the modification shifts the point of zero charge slightly toward near-neutral pH, which can enhance electrostatic attraction under typical groundwater conditions. Third, the presence of the $\text{Fe}(\text{OH})_3$ layer is expected to limit direct exposure of the alumina surface to solution, thereby helping to reduce Al^{3+} release and the formation of soluble Al-F complexes. Taken together, these effects provide a plausible explanation for the higher and more stable fluoride adsorption capacity observed for FMAA.

The enhanced fluoride adsorption observed for FMAA compared to pristine AA can be attributed to the synergistic interaction between Al–OH and Fe–OH surface sites. In pristine activated alumina, fluoride adsorption primarily occurs through interactions with surface hydroxyl groups (Al–OH), which may involve electrostatic attraction and limited ligand exchange. However, under near-neutral conditions, the surface of AA becomes less positively charged, reducing its affinity for fluoride. Upon Fe(III) modification, additional Fe–OH sites are introduced on the surface, which exhibit a stronger affinity for fluoride ions due to their ability to form inner-sphere complexes through ligand exchange reactions. In this process, surface hydroxyl groups are replaced by fluoride ions, forming stable Fe–F bonds:



At the same time, Al–OH sites continue to contribute to adsorption, although with comparatively weaker interactions. The coexistence of Fe–OH and Al–OH functional groups increases the overall density of active sites and provides multiple binding environments for fluoride ions.

In addition, Fe(III) modification slightly shifts the point of zero charge toward lower pH, enhancing electrostatic attraction under near-neutral conditions. The presence of Fe(III) species also helps reduce Al^{3+} leaching and the formation of soluble fluoroaluminate complexes, thereby improving the effective adsorption capacity. Therefore, the improved performance of FMAA can be attributed to a combination of stronger inner-sphere complexation at Fe sites, continued contribution from Al sites, and favourable surface charge characteristics, resulting in a synergistic enhancement of fluoride adsorption.

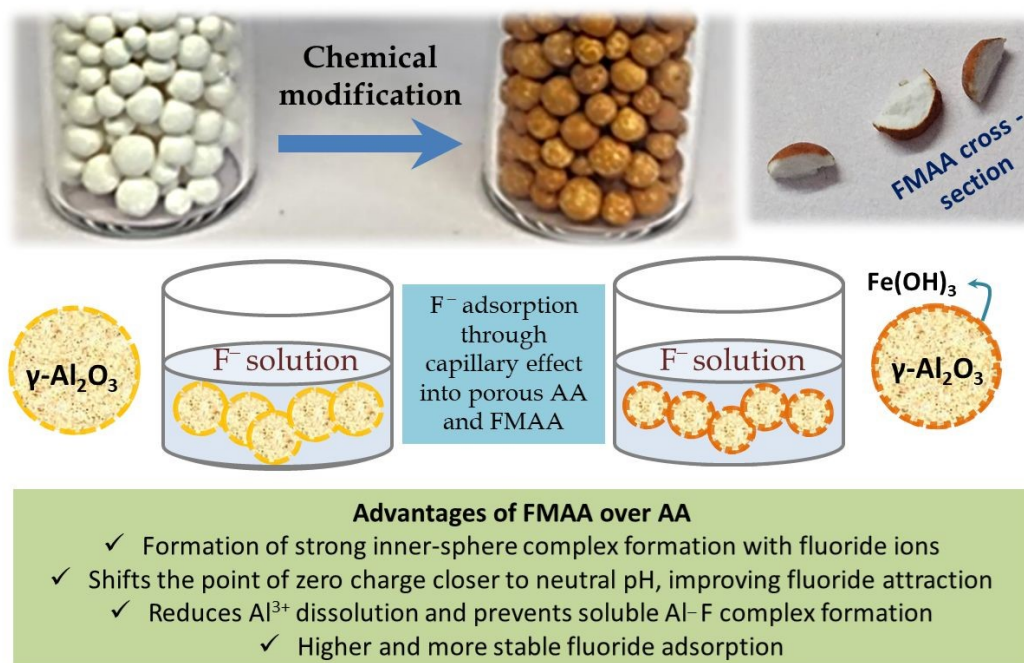


Figure 7. Schematic illustration of the proposed mechanisms by which $\text{Fe}(\text{OH})_3$ modification enhances the fluoride adsorption capacity of activated alumina.

Kinetics of fluoride adsorption on AA and FMAA. The time-dependent fluoride adsorption capacities of AA and FMAA at different initial fluoride concentrations (2–10 mg/L) are shown in Figures 5a and 5b, respectively. The adsorption capacities measured at 24 h for each concentration were taken as the corresponding equilibrium adsorption capacities, q_e .

The pseudo-first-order and pseudo-second-order kinetic models were analyzed using the following integral forms [43]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

Equation (4) can be rearranged to the linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where q_e is the equilibrium adsorption capacity (mg/g), q_t is the adsorption capacity at time t (mg/g), and k_1 and k_2 are the rate constants for the pseudo-first-order and pseudo-second-order models, respectively. To evaluate the pseudo-first-order model, linear fits of $\ln(q_e - q_t)$ versus t were constructed for different initial fluoride concentrations, as shown in Figures 8a and 8b for AA and FMAA, respectively. The corresponding pseudo-second-order plots of t/q_t versus t are presented in Figures 8c and 8d.

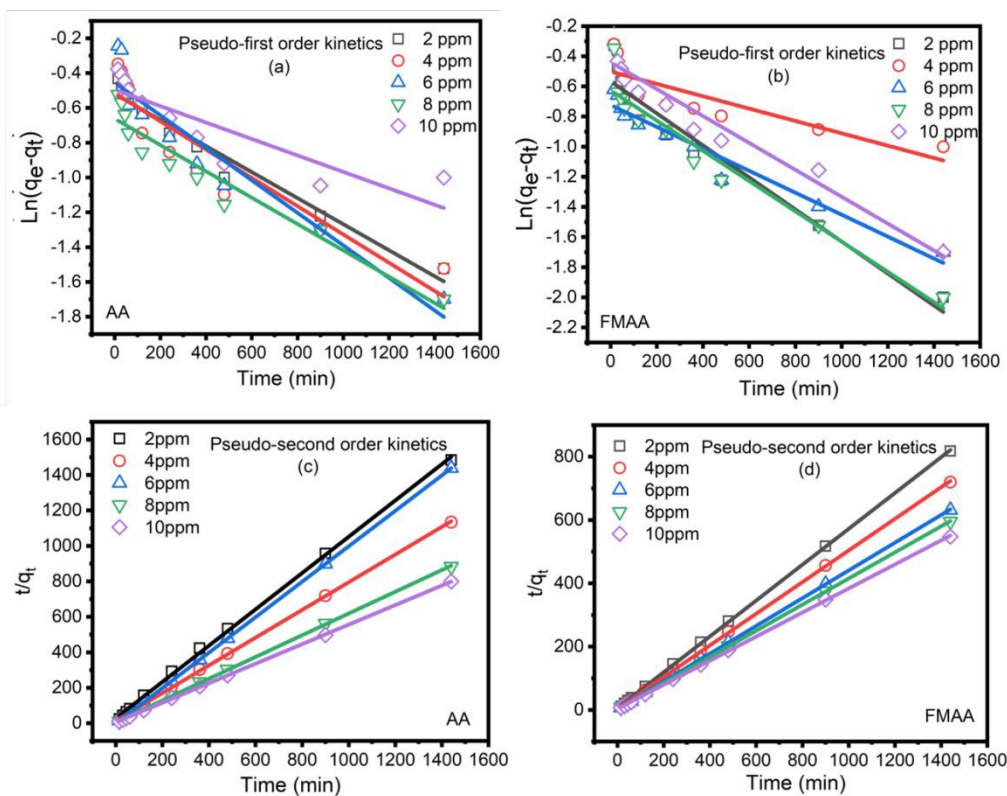


Figure 8. Pseudo-first-order kinetic fits for fluoride adsorption on (a) AA and (b) FMAA, and pseudo-second-order kinetic fits for fluoride adsorption on (c) AA and (d) FMAA. Contact time up to 1440 min = 24 h.

Figures 8c and 8d show the pseudo-second-order kinetic plots (t/q_t vs. t) for fluoride adsorption on AA and FMAA at different initial concentrations. The kinetic parameters obtained from the linear fits of the pseudo-first-order and pseudo-second-order models for AA and FMAA are summarized in Table 1 and Table 2, respectively.

Table 1. Kinetic parameters obtained from the pseudo-first-order model for fluoride adsorption on AA and FMAA at different initial fluoride concentrations. Here, q_e is the equilibrium adsorption capacity, k_1 is the pseudo-first-order rate constant, Adj. R^2 is the adjusted coefficient of determination, and R^2 (COD) is the coefficient of determination obtained from the linear regression fits.

Fluoride concentration (mg/L)	AA				FMAA			
	q_e (mg/g)	k_1 (min ⁻¹)	Adj. R^2	R^2 (COD)	q_e (mg/g)	k_1 (min ⁻¹)	Adj. R^2	R^2 (COD)
2	0.5950	0.0017	0.9621	0.9663	0.568	0.0024	0.9275	0.9355
4	0.5981	0.0018	0.8486	0.8654	0.606	0.0009	0.7211	0.7521
6	0.6347	0.0021	0.9018	0.9127	0.485	0.0016	0.9462	0.9522
8	0.5162	0.0017	0.9228	0.9313	0.534	0.0023	0.9321	0.9396
10	0.6099	0.0010	0.7400	0.7689	0.645	0.0020	0.9083	0.9184

Table 1. Kinetic parameters obtained from the pseudo-second-order model for fluoride adsorption on AA and FMAA at different initial fluoride concentrations. Here, q_e is the equilibrium adsorption capacity, k_2 is the pseudo-second-order rate constant, Adj. R^2 is the adjusted coefficient of determination, and R^2 (COD) is the coefficient of determination obtained from the linear regression fits.

Fluoride concentration (mg L ⁻¹)	AA				FMAA			
	<i>q_e</i> (mg/g)	<i>k₂</i> (min ⁻¹)	Adj. R ²	R ² (COD)	<i>q_e</i> (mg/g)	<i>k₂</i> (min ⁻¹)	Adj. R ²	R ² (COD)
2	0.9768	0.0366	0.9986	0.9988	1.7661	0.0519	0.9998	0.9998
4	1.2798	0.0430	0.9998	0.9998	2.0016	0.0573	0.9998	0.9998
6	1.0003	0.8653	1	1	2.2818	0.0728	0.9999	0.9999
8	1.6308	0.0615	0.9997	0.99981	2.4241	0.0592	0.9999	0.9999
10	1.8144	0.0551	0.9998	0.99986	2.6315	0.0373	0.9997	0.9998

When the model fits are compared with the experimental data, the pseudo-second-order model provides a markedly better description of fluoride adsorption on both AA and FMAA than the pseudo-first-order model. In particular, there is close agreement between the experimental equilibrium capacities *q_e* and the values calculated from the pseudo-second-order fits. By contrast, the pseudo-first-order model reproduces the data less accurately for both adsorbents. These observations are consistent with a rate-limiting step that involves chemisorption or valence forces between fluoride ions and surface sites on AA and FMAA.

The better agreement of the experimental data with the pseudo-second-order kinetic model for both AA and FMAA indicates that fluoride adsorption is primarily controlled by chemisorption processes. In this mechanism, fluoride ions interact strongly with surface hydroxyl groups (≡M–OH, where M = Al or Fe) through ligand exchange reactions, forming inner-sphere surface complexes:



Such interactions involve valence forces or electron sharing between the adsorbent surface and the fluoride ions, which are characteristic of chemisorption. The pseudo-second-order model assumes that the adsorption rate depends on the availability of active sites and is therefore well suited to describe adsorption processes controlled by surface chemical reactions. In addition, the close agreement between the experimentally observed and calculated equilibrium adsorption capacities further supports the applicability of the pseudo-second-order model. These results suggest that fluoride adsorption on both AA and FMAA is dominated by surface chemical interactions rather than purely diffusion-controlled physical adsorption.

Isotherm studies for fluoride adsorption on AA and FMAA. To further interpret the equilibrium adsorption behavior of AA and FMAA, the fluoride uptake data obtained at 25 °C were analyzed using common adsorption isotherm models. Figure 9a shows the variation of the equilibrium adsorption capacity (q_e) as a function of the equilibrium fluoride concentration (C_e). These data were fitted with the Langmuir and Freundlich isotherms, which are widely used to describe adsorption on solid surfaces [44]. The Langmuir model assumes monolayer adsorption on a surface with energetically uniform binding sites and is expressed in linear form as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (7)$$

whereas the Freundlich model is an empirical relationship that accounts for adsorption on heterogeneous surfaces and is given by:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (8)$$

where Q_0 is the Langmuir monolayer adsorption capacity, b is the Langmuir affinity constant, and K_f and n are the Freundlich constants related to adsorption capacity and surface heterogeneity, respectively. The corresponding Langmuir and Freundlich plots for fluoride adsorption on AA and FMAA are presented in Figures 9b and 9c.

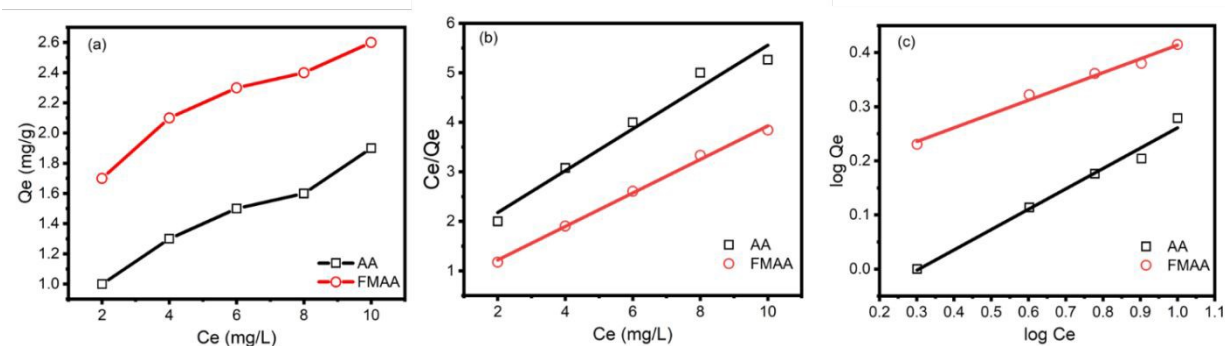


Figure 9. (a) Fluoride adsorption isotherms for AA and FMAA at 25 °C. (b) Langmuir plots for fluoride adsorption on AA and FMAA. (c) Freundlich plots for fluoride adsorption on AA and FMAA.

Isotherm analysis (Table 3) shows that both Langmuir and Freundlich models provide good fits for the fluoride adsorption data, but the preferred model differs between the two adsorbents. For pristine AA, the Freundlich model yields the higher adjusted R^2 value (0.977), indicating adsorption on a heterogeneous surface with a broad distribution of binding sites. In contrast, for FMAA, the Langmuir model provides the best fit (adjusted $R^2 = 0.995$), slightly outperforming the Freundlich model (0.985). This suggests that Fe(III) modification produces a more uniform set of adsorption sites, consistent with a more homogeneous Fe–OH surface layer.

Table 3. Linear isotherm fitting parameters for fluoride adsorption on AA and FMAA.

Langmuir	Intercept	Slope	Statistics
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	Value	Error	Value	Error	Adj. R ²
C_e/q_e (AA)	1.3332	0.28487	0.42247	0.04295	0.95991
C_e/q_e (FMAA)	0.5435	0.0781	0.3384	0.01177	0.99517
Freundlich	Intercept		Slope		Statistics
	Value	Error	Value	Error	Adj. R ²
$\log q_e$ (AA)	-0.11515	0.02165	0.37626	0.02855	0.97736
$\log q_e$ (FMAA)	0.15924	0.01187	0.25482	0.01565	0.98508

For the Langmuir model, the intercept and slope of the C_e/q_e vs. (C_e) plots correspond to $1/Q_0b$ and $1/Q_0$, respectively. For the Freundlich model, the intercept and slope of the $\log q_e$ vs. $\log C_e$ plots correspond to $\log K_f$ and $1/n$, respectively. Adj. R² denotes the adjusted coefficient of determination for each linear fit. The Freundlich slopes ($1/n$) are 0.38 for AA and 0.25 for FMAA, confirming that adsorption is favourable in both cases ($0 < 1/n < 1$). The lower $1/n$ value for FMAA reflects a stronger affinity toward fluoride and a narrower distribution of site energies relative to unmodified AA. Langmuir parameters also support this trend: FMAA exhibits a higher monolayer adsorption capacity and affinity constant than AA. Collectively, these results indicate that Fe(III) modification enhances both the strength and uniformity of fluoride-binding sites on activated alumina, which aligns with the higher adsorption capacities observed for FMAA.

To further evaluate the performance of the developed adsorbent, FMAA was compared with a range of reported materials used for fluoride removal, including alumina-based adsorbents and other metal oxide systems. As shown in Table 4, several adsorbents exhibit higher maximum adsorption capacities; however, these values are typically obtained under optimized conditions

such as acidic pH and elevated fluoride concentrations, which enhance adsorption driving forces. In contrast, the adsorption performance of FMAA was evaluated under near-neutral pH and relatively low initial fluoride concentration (~10 mg/L), conditions that are more representative of natural groundwater systems. Under these conditions, FMAA achieves an adsorption capacity of 2.63 mg/g, which is comparable to or better than several reported adsorbents tested under similar conditions. Furthermore, the simple preparation method and use of commercially available activated alumina make FMAA a practical and scalable option for defluoridation applications. Therefore, while direct comparison of adsorption capacities must consider differences in experimental conditions, the present results demonstrate that Fe(III)-modified activated alumina offers a favorable balance between performance and practical applicability.

Table 4. Comparison of fluoride adsorption capacities of alumina-based and related adsorbents.

Adsorbent	Maximum adsorption capacity (mg/g)	pH	Initial F ⁻ concentration (mg/L)	Reference
MnOOH-AA	~6–10	4–5	>20	[28]
Activated Alumina (AA)	1.08	4–7	~10	[29]
Manganese-oxide-coated alumina (MOCA)	2.85	4–7	~10	[29]
Fe(III)–Al mixed oxide	3–15	<6	>20	[45]
Activated Alumina (AA)	~1–3	~7	~10	[46]
AA	1.8	~7	10	This work
FMAA	2.63	~7	10	This work

Although the increase in adsorption capacity from 1.8 mg/g for AA to 2.63 mg/g for FMAA may appear moderate, it is important to consider the operating conditions under which these values were obtained. The present study was conducted at near-neutral pH and relatively low initial fluoride concentration (~10 mg/L), conditions that closely resemble natural groundwater systems. Under such conditions, the adsorption capacity of activated alumina is typically limited to approximately 1–3 mg/g, as reported in the literature. Therefore, the observed increase corresponds to an improvement of approximately 46%, which is significant within this realistic operating range.

In contrast, many studies reporting higher adsorption capacities employ acidic pH and/or elevated fluoride concentrations, which enhance adsorption driving forces but may not reflect practical water treatment scenarios. In addition, the Fe(III) modification used in this work involves a simple wet-chemical treatment of commercially available activated alumina, making the approach cost-effective and scalable. These factors collectively highlight the practical relevance of the observed improvement.

4. Conclusions

In summary, this study reports the preparation of a Fe(III)-modified activated alumina (FMAA), in which iron is present predominantly as amorphous Fe(III) hydroxide/oxyhydroxide species resembling $\text{Fe}(\text{OH})_3$, obtained through a simple wet-chemical treatment of commercially available activated alumina (AA) beads. Fluoride adsorption on AA and FMAA was evaluated as a function of adsorbent dose, initial fluoride concentration, contact time, solution pH, and coexisting ions. Both adsorbents exhibited their highest fluoride uptake at acidic pH (~4), consistent with electrostatic attraction below their points of zero charge. At near-neutral pH, FMAA achieved a

higher adsorption capacity (2.63 mg/g) than AA (1.8 mg/g). Adsorption capacity (mg/g) decreased with increasing adsorbent dosage, reflecting reduced utilization of adsorption sites, while higher initial fluoride concentrations (2–10 mg/L) increased the measured capacities. Fluoride uptake was rapid during the first 60 min and approached equilibrium within approximately 240 min. Most common coexisting ions (Cl^- , NO_3^- , PO_4^{3-}) had minimal impact on fluoride removal, whereas high concentrations of HCO_3^- and SO_4^{2-} reduced adsorption for both materials. Kinetic analysis showed that the pseudo-second-order model provides the best fit for both AA and FMAA, consistent with a rate-limiting step involving surface interaction or chemisorption. Isotherm analysis revealed that AA is better described by the Freundlich model, indicating adsorption on heterogeneous surface sites, while FMAA fits the Langmuir model more closely, suggesting the formation of a more uniform population of fluoride-binding sites following Fe(III) modification. Present findings indicate that $\text{Fe}(\text{OH})_3$ modification enhances fluoride adsorption by increasing the density of favorable binding sites, shifting the point of zero charge toward near-neutral pH, and reducing Al^{3+} release.

Credit to Authorship:

Vaishali Chauhan: Experiment design and performing; Methodology; Investigation; Data collection; Formal analysis; Writing-original draft; Review & editing. **Felipe Fantuzzi:** Formal analysis; Investigation; Writing-original draft; Data analysis; Review & editing. **Anirban Das:** Experiment design; Funding acquisition; Project administration; Supervision, Resources, editing; **Kalisadhan Mukherjee:** Experiment design; Data analysis; Funding acquisition; Project administration; Supervision, Resources, Writing-review & editing.

Statement of Conflict of Interest:

There are no conflicts to declare.

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Data availability statement

The data in the form of figures and tables are provided in the manuscript