Simultaneous removal of fluoride, manganese and iron by manganese oxide supported activated alumina: characterization and optimization via response surface methodology

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ABSTRACT

Fluoride, iron and manganese simultaneous exceedance of standard can be observed in groundwater in northeastern China. This work aims to apply a highly efficient method combining adsorption and oxidation for the synchronous removal of the inorganic ions. An innovative adsorbent (manganese-supported activated alumina) was synthesized by the impregnation method and showed a significant adsorption capacity better than that of fresh activated alumina. The characterization (scanning electron microscope; Brunauer, Emmett and Teller; X-ray diffraction and Fourier transform infrared spectroscopy) results verified the successful introduction of MnOOH and MnO\textsubscript{2}, and the improvement of surface microstructure enhanced the removal ability. The effect of single factors, such as pH value, reaction time or dosage on the removal performance has been verified. The maximum removal efficiencies of fluoride, iron and manganese were optimized via Response surface methodology considering the independent factors in the range of MO@AA dosage (5–9 g/L), pH (4–6) and contact time (4–12 h). Noted that compared with control, MO@AA exhibited 59.4\% of improved fluoride performance. At pH of 5.79, contacting time of 12 h and 8.21 g/L of MO@AA, fluoride, iron and manganese removal were found to be 91, 100 and 23\%, respectively. Herein, MO@AA was distinguished as good applicability for the treatment of fluoride-, iron- and manganese-containing groundwater.

Key words: activated alumina, adsorption, oxidation, response surface methodology

HIGHLIGHTS

- The modified activated alumina were prepared by impregnation method.
- Response surface methodology model is used in this research to find out the relationships among the factors.
- The modified activated alumina can be applied for the removal of fluoride, manganese and iron.

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1. INTRODUCTION

Groundwater, utilized as a main drinking water resource in China, suffers from simultaneous exceedances of iron, manganese, and fluoride standards, especially in northeastern China (Xilin et al. 2021). Excessive intake of fluoride ions (>0.08 mmol/L) can threaten human health for example in fluorosis (Yadav et al. 2019; Chen et al. 2021). Exposure to high-manganese and high-iron media can result in damage to body organs (Khatri et al. 2017; Yang et al. 2019). In addition, excess iron ions can be deposited in the transport pipeline which may result in operational problems (Yang et al. 2021). Nevertheless, few researchers have studied the simultaneous removal of the pollutants mentioned. Therefore there is an urgent need to develop techniques for simultaneous removal of fluoride, manganese and iron contaminants.

Technologies such as ion exchange (Li et al. 2016), coagulation, adsorption (Boubakri et al. 2014) and membrane separation (Dhawane et al. 2018) have been developed for the defluoridation process. Methods including oxidation (Yang et al. 2021), flocculation, ion exchange (Virolainen et al. 2021), adsorption (Rudi et al. 2020), and membrane filtration (Tang et al. 2020) have been applied to eliminate the presence of manganese ions. Iron removal approaches are mainly oxidation, ion exchange (Virolainen et al. 2021), membrane (Tang et al. 2020) and adsorption (Ahmed et al. 2021; Ma et al. 2021) methods. By comparing the main advantages and shortcomings (Table 1) (Khatri et al. 2017; Kimambo et al. 2019), no single technique is considered perfect. Adsorption methods, which are recognized as an environmental-friendly and sustainable way to remove contaminants from high fluoride distributed area, can prevent secondary pollutants forming (Yu et al. 2020). Many adsorbents (porous carbon, chitosan, zeolite, activated alumina) have been used for contaminants reduction (Mandal & Mayadevi 2008). Although the good performance of adsorption ability has been shown (Table 2) (Tahir & Rauf 2004; Taffarel & Rubio 2009; Thakre et al. 2010; Modin et al. 2011; Zhang et al. 2011; Shavandi et al. 2012; Khobragade & Pal 2014; Al-Wakeel et al. 2015; Elwakeel et al. 2015; Mudzielwana et al. 2017; Singh et al. 2018), their shortcomings are inevitable. Here, attempts have been made to modify the adsorbent to improve adsorption capacity. MnOOH exhibited a large specific surface area, which can provide more active sites for the reaction. MnO₂ showed an excellent oxidation performance in the removal of manganese ions (Yang et al. 2021). Based on that, the manganese-supported AA was tested for fluoride removal.

Response surface methodology is an experimental statistical method to investigate the functional relationship between explanatory variables and response values by determining a regression model (Fakhri 2014; Gao et al. 2020). The factors and levels were set based on the single-factor experiments conducted previously, and the scheme was performed according...
to the limited set of experimental conditions provided by the software. Meanwhile, the optimal process parameters and operating conditions can be found (Zhang et al. 2020; Zhao et al. 2020). Response surface methodology, which has been confirmed with high accuracy, is suitable for multi-factor experiments.
This paper is mainly describes synthesis of a promising adsorbent by impregnation methods. Characterizations of the adsorbent and the effect of various parameters like adsorption time, adsorbent dosage and initial pH were conducted using manganese oxide supported activated alumina (MO@AA). In addition, Response surface methodology and Design-Expert software were used to determine optimal operating parameters.

2. MATERIALS AND METHODS

2.1. Materials

Chemicals for the experimental study were bought from Sinopharm Chemical Reagent Co., Ltd. These chemicals included fresh alumina, hydroxylamine hydrochloride (H4ClNO), manganese chloride (MnCl2), sodium fluoride (NaF), ammonia (NH3·H2O), potassium pyrophosphate (K4P2O7), potassium periodate (KIO4), ammonium acetate (CH3COONH4), nitric acid (HNO3) and ferrous sulfate ((NH4)2Fe(SO4)2·6H2O). As provided by Tianjin Damao Chemical Reagent Factory and America HACH company, hydrogen peroxide (H2O2) and SPADNS reagent were used in this experiment. The remaining chemical reagents were aluminum sulfate (Al2(SO4)3), manganese sulfate (MnSO4), hydroxylamine hydrochloride, o-phenanthroline, hydrochloric acid (HCl), phenanthroline (C12H8N2), ammonium acetate (CH3COONH4), and glacial acetic acid (CH3COOH). All were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. All chemicals were of analytical grade, and experimental solutions were made with deionized water (DI water).

2.2. Preparation of the adsorbent

As shown in Figure 1, the MO@AA were prepared by the impregnation method (Liping 2011). Briefly, 30 g of the particles were impregnated in 150 mL of MnSO4 solution (0.05 mol/L) with continuous stirring and heating for 6 h at 115 °C (magnetic stirrer), then 2.76 mL H2O2 with a concentration of 30% were immersed. At this point, the particles turned light yellow. Subsequently, 45 mL 25% NH3·H2O were poured into the mixture. The brown precipitates, generated on the surface of the samples in this step, were confirmed as MnOOH and MnO2. Next, the mixture was washed thoroughly in a constant temperature oscillation incubator with hot DI water (30–40 °C) for 40 min at the speed of 150 r/min. After several rounds of flushing, the adsorbent was dried for 4 h at 100 °C and cooled to room temperature for further use.

2.3. Characterizations of the adsorbent

The surface microstructure of MO@AA was explored by scanning electron microscope (SEM) (S-4800, Hitachi, Japan). When the accelerating voltage was 5 kV and the temperature was constant, the photomicrographs were recorded. The measurement of particle surface areas and pore sizes were conducted by N2 air-suction desorption on an automatic static physical adsorption instrument (Autosorb-IQ2-MP, Quantachrome, America). The total specific surface was calculated based on the multipoint Brunauer, Emmett and Teller (BET) equation (P/P0 = 0.005–0.3). The total pore volume was measured at P/P0 = 0.99.

Figure 1 | Fabrication of MO@AA.
X-ray diffraction (XRD) was measured using an X’Pert Pro instrument (Spectris, Holland). Measurement conditions were as follows: tube voltage 40 kV, tube current 40 mA, Cu K-alpha radiation source, $\gamma = 0.15406$ nm, scanning range 5–90°, and scanning at the speed of 5°/min. Lastly, transmission spectra were analyzed using Fourier transform infrared spectroscopy (FTIR) (NICOLET iS50, Thermo Nicolet Corporation, America) for infrared absorption spectra. The infrared range was set to 4,000–400 cm$^{-1}$, and each scanned 32 times.

2.4. Single-factor study

The prepared MO@AA were used for the removal of fluoride, manganese and iron from the aqueous solution. All trials were conducted under the conditions of room temperature (25 ± 0.1 °C) and acid condition (hydrochloric acid was used to adjust the pH) by batch scale. Here, 100 mL of fluoride, iron and manganese solution with the initial concentrations of 0.26 mmol/L, 0.04 mmol/L, and 0.02 mmol/L were mixed with a certain mass of adsorbents. Then, the mixture was shaked in a constant temperature oscillation chamber for a predetermined period of reaction time at the speed of 120 r/min. The residual concentrations of fluoride, manganese, and iron were detected and accessed using fluorometric spectrophotometry and spectrophotometer, respectively. The limits of fluoride, manganese, and iron concentrations from the Standard Test Method for Drinking Water (GB/T 57750–2006), were 0.05 mmol/L, 0.01 mmol/L and 0.002 mmol/L.

In the previous study, pH value, adsorbent dosage, contacting time were basic factors affecting the effect of removal efficiency. Then, based on the range of the single-factor test, Response surface methodology was conducted to obtain the corresponding response values. The concentrations of contaminants were detected at certain time intervals, and the adsorption quantity ($q_t$, mg/g) was investigated using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{w} \quad (1)$$

where $C_t$ (mg/L), $w$ (g) and $V$ (L) represent the concentration of fluoride ions at time $t$ (min), the weight of the adsorbent and the volume of the solution, respectively. The removal efficiency of contaminants (%) was calculated using the following mathematical expression:

$$\text{Removal rate} \% = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where $C_0$ (mg/L) and $C_t$ (mg/L) were taken as the initial and final solution concentration.

2.5. Box–Behnken experimental design

Box–Behnken experiments were carried out to investigate the interaction of three independent process variables (pH, adsorbent dosage, contact time) and optimize the maximum percent removal efficiency. The scheme, a total of 17 runs, consisted of three levels (low, medium and high). Independent factors, including pH, contact time, adsorbent dosage, were written as A, B, and C. Response value (removal rate of fluoride, iron and manganese) were denoted as $Y_1$, $Y_2$ and $Y_3$, respectively. Analysis of variance was generated to manifest the influence of individual linear, quadratic and interaction terms. The applicability of the model was checked using the coefficient of determination ($R^2$) and coefficient of variation (C.V. %). The commonly used second-order polynomial equation can be expressed as:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

where $Y$ is the response value (%), $\beta_i$ is the regression coefficient, and $\varepsilon$ is the error of the model. The main effects and interactions between factors were determined. Through the Response surface methodology model, the parameters (coefficients of correlation, $P$-value, F-value, residual analysis and predicted values) were validated by the data obtained. Then, the mechanism of fluoride, manganese and iron removal can be discussed.
3. RESULTS AND DISCUSSION

3.1. Characterization of the adsorbent

3.1.1. SEM analysis

As depicted in Figure 2, the surface microstructures of fresh alumina and MO@AA were observed by SEM. It manifested that the surface appearance changed obviously in the modification process. As shown in Figure 2(a), the pore structure of AA was inconspicuous with only a few pores and obvious bulks were heaped up on the surface. Whereas, Figure 2(b) shows that after impregnation of AA, certain pores became uniformed and extensive impurities removed, which improved the adsorption performance. In addition, the surface of modified AA presented a convex spinous structure. These alterations that occurred may be possibly for the sake of the introduction of functional groups into the surface of AA by manganese oxides, which destroyed the crystal structure to manifest higher energy of adsorption. Thus, it can be inferred that manganese oxides were successfully loaded on to AA.

3.1.2. BET analysis

To examine the pore properties of AA before and after modification, BET analysis was carried out. As displayed in Table 3, the specific surface increased 24% compared with unloaded alumina beads, which is expected to improve adsorption ability. However, total pore volume and average pore diameter were slightly reduced, attributed to a small amount of manganese oxides entering the pore channel. With respect to the adsorption–desorption isotherm plot shown in Figure 3(a) and 3(b), its nature was similar to type II isotherms with a typical H2 hysteresis loop (Thommes 2016). It was indicated that the process was unrestricted monolayer–multilayer and the MO@AA were mesoporous. Additionally, the N2 adsorption capacity increased with the build-up of relative pressure, revealing that the pore structure was not damaged during the modification process. The curves of MO@AA did not coincide but formed the larger hysteresis loops, which exhibited better mesoporous properties, being consistent with SEM analysis. The hysteresis loop at high pressure resulted from the occurrence of condensation and evaporation at different relative pressures. The above results indicated that loading with manganese oxides had little effect on the pore structure of the samples.

![Figure 2](image1.png)  
**Figure 2** | SEM image of (a) fresh alumina, (b) MO@AA.

| Sample  | S<sub>BET</sub> (m<sup>2</sup>/g) | V<sub>Total</sub> (cc<sup>2</sup>/g) | Pore diameter (nm) |
|---------|---------------------------------|---------------------------------|-------------------|
| AA      | 2.324                           | 4.636                           | 3.059             |
| MO@AA   | 2.892                           | 4.079                           | 2.453             |
3.1.3. XRD analysis

XRD measurements were conducted to investigate the main constituent elements and chemicals of AA and modified AA, respectively. XRD analysis of AA before and after treatment is exhibited in Figure 4. It can be concluded that the modification process had little effect on the crystal structure of the samples, indicating that the basic framework of AA showed no obvious change. Taking a step further, some wide and sharp diffraction peaks were demonstrated as Al₂O₃, which emerged at 2θ of 25.578°, 35.154°, 37.779°, 43.357°, 52.556°, 68.214° and 77.248°. Besides, the intensities of MnOOH and MnO₂ were in 2θ of 26.379°, 34.263°, 37.327°, 51.563°, 54.303°, 65.799°, 71.361°, 79.585° and 12.784°, 18.107°, 28.841°, 37.622°, 41.968°, 60.274°, 67.648°, 71.189°. All were compatible with current literature values (JCPDS No. 78-2427, JCPDS No. 74-1842 and JCPDS No. 44-0141), respectively (Yang et al. 2021). This revealed that the major oxide of fresh AA was Al₂O₃ and manganese oxide was successfully loaded onto the surface of the modified samples after impregnation.

Figure 3 | N₂ adsorption–desorption isotherm plot of (a) fresh alumina (b) MO@AA from BET analysis.

Figure 4 | XRD analysis of fresh alumina and MO@AA.
3.1.4. FTIR analysis

It was well known that the chemical groups involved in the adsorption process were directly affected the performance of fluoride removal. Hence, to verify the functional groups, the FTIR spectroscopy was performed. Figure 5 shows the FTIR spectra of fresh alumina and MO@AA. The peaks located at around 3,455 cm\(^{-1}\), 1,617 cm\(^{-1}\), 1,384 cm\(^{-1}\) and 586 cm\(^{-1}\) were observed, respectively.

The adsorption band in between 3,455 cm\(^{-1}\) and 3,626 cm\(^{-1}\) was due to -OH stretching vibrations and the peak became sharp. The shift was possibly caused by the increase in hydroxyl groups after manganese oxides loaded. When the concentration of hydroxyl group increased, the association effect would be enhanced, and the stretching vibration peak would become sharp. The intensified water molecule bending vibration at 1,617 cm\(^{-1}\) indicated that the adsorption process might be hydrogen bonding with the hydroxyl group. As can be seen from the images no other chemical groups were formed, which was speculated to be electrostatic adsorption. After adsorption, the sharpness of peaks of the hydroxyl group implied that the ion exchange reaction had occurred and the hydroxyl group had been replaced. The bands at 1,384 cm\(^{-1}\) were CO\(_3^{2-}\) symmetric stretching vibration. This phenomenon can be explained in that AA hydrophilicity inevitably absorbed H\(_2\)O and CO\(_2\) in the air. The peak at 592 cm\(^{-1}\) was attributed to Al-O bond vibration in unmodified AA, while higher bands at 586 cm\(^{-1}\) were due to the combination of Al-O and Mn-O bonds. In general, the peak position of activated alumina before and after modification had little variation, and the peak shape was basically the same, which demonstrated that the basic skeleton of AA had no obvious change in the process of modification. In the process of adsorption, not much had changed for the functional groups, but these obtained an increased -OH stretching vibration peak, so the content of hydroxyl groups and the number of active sites increased.

3.2. Single-factor study

3.2.1. Effect of contact time

The contacting time is related to the degree of reaction. The longer the reaction time, the better the effect of pollutant removal. As shown in Figure 6, the contact time exhibited a major influence on the pollutant removal. It expressed a similar increasing tendency in the removal of fluoride and iron with a further increment of time. The adsorption capacity of fluoride calculated by Equation (1) was dramatically accelerated in the preliminary stage (0–4 h), which was mainly due to external diffusion. Subsequently, from 4 to 12 h, the adsorption growth rate slowed down. This phenomenon can be explained in that MO@AA was gradually covered by fluoride ions, especially on active sites and pores. Then, in the final stage (12–24 h), the amount of fluoride adsorbed tended to be stable. That is to say, the adsorption came to an equilibrium state, the maximum
achieved fluoride removal efficiency was 98% (Equation (2)). In the process of reducing the concentration of iron and manganese ions, the adsorption and contact oxidation processes worked together. The manganese oxide accumulated on the surface of MO@AA, and the contact oxidation capacity was enhanced. After 24 h of reaction, the maximum iron and manganese removal rates of the effluent water reached 83 and 12% (Equation (2)), respectively. When set as a long period of contact time in acid solution (pH < 4), leaching of manganese was observed. This can be explained by the reaction of excess hydrogen ions with MnOOH (Bochatay & Persson 2000):

\[
2\text{MnOOH} + 2\text{H}^+ = \text{Mn}^{2+} + \text{MnO}_2 + 2\text{H}_2\text{O}
\]  

(4)

3.2.2. Effect of adsorbent dosage

With the increase in adsorbent dosage, the active sites and the amount of manganese oxide provided by MO@AA was reinforced, and the fluoride and iron removal rate gradually improved, as observed from Figure 7. This may be due to the enhanced attraction between MO@AA and the contaminants. The fluoride, iron and manganese rates of removal increased 50, 63 and 9% (Equation (2)) in the dosage range selected (1–11 g/L), respectively. It was observed that this further increased the amount of dosage, but removal efficient did not markedly change. This may be due to saturation on the surface of MO@AA.

3.2.3. Effect of pH value

In a strong acid medium (pH < 2.00), HF generation affects the removal of fluoride ions. Here, the initial pH was set from 3.00 to 10.00 (Chen et al. 2021). Apparently, as demonstrated in Figure 8, pH had a significant monitoring force driving the removal process. The increase in pH led to an increase in the removal of fluoride, which could be attributed to the fact that positively charged MO@AA in acidic conditions was combined with negatively charged fluoride ions. When pH increased, the existence of excess OH⁻ ions may compete with negatively charged fluoride ions that weakened the interaction of electrostatic forces (Roy et al. 2018). In general, the removal capacity for fluoride was high at low pH, whereas high pH favors the oxidation of iron and manganese ions. Therefore, pH 4–6 was chosen as the optimum range for pH value for the simultaneous removal of fluoride, manganese and iron.

3.3. The scheme of Box–Behnken design under response surface methodology

As listed in Table 4, independent factors, including pH, contact time, adsorbent dosage, were denoted as A, B, and C. Meanwhile, three levels based on the above single factor results of −1, 0 and 1 were given. Response values \((Y_1, Y_2, Y_3)\) were
Figure 7 | Removal efficiency of adsorbent dosage on fluoride, iron, manganese. (Co = 0.26 mmol/L, 0.04 mmol/L, and 0.02 mmol/L, speed = 120 r/min, contact time = 8 h, pH = 4, T = 298 K.)

Figure 8 | Removal efficiency of pH on fluoride, iron, manganese. (Co = 0.26 mmol/L, 0.04 mmol/L, and 0.02 mmol/L, speed = 120 r/min, contact time = 8 h, adsorbent dosage = 5 g/L, T = 298 K.)

Table 4 | Factors and levels used in response surface methodology design

| Factor                | Levels          |
|-----------------------|-----------------|
|                       | Low (-1)        | Medium (0) | High (+1) |
| pH (A)                | 4               | 5          | 6         |
| Contact time (B)      | 4 h             | 8 h        | 12 h      |
| Adsorbent dosage (C)  | 5 g/L           | 7 g/L      | 9 g/L     |
calculated from Equation (3) and represented the removal efficiency of fluoride, iron and manganese, respectively. In total, 17 runs were performed using Design-Expert 8.0 software (Table 5). Then, using the following second-order polynomial equation to explore the relationship between factors and response values:

\[
Y_1 = 88.51 - 5.87 \times A + 8.75 \times B + 5.77 \times C + 5.69 \times AB - 0.87 \times AC - 3.25 \times BC - 1.11 \times A^2 - 6.78 \times B^2 - 2.47 \times C^2
\]

(5)

\[
Y_2 = 78.79 + 0.84 \times A + 15.67 \times B + 3.29 \times C + 1.80 \times AB + 0.94 \times AC - 3.25 \times BC - 3.34 \times A^2 + 4.83 \times B^2 + 0.62 \times C^2
\]

(6)

\[
Y_3 = 12.11 + 5.85 \times A + 5.76 \times B + 1.97 \times C + 2.48 \times AB + 0.4 \times AC + 0.35 \times BC - 1.81 \times A^2 - 0.56 \times B^2 - 0.97 \times C^2
\]

(7)

### 3.4. Analysis of response surface methodology and the model fitting

The ANOVA results for fluoride, iron and manganese are shown in Tables S1–S4 in Supplementary Materials. The values for F and P implied the significance of the fitted equations and the extent to which the original hypothesis is not rejected. The smaller the P-value and the larger the F-value, the more significant is the effect of this item on the response value (Thommes 2016). By analyzing the results obtained, all three Response surface methodology models showed good predictability.

In the regression equation for fluoride (Table S1), the F-value was 9.59, the P-value was 0.0035, 0.005. Values of P less than 0.005 indicated model terms were significant. In this case, A, B, C, AB, and B^2 were significant factors. Adeq precision measures the signal-to-noise ratio. A value greater than 4 is desirable. Thus, 11.357 indicates an adequate signal. This model can be used to navigate the design space. The values of the correlation coefficient (R^2) and adjusted R^2 were 0.9250 and 0.8296, respectively. A high R^2 value (more than 0.8) is expected. There was only 2% of the total variation that was not explained by the model. All demonstrated the good fitness for the model.

### Table 5 | BBD and results for the study of three experimental variables in coded units

| Run | Factor 1: pH | Factor 2: contact time (h) | Factor 3: adsorbent dosage (g/L) | Response 1: removal rate of fluoride (%) | Response 2: removal rate of iron (%) | Response 3: removal rate of manganese (%) |
|-----|--------------|---------------------------|-------------------------------|------------------------------------------|-------------------------------------|------------------------------------------|
| 1   | 6            | 12                        | 7                             | 86.41                                    | 100                                 | 23.98                                    |
| 2   | 5            | 4                         | 9                             | 80.78                                    | 74.94                               | 7.00                                     |
| 3   | 6            | 8                         | 9                             | 87.61                                    | 79.68                               | 17.27                                    |
| 4   | 6            | 8                         | 5                             | 78.18                                    | 71.12                               | 13.21                                    |
| 5   | 5            | 8                         | 7                             | 88.56                                    | 77.01                               | 12.18                                    |
| 6   | 5            | 8                         | 7                             | 88.69                                    | 78.07                               | 12.21                                    |
| 7   | 5            | 12                        | 5                             | 84.25                                    | 100                                 | 13.48                                    |
| 8   | 6            | 4                         | 7                             | 55.42                                    | 65.24                               | 7.07                                     |
| 9   | 4            | 12                        | 7                             | 94.44                                    | 91.71                               | 7.45                                     |
| 10  | 5            | 12                        | 9                             | 89.67                                    | 100                                 | 18.79                                    |
| 11  | 4            | 8                         | 9                             | 93.4                                     | 79.14                               | 4.65                                     |
| 12  | 4            | 8                         | 5                             | 80.51                                    | 74.33                               | 2.19                                     |
| 13  | 4            | 4                         | 7                             | 86.21                                    | 64.17                               | 0.47                                     |
| 14  | 5            | 8                         | 7                             | 88.24                                    | 79.14                               | 11.9                                     |
| 15  | 5            | 8                         | 7                             | 88.63                                    | 79.5                                | 12.2                                     |
| 16  | 5            | 4                         | 5                             | 62.35                                    | 62.03                               | 3.08                                     |
| 17  | 5            | 8                         | 7                             | 88.43                                    | 80.21                               | 12.08                                    |
Results of ANOVA for iron are shown in Table S2. The model F-value of 71.53 demonstrated that the model was accurate. There was only a 0.01% chance that a Model F value this large could occur due to noise. P-values less than 0.05 indicate model terms were significant. In this case, B, C, BC, A^2 and B^2 are significant factors. The sequence of the independent factors was B^2 > C > A^2 > BC > AB > A > AC > C^2. The R^2 of 0.8680 (>.8) was in reasonable agreement with the adjusted R^2 of 0.9754 (>.8). Furthermore, the Adeq precision in this model was 26.409 > 4. It showed that this model fits well with the actual situation, has good stability, high test reliability, and accuracy.

The ANOVA result of manganese model is given in Table S3. The high F-value (347.5) implied the reliability of the model. The existed chance of P < 0.0001 indicated that the model was highly significant. In this manner, A, B, C, AB, A^2, B^2 and C^2 were significant variables. The high Adeq precision value of 35.942, high R^2 of 0.9924 and adjusted R^2 of 0.9826 were found. It reflected that only 1% of the total variations cannot be explained. Here, this model can be used.

The correlation between actual and predicted values of removal efficiency is displayed in Figure 9(a)–9(c). The points distribution was in the vicinity of a straight line, suggesting that the developed model was adequate in predicting the response variables for the experiment, the reliability of the data was proven. The simulation results showed that the model could be evaluated with a 95% confidence level.
3.5. Effect of interactive variables

3.5.1. Effect of variation in pH and contact time
To further investigate the effect of pH, and the time of reaction, a multivariate coupling experiment was carried out. The 3D images of Response surface methodology plot shown in Figure 10(a)–10(c) verified the connection of the two parameters on the simultaneous removals of fluoride, iron and manganese. With the increase in pH from 4 to 6, fluoride removal capacity slowed down and the removal efficiency of manganese and iron was enhanced. While, with increase in contacting time, removal rate correspondingly improved. In addition, the slope of the plots was large, and the large plot indicated a huge impact of independent factors on the response values.

3.5.2. Effect of variation in pH and dosage
Figure 11(a)–11(c) shows 3D surface of the impact of pH and dosage on response value. When the pH value rose continually, it an increase was observed in the removal of fluoride along with a decrease in iron and manganese removal efficiency. As the time of reaction was extended, the solid–liquid two-phase system gradually reached an equilibrium, leading to an increase in the removal effect. Maximum efficiency of 94, 100 and 24% was observed in this plot, for 8 g/L of adsorbent.

3.5.3. Effect of variation in contact time and dosage
In Figure 12(a)–12(c), the interaction of contact time and adsorbent dosage is explored. In the range selected, contact time and adsorbent dosage had a positive effect on reduction of fluoride, iron and manganese concentration. The contact time

![Figure 10](image-url) | 3D images of the effects of pH and contact time on fluoride (a), iron (b) and manganese (c) removal.
3.6. Optimization and validation of the model

To meet the drinking water standards, an optimal condition can be selected based on the Response surface methodology model. In this work, the raw fluoride, iron and manganese ion mass concentrations of 0.26 mmol/L, 0.04 mmol/L, and 0.02 mmol/L were mixed with MO@AA at an initial pH of 5.79, the reaction time of 12 h, adsorbent dose of 8.21 g/L (Table 6). Optimum process condition was 0.955. Under the optimized conditions, the maximum removal rate was achieved. The measured value had an error of only 1, 0 and 1%, with the simulation result. Consistent with the above analysis, the Response surface methodology model has good accuracy and desirability.

3.7. Mechanism of fluoride, manganese and iron removal

Compared with the reported adsorbents in Table 2 which showed good performance in the removal of fluoride, iron and manganese, respectively, MO@AA can take effect in the simultaneous removal of these three inorganic solutes. In addition, MO@AA worked effectively over a wider range of pH (3–9). The comparison of fresh alumina and MO@AA is demonstrated in Figure 13. It manifested that the adsorption capacity of fluoride rose sharply on MO@AA as compared to the control. The possible reasons analyzed on the basis of characterization (SEM and BET) were given as follows: the number of active sites enhanced, the specific surface increased, convex spinous structure presented and the pore structure improved.

Figure 11 | 3D images of the effects of pH and adsorbent dosage on fluoride (a), iron (b) and manganese (c) removal.
The mechanism of adsorption on MO@AA was based on the experimental results and the analysis of XRD and FTIR. It can be deduced that the adsorption process may be the reason for electrostatic attraction and ion exchange. For one thing, at acidic conditions, the surface hydroxyl group was protonated and led to the surface of MO@AA being electropositive (Kumari et al. 2020). Thus, the negative fluoride ions charged primely onto the positively surface by the electrostatic force as follows:

\[
\text{AlOH} + \text{H}_2\text{O}^+ + \text{F}^- \rightarrow \text{AlOH}\cdot\text{H}^+ + \text{F}^- + \text{H}_2\text{O}
\]  

(8)

In addition, hydroxyl released when in acidic medium, resulting in the increase in pH. Furthermore, MO@AA absorbed water molecules led to surface hydroxylation (Teng et al. 2009). Active sides enhanced in this process and MnOOH was reduced to Mn(OH)$_2$. Simultaneously, fluoride ions exchanged with hydroxyl groups due to the similar hydrated ionic radius. The chemical reaction equations could be expressed as (Yang 2013):

\[
\begin{align*}
\text{(Al}_2\text{O}_3)_n \cdot \text{MnOOH} + \text{H}_2\text{O} & \rightarrow (\text{Al}_2\text{O}_3)\text{Mn(OH)}_2 + \text{OH}^- \\
\text{R-(Al}_2\text{O}_3)_n \cdot \text{Mn(OH)}_2 + 2\text{F}^- & = \text{R-(Al}_2\text{O}_3)_n\text{MnF}_2 + 2\text{OH}^-
\end{align*}
\]  

(9)

\[10\]

**Figure 12** | 3D images of the effects of contacting time and adsorbent dosage on fluoride (a), iron (b) and manganese (c) removal.

**Table 6** | The predicted and experimental values under optimized process parameters

| pH  | Reaction time (h) | Dosage (g/L) | Removal rate of fluoride (%) | Removal rate of iron (%) | Removal rate of manganese (%) |
|-----|-----------------|--------------|------------------------------|--------------------------|-------------------------------|
|     |                 |              | Actual value | Predicted value | Actual value | Predicted value | Actual value | Predicted value |
| 5.79 | 12              | 8.21         | 91            | 90            | 100           | 100           | 23            | 24            |

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\end{align*}
\]  

(9)

\[10\]
The removal of ferrous ions may be due to the oxidation of MnOOH by dissolved oxygen in the aquatic environment, which generated a high-valent manganese compound. Subsequently, MnO·Mn2O7 was further oxidized with divalent iron in solution to form Fe(OH)3 (Weili 2020). The equations are shown below:

\[
\text{MnOOH} + O_2 + H_2O \rightarrow \text{MnO·Mn_2O_7} \quad (11)
\]
\[
\text{MnO·Mn_2O_7} + 2\text{Fe}^{2+} + H_2O \rightarrow \text{MnO}_2 + \text{Fe(OH)}_3 \quad (12)
\]
\[
\text{Fe(OH)}_3 + 2\text{H}_2\text{O} + \text{Fe}^{2+} \rightarrow [\text{Fe(OH)}_2(\text{Fe})\text{·2H}_2\text{O}]^+ + \text{H}^+ \quad (13)
\]
\[
[\text{Fe(OH)}_2(\text{Fe})\text{·2H}_2\text{O}]^+ + 1/4\text{O}_2 + 5/2\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3\text{·2H}_2\text{O} + \text{H}^+ \quad (14)
\]

For manganese removal, two steps were involved: (i) the dissolved Mn2⁺ adsorbed by MnO2; (ii) the adsorbed Mn2⁺ oxidized to high valence manganese compounds. At the beginning of the reaction, influenced by low pH, MO@AA showed poor performance in oxidation. A small amount of Mn2⁺ was adsorbed on the surface of the particles (Equation (15)). As the hydroxyl group undergoes ion exchange with the fluoride ion, the hydroxide is released into the aqueous solution, while the high pH facilitates the oxidation of the manganese ion. As the contact time increases, its contact oxidation capacity becomes stronger and stronger, and then contact oxidation for manganese removal is the main focus (Equation (16)–(18)). The equations are shown below (Liping 2011):

\[
\text{Mn}^{2+} + \text{MnO}_2\cdot x\text{H}_2\text{O} = \text{MnO}_2\cdot \text{MnO} \cdot (x-1)\text{H}_2\text{O} + 2\text{H}^+ \quad (15)
\]
\[
\text{MnO}_2\cdot \text{MnO} \cdot (x-1)\text{H}_2\text{O} + 1/2\text{O}_2 + \text{H}_2\text{O} = 2\text{MnO}_2\cdot x\text{H}_2\text{O} \quad (16)
\]
\[
\text{MnO}_2 + \text{Mn}^{2+} + \text{H}_2\text{O} = \text{Mn}_2\text{O}_3 + 2\text{H}^+ \quad (17)
\]
\[
\text{Mn}_2\text{O}_3 + \text{Mn}^{2+} + \text{H}_2\text{O} = \text{Mn}_3\text{O}_4 + 2\text{H}^+ \quad (18)
\]

4. CONCLUSIONS

In this work, a novel adsorbent was successfully fabricated on containments reduction. The percent fluoride removal varied from 31% to 91% after the impregnation method. Results obtained from SEM proved better adsorption performance with the convex spinous structure and more active sides on the surface of MO@AA. XRD also manifested the introduction of MnOOH and MnO2 after impregnation. The specific surface increased 24% compared with unloaded alumina beads on the basis of BET, with respect to the adsorption-desorption isotherm, it verified that the process was multilayered and the modified AA was mesoporous. The FTIR spectroscopy analysis implied that the ion exchange reaction had occurred. By modelling, the effects of the three parameters including pH, contacting time and the amount of dosage were evaluated. Under optimized
conditions, maximum removal efficiency reached 90.59%, 100% and 23.46%. Furthermore, it can be deduced that the mechanism of adsorption consisted of electrostatic attraction and ion exchange. The oxidation process played a major role in treating iron and manganese-containing simulated water. Thus, MO@AA showed the great potential of fluoride, iron and manganese removal and was a promising adsorbent for groundwater treatment. In the follow-up trials, MO@AA would be applied in real groundwater to remove the excess fluoride, iron and manganese ions. More cost-effective methods can be explored in the next phase.

**AUTHOR CONTRIBUTIONS**

**Kun You**: Review & editing, Methodology, Formal Analysis; **Yujia Gao**: Writing – original draft, Methodology, Formal Analysis; **Weiye Qian**: Writing – review & editing, Formal Analysis; **Jinxiang Fu**: Writing – review & editing, Methodology; **Juliang Wang**: Formal Analysis, Resources; **Weiwei Zhou**: Resources.

**CONFLICT OF INTEREST**

The authors declare that they have no conflict of interest.

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**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

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