The performance of calcined serpentine to simultaneously remove fluoride, iron and manganese

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ABSTRACT

To solve the problem of high fluoride, iron and manganese concentrations in groundwater, serpentine (Srp) was modified by metal salt impregnation, acid-base activation and calcination, and the effects of these three modifications on removal performance of Srp were compared. Specifically, the effects of the calcined serpentine (Csrp) dose, reaction time, pH, and temperature on the removal performance of F\(^-\), Fe\(^{2+}\) and Mn\(^{2+}\) on Csrp were analysed. An isothermal adsorption model and adsorption kinetic equation were established and confirmed through SEM, EDS, XRD and FTIR spectroscopy to analyse the mechanism of removing F\(^-\), Fe\(^{2+}\) and Mn\(^{2+}\) by Csrp. The results show that when 3 g/L Csrp was used to treat water samples with 5 mg/L F\(^-\), 20 mg/L Fe\(^{2+}\), and 5 mg/L Mn\(^{2+}\) (pH of 6, reaction temperature of 35 °C, and time of 150 min), the removal rates of F\(^-\), Fe\(^{2+}\), and Mn\(^{2+}\) were 94.3%, 99.0%, 98.9%, respectively. The adsorption of F\(^-\), Fe\(^{2+}\) and Mn\(^{2+}\) on Csrp follows the quasi-second-order kinetic equation and Langmuir isotherm adsorption model. After 5 cycles of regeneration of Csrp, Csrp can still maintain good properties of fluoride, iron and manganese removal.

Key words: calcined modification, fluoride, iron, manganese, removal mechanism, serpentine

HIGHLIGHTS

- Microscopic characterization of calcined serpentine was carried out.
- Calcined serpentine can achieve the synchronous removal of high fluoride, iron and manganese concentrations in groundwater.
- The adsorption isothermal model and adsorption kinetic equation of calcined serpentine were established.
- The mechanism for the simultaneous removal of fluoride, iron and manganese by calcined serpentine was analysed.

GRAPHICAL ABSTRACT

INTRODUCTION

Excessive fluoride, iron and manganese in groundwater have an impact on the health of residents, and there are problems related to high levels of fluoride, iron and manganese in groundwater both at home and abroad (Li et al. 2021a, 2021b).

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Fluoride is widely present in minerals, natural water systems and geological deposits and enters the food chain through human consumption or vegetation (Jin et al. 2016). The excessive intake of fluoride affects human health and causes fluorosis (Cai et al. 2015). Iron and manganese ions exist in nature in the form of dissolved single ions (Fe$^{2+}$, Mn$^{2+}$) or in the form of undissolved Fe(OH)$_3$ and MnO$_2$ (Barloková & Ilavský 2010). Fe$^{2+}$ and Mn$^{2+}$ form hydroxides after oxidation, which affects the colour, taste and turbidity of water (Homoncik et al. 2010). These insoluble hydroxides can produce toxic derivatives in the body and cause many physical diseases. The World Health Organization stipulates that the maximum limit of fluoride is 1.5 mg/L (Zawar et al. 2020). The EU Directive 2020/2184 sets the following limits for aesthetic reasons: Fe < 0.2 mg/L and Mn < 0.05 mg/L. Therefore, the removal of fluoride, iron, and manganese from groundwater is an urgent need to solve the problem of using groundwater that contains fluoride, iron, and manganese as drinking water.

There are many studies on the separate removal of fluoride, iron and manganese both at home and abroad (Kwakye-Awuah et al. 2019; Yadav et al. 2019; Aziz et al. 2020). However, there are few studies on their simultaneous removal, and thus, it is essential to explore how to simultaneously remove fluoride, iron and manganese in groundwater (Zhang et al. 2009). At present, the methods for treating fluoride-containing groundwater mainly include ion exchange, electrolysis, reverse osmosis, nanofiltration and adsorption (Abri et al. 2019). The main approaches to treat groundwater containing iron and manganese include filtration, contact oxidation, microbial treatment, ion exchange, ultra/microfiltration membranes, and adsorption (Chaturvedi & Dave 2012; Patil et al. 2016). Among the above methods, the adsorption method is the first choice to remediate groundwater pollution due to its low cost, high adsorption capacity, and low energy consumption (Meski et al. 2019). Optimizing adsorbents for the simultaneous removal of fluorine, iron and manganese is the key to research and application. Natural minerals are inexpensive and have good chemical stability; thus, they are often used to adsorb fluoride or heavy metal ions from water. Serpentine, as a magnesium-rich silicate mineral, has abundant reserves in China and is widely distributed throughout areas such as the Liaoning Province and Shanxi Province. Serpentine itself contains a large number of active groups, such as hydroxyl groups and unsaturated Si-O-Si, O-Si-O, magnesium and hydrogen bonds, which can be combined with metal ions to undergo ion exchange and surface coordination reactions (Cattaneo et al. 2003; Shaban et al. 2018). Thus, the adsorption performance of modified serpentine can be significantly improved. Mobarak et al. (2019) used chemically modified serpentine to remove Cr$^{6+}$ and F$^-$ at rates of 87.31% and 94.72%, respectively. Huang et al. (2017) used mechanically activated serpentine to remove Cu$^{2+}$ from water, and this modified serpentine exhibited a significant increase in adsorption capacity compared to natural serpentine.

Based on the above results, this article first studies the modification of Srp and selects the best modification method. The effects of the Csrp dose, reaction time, pH, and temperature on the removal effect of F$^-$, Fe$^{2+}$, Mn$^{2+}$ were also explored. An isothermal adsorption model and adsorption kinetic equation were established to investigate the adsorption behaviour of Csrp for F$^-$, Fe$^{2+}$ and Mn$^{2+}$. The adsorption performance of Csrp for F$^-$, Fe$^{2+}$ and Mn$^{2+}$ in water was compared with other adsorbents. The removal mechanism of Csrp for F$^-$, Fe$^{2+}$ and Mn$^{2+}$ was revealed by SEM, EDS, XRD, and FTIR spectroscopy, which provides a reference for further studies on the simultaneous removal of F$^-$, Fe$^{2+}$ and Mn$^{2+}$ from groundwater.

**MATERIALS AND METHODS**

**Experimental materials**

Srp was obtained from the boron mining area in Yingkou City, Liaoning Province, China, and ground to 120 mesh. The test reagents included Al$_2$(SO$_4$)$_3·18$H$_2$O, CaCl$_2$, NaOH, HCl, MnSO$_4·3$H$_2$O, FeSO$_4·7$H$_2$O, NaF, NaCO$_3$, HNO$_3$, H$_3$PO$_4$, C$_{12}$H$_8$N$_2·2$H$_2$O, CH$_3$COOH, and C$_{14}$H$_{22}$N$_2$O$_8·$H$_2$O, all of analytical grade, which were purchased from the Liaoning Quanrui Reagent Co., Ltd.

**Test instrument**

An electronic balance (e-10d) was used to weigh the test materials. The adsorption reaction was carried out in an intelligent precision shaker (BXD-YX-2000), and calcination was carried out in a box resistance furnace (SRJX-4-10). The F$^-$ concentration was determined by a fluoride ion selective electrode (PF-2-01), and the concentrations of Fe$^{2+}$ and Mn$^{2+}$ were determined by an atomic absorption spectrophotometer (Z-2000). A precision pH meter (PHS-3C) was used to measure the pH. Scanning electron microscopy (SEM, Hitachi S-3400N) was used to observe the apparent morphological changes in the sample. Energy dispersive X-ray spectroscopy (EDS, FEI Quanta TM250) was used to qualitatively and quantitatively analyse each element in the sample. X-ray diffraction (XRD, D8 ADVANCE) was used for phase analysis of Csrp before and
after the reaction. Fourier transform infrared (FTIR, AVATAR 330) spectroscopy was used to analyse changes in the functional groups before and after adsorption by the sample.

**Preparation of modified serpentine**

Srp was modified by the following methods:

- Impregnation of a metal salt: Two hundred millilitres of aluminium sulfate solution and calcium chloride solution with mass fractions of 1, 2, 3, 4, 5, 6, and 7% were prepared. Then, 10 g of 120 mesh Srp was added to each solution, which was fully stirred for 3 h, aged for 24 h, filtered to remove the Srp, washed with distilled water and dried for later use.

- Acid-base activation: Two hundred millilitres of hydrochloric acid solution and sodium hydroxide solution with mass fractions of 1, 2, 3, 4, 5, 6, and 7% were prepared. Then, 10 g of 120 mesh Srp was added to each solution, fully stirred for 3 h, aged for 24 h, filtered to remove the Srp, washed with distilled water and dried for later use.

- Calcination: Srp (50 g, 120 mesh) was calcined for 120 min in a box resistance furnace at 100 °C, 200 °C, 300 °C, 400 °C, 500 °C, 600 °C and 700 °C. After calcination was completed, the serpentine was sealed and stored.

**Preparation of dealkalized Csrp**

Ten grams of Csrp was placed in a 500 mL conical flask, and a certain amount of distilled water was added to dealkali the particles. The distilled water in the conical bottle was replaced at regular intervals until the particles no longer release alkalinity. The dealkalized particles were put into the oven to dry until a constant weight was reached.

**Test water sample**

The groundwater in Fuxin City, Liaoning Province, China contains high concentrations of fluoride (1.5–5.0 mg/L), iron (3.5–19.5 mg/L) and manganese (0.9–4.8 mg/L), and the pH is between 6.0 and 6.8. Due to the low oxygen content in the groundwater, iron and manganese are not easily oxidized and are often dissolved in the groundwater in the forms of Fe$^{2+}$ and Mn$^{2+}$. Thus, they were used as the research objects in this work. Considering the instability and complexity of actual groundwater, experimental water samples were configured to simulate the groundwater quality in the Fuxin area. The mass concentrations of F$^{-}$, Fe$^{2+}$ and Mn$^{2+}$ in the water samples were 5 mg/L, 20 mg/L and 5 mg/L, respectively, and the pH was adjusted to 6.5. In addition, to prevent Fe$^{2+}$ and Mn$^{2+}$ from being oxidized during the adsorption process, a nitrogen cylinder was used to keep the shaker box filled with nitrogen. Xie et al. (2015) also used this method when studying the adsorption of Fe$^{2+}$ and S$^{2-}$ by fermented rice husks.

**Experiment method**

**Modified Srp to remove fluoride, iron and manganese experiment**

Briefly, 150 mL of a composite water sample was added to an Erlenmeyer flask. Then, 300 mg of differently modified Srp was added to the flask, shaken, and then allowed to react for 120 min in a shaker at 180 rpm and 25 °C. Finally, the mass concentrations of F$^{-}$, Fe$^{2+}$, and Mn$^{2+}$ were measured.

**Experiments on the influence of Csrp removal performance**

The effects of the dose, reaction time, pH and reaction temperature on the removal of F$^{-}$, Fe$^{2+}$ and Mn$^{2+}$ by Csrp were investigated through batch tests. The adsorption capacity and removal rate of F$^{-}$, Fe$^{2+}$ and Mn$^{2+}$ by Csrp can be calculated using Equations (1) and (2):

$$q_e = \frac{(c_0 - c_e)V}{m}$$  \hspace{1cm} (1)

$$R = \frac{(c_0 - c_e)}{c_0} \times 100\%$$  \hspace{1cm} (2)

where $q_e$ is the adsorption capacity at equilibrium, mg/g; $c_0$ is the initial concentration of solution, mg/L; $c_e$ is the concentration of solution at adsorption equilibrium, mg/L; $V$ is the volume of solution, L; and $m$ is the mass of adsorbent, g.
Experiments on the influence of dealkalized Csrp removal performance

A total of 450 mg of dealkalized Csrp was weighed and added into 150 mL of a composite water sample containing F⁻, Fe²⁺ and Mn²⁺. The reaction was carried out in a constant temperature shaker at 35 °C, and the samples were sampled and filtered at a predetermined time to determine the concentrations of F⁻, Fe²⁺ and Mn²⁺ in the filtrate.

Adsorption kinetics

Briefly, 450 mg of Csrp was weighed and added to 150 mL of a composite water sample containing F⁻, Fe²⁺ and Mn²⁺. The oscillating reaction was carried out under optimal adsorption conditions (pH of 6, temperature of 35 °C). Samples were taken and filtered at predetermined times to determine the concentrations of F⁻, Fe²⁺ and Mn²⁺ in the filtrate. Quasi-first-order and quasi-second-order rate equations are often used to describe and analyse the kinetic process of solid-liquid adsorption, and the fitted correlation coefficient $R^2$ is used for fitting evaluation (Ijagbemi et al. 2010). The equations are as follows (Equations (3) and (4)):

Quasi-first-order kinetic equation:

$$\ln\left(\frac{q_e - q_t}{q_e}\right) = \ln\left(\frac{k_1}{2.303}\right) - k_1 \frac{t}{2.303}$$

(3)

Quasi-second-order kinetic equation:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$$

(4)

where $q_t$ (mg/g) is the amount of adsorbent at time t (min) and $k_1$ and $k_2$ are the adsorption rate constants, min⁻¹.

Adsorption isotherm

Briefly, 450 mg of Csrp was weighed and added to 150 mL of a composite water sample containing F⁻, Fe²⁺ and Mn²⁺. The sample was allowed to react at 25 °C, 30 °C, and 35 °C for 150 min before being filtered. The concentrations of F⁻, Fe²⁺ and Mn²⁺ in the filtrate were measured. Langmuir and Freundlich isotherm models were used to evaluate the maximum adsorption capacity and adsorption difficulty of Csrp for F⁻, Fe²⁺ and Mn²⁺ (Matouq et al. 2015). The equations are as follows (Equations (5) and (6)):

Langmuir isotherm adsorption equation:

$$\frac{c_e}{q_e} = \frac{1}{K_L q_m} + \frac{c_e}{q_m}$$

(5)

Freundlich isotherm adsorption equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e$$

(6)

where $q_m$ is the adsorption capacity at adsorption saturation, mg/g; $K_L$ is the Langmuir constant, L/mg; and $K_F$ and $n$ are Freundlich empirical constants.

Desorption and regeneration

To evaluate the availability of Csrp, Csrp with adsorbed ions was regenerated with 0.1 M NaCO₃ and 0.1 M HNO₃ solutions. Before this process, the adsorbed Csrp was pretreated, the unadsorbed ions on the surface of the Csrp were washed off with deionized water, filtered, and the Csrp was dried. The dried Csrp was added to 150 mL of Na₂CO₃ solution, and the mixture was shaken at 35 °C and 180 rpm for 150 min. Then, the Csrp was washed with deionized water to remove Na₂CO₃ from the surface. Subsequently, 150 mL of nitric acid solution was added to Csrp, and the mixture was shaken at 35 °C and 180 rpm for 150 min. Next, Csrp was washed with deionized water to remove nitric acid from the surface. Finally, the Csrp was dried at 110 °C for 2 h. After drying, Csrp was regenerated, and the adsorption test was carried out again for completely desorbed Csrp for a total of five cycles.
RESULTS AND DISCUSSION

Optimization the Srp modification methods

Natural Srp was modified by metal salt impregnation, acid-base activation and calcination, and the performance of the modified Srp in removing fluoride, iron and manganese was compared. The results are shown in Figure 1.

As shown in Figure 1(a), when the reaction time was less than 120 min, the removal rates of $F^-$, $Fe^{2+}$ and $Mn^{2+}$ by natural Srp all increased with increasing reaction time. As the reaction time continued to increase, the removal rates of $Fe^{2+}$ and $Mn^{2+}$ remained stable, while the removal rate of $F^-$ showed a downward trend. This is because with increasing reaction time, the increase in $OH^-$ released by Srp increases the electrostatic repulsion towards $F^-$, which affects the removal of $F^-$. In summary, 120 min was determined to be the best reaction time for natural Srp to adsorb $F^-$, $Fe^{2+}$, and $Mn^{2+}$. At this time, the removal rates of $F^-$, $Fe^{2+}$, and $Mn^{2+}$ were 73.4%, 92.1%, and 89.8%, respectively.

As shown in Figure 1(b), the removal rate of $F^-$ by metal salt-impregnated Srp increased with increasing metal salt concentration. This is because aluminium sulfate and calcium chloride adhere to the pores and surface of Srp, and when in contact with $F^-$ in solution, aluminium fluoride and calcium fluoride are generated and adsorbed on Srp, thus reducing the concentration of $F^-$ in solution (Zhai et al. 2010). The removal rates of $Fe^{2+}$ and $Mn^{2+}$ decreased with increasing metal salt concentration due to the enrichment of a large amount of $Al^{3+}$ and $Ca^{2+}$ in the modified Srp. These metal ions combine with the active groups in Srp to form complexes, occupying the effective sites for $Fe^{2+}$ and $Mn^{2+}$ adsorption on Srp. Additionally, due to a large amount of positively charged ions, the electrostatic repulsion towards $Fe^{2+}$ and $Mn^{2+}$ increases, which

Figure 1 | Removal rates of natural and modified Srp for fluoride, iron and manganese. (a) Natural, (b) metal salt impregnation, (c) acid-base activation, and (d) calcination.
affects the removal of Fe$^{2+}$ and Mn$^{2+}$. In summary, fluoride, iron and manganese removal effect on the same concentration of metal salt-impregnated Srp were opposite; thus, the simultaneous removal of all three ions could not be achieved.

Figure 1(c) shows that the removal rates of F$^-$, Fe$^{2+}$, and Mn$^{2+}$ are improved by modifying Srp with a proper amount of acid and base. This is because hydrochloric acid can dissolve impurities in Srp pores, thus improving its adsorption performance. Sodium hydroxide can chemically react with silica inside Srp to dissolve silicon, reduce the zeta potential, and improve the adsorption performance of Srp (Chen et al. 2021). When the concentration of hydrochloric acid exceeded 4%, the removal rates of F$^-$, Fe$^{2+}$, and Mn$^{2+}$ began to decrease, which may be due to the excessive acidity destroying the pores of Srp and resulting in reduced adsorption performance (Gong et al. 2020). When the concentration of sodium hydroxide exceeded 2%, the F$^-$ removal rate showed a downward trend. This is because with increasing alkalinity, some surface particles are negatively charged and electrostatically repel F$^-$, which reduces the adsorption of F$^-$ on Srp. The removal rates of Fe$^{2+}$ and Mn$^{2+}$ increased with increasing sodium hydroxide concentration because OH$^-$ can form Fe(OH)$_2$ and Mn(OH)$_2$ precipitates with Fe$^{2+}$ and Mn$^{2+}$, thereby increasing the removal of Fe$^{2+}$ and Mn$^{2+}$. The acid-base activated Srp could not achieve the simultaneous removal of fluoride, iron and manganese.

As shown in Figure 1(d), when the calcination temperature did not exceed 500 °C, the removal rates of F$^-$, Fe$^{2+}$ and Mn$^{2+}$ gradually increased with increasing calcination temperature. This is because the surface water and interlayer water of Srp will be lost after calcination at a high temperature, which further enhances the hydrophilicity of the silicon oxygen structure in Srp and increases the contact performance between Srp and various ions. When the temperature exceeded 500 °C, the removal rates of F$^-$, Fe$^{2+}$ and Mn$^{2+}$ began to decrease because the high temperature may change the internal skeletal structure of Srp, resulting in changes in its crystal lattice, morphology and phase and a reduction in the removal of F$^-$, Fe$^{2+}$ and Mn$^{2+}$. Cao et al. (2017) used thermally activated Srp to adsorb cadmium and reached a similar conclusion. The adsorption capacity of thermally activated Srp was higher than that of natural Srp, and its adsorption capacity was strongly dependent on the activation temperature. After analysis and comparison, Srp calcined at 500 °C showed the best simultaneous removal of F$^-$, Fe$^{2+}$ and Mn$^{2+}$.

In conclusion, compared with natural Srp, the removals of F$^-$, Fe$^{2+}$ and Mn$^{2+}$ by Srp modified with metal salt impregnation, acid-base activation and calcination all improved. Overall, calcination at 500 °C showed the best effect among the various modifications, with F$^-$, Fe$^{2+}$ and Mn$^{2+}$ removal rates of 91.8%, 95.7% and 94.7%, respectively.

Analysis of the factors influencing the removal of F$^-$, Fe$^{2+}$ and Mn$^{2+}$ on Csrp

Influence of the adsorbent dose

The pH was kept at 6.5, the temperature was 25 °C, and the reaction time was 120 min. The effects of the Csrp dose on the removal rates of F$^-$, Fe$^{2+}$ and Mn$^{2+}$ were analysed, and the results are shown in Figure 2(a). When the dose of Csrp did not exceed 450 mg, the removal rates of F$^-$, Fe$^{2+}$, and Mn$^{2+}$ increased with an increasing dose of Csrp. This is because with an increasing Csrp dose, the relative specific surface area and adsorption sites of Csrp increase; thus, the removal rates of F$^-$, Fe$^{2+}$ and Mn$^{2+}$ gradually increase (Xie et al. 2020). When the dose of Csrp exceeded 450 mg, the removal rate of F$^-$ began to decrease, and the removal rates of Fe$^{2+}$ and Mn$^{2+}$ tended to be stable. This was because the OH$^-$ released into the water by Csrp increased when the Csrp dose was increased. It can also be seen from the figure that the pH of the solution after the reaction increased as the Csrp dose increased. A large amount of OH$^-$ and F$^-$ resulted in electrostatic repulsion and a decrease in the F$^-$ removal rate. However, since the concentrations of Fe$^{2+}$ and Mn$^{2+}$ in the solution were constant, the removal rates of Fe$^{2+}$ and Mn$^{2+}$ remained basically unchanged as the Csrp dose continued to increase. In conclusion, when the Csrp dose was 450 mg (5 g/L), the removal effect of F$^-$, Fe$^{2+}$ and Mn$^{2+}$ was the best; the removal rates of F$^-$, Fe$^{2+}$ and Mn$^{2+}$ were 92.3%, 97.2% and 97.5%, respectively.

Effect of the reaction time

The Csrp dose was kept at 450 mg, the pH was 6.5, and the temperature was 25 °C while the Csrp reaction time was changed to analyse its influence on the removal rates of F$^-$, Fe$^{2+}$ and Mn$^{2+}$. The results are shown in Figure 2(b). Over the period of 30–150 min, with increasing reaction time, the removal rates of F$^-$, Fe$^{2+}$ and Mn$^{2+}$ increased significantly. This is because during the initial stage of the reaction, the surface of the adsorbent contains a large number of adsorption sites, which fully combine with each ion in the test water sample and result in a large increase in the removal of each ion. When the reaction time exceeded 150 min, the removal rate of F$^-$ began to decrease, while the removal rates of Fe$^{2+}$ and Mn$^{2+}$ tended to be

Uncorrected Proof
Considering the adsorption effects of $\text{F}^-/\text{C}_0$, $\text{Fe}^{2+}$ and $\text{Mn}^{2+}$, the optimal reaction time was determined to be 150 min, and the removal rates of $\text{F}^-/\text{C}_0$, $\text{Fe}^{2+}$ and $\text{Mn}^{2+}$ were 93.1%, 98.1% and 98.5%, respectively.

**Influence of the initial pH**

The Csrp dose was maintained at 450 mg, the reaction time was 150 min, and the temperature was 25 °C while the initial pH of the water sample was changed to analyse its effect on the removal rates of $\text{F}^-$, $\text{Fe}^{2+}$ and $\text{Mn}^{2+}$ by Csrp, as shown in Figure 2(c). The removal efficiencies of $\text{F}^-$, $\text{Fe}^{2+}$ and $\text{Mn}^{2+}$ were poor when the pH was less than 4, probably due to the loss of the $\text{Mg}^{2+}$ active sites of Csrp at lower pH (Sun et al. 2011). When the pH was 6, the $\text{F}^-$ removal rate reached its maximum because the Csrp surface was protonated and a positive charge was obtained. This increases the electrostatic attraction to $\text{F}^-$ and reduces the $\text{F}^-$ concentration. When the pH continued to increase, the $\text{F}^-$ removal rate began to decline because with increasing alkalinity, $\text{OH}^-$ in the solution began to compete with $\text{F}^-$ for adsorption, thereby decreasing the number of available adsorption sites. The removal rates of $\text{Fe}^{2+}$ and $\text{Mn}^{2+}$ increased with increasing pH. Due to the increase in pH, the content of $\text{OH}^-$ in solution increased, which promoted the removal of $\text{Fe}^{2+}$ and $\text{Mn}^{2+}$. After comprehensive consideration, the optimal reaction pH was determined to be 6, and the removal rates of $\text{F}^-$, $\text{Fe}^{2+}$ and $\text{Mn}^{2+}$ were 93.8%, 98.3% and 99.2%, respectively.

**Effect of the reaction temperature**

The Csrp dose was kept at 450 mg, the reaction time was 150 min, and the pH was 6 while the reaction temperature was changed to analyse its influence on the removal rates of $\text{F}^-$, $\text{Fe}^{2+}$ and $\text{Mn}^{2+}$. The results are shown in Figure 2(d). When
the reaction temperature was between 20 °C and 35 °C, the removal rates of F\(^-\), Fe\(^{2+}\) and Mn\(^{2+}\) increased with increasing temperature because the increase in temperature increased the activity of the reactants. From 35 to 45 °C, the removal rate of F\(^-\) began to decrease, and the removal rates of Fe\(^{2+}\) and Mn\(^{2+}\) increased. This was caused by the increase in reaction temperature promoting the release of OH\(^-\) from Csrp. When the temperature exceeded 45 °C, the removal rates of F\(^-\), Fe\(^{2+}\) and Mn\(^{2+}\) all began to decrease. This may be due to the weakness of the adsorptive forces between the active site of the adsorbent and the adsorbate species and between the adjacent molecules of the adsorbed phase (Al-Anber & Al-Anber 2008). After comprehensive analysis, the optimal reaction temperature was determined to be 35 °C, and the removal rates of F\(^-\), Fe\(^{2+}\) and Mn\(^{2+}\) were 94.3%, 99.0% and 98.9%, respectively.

Our research group previously studied a new type of adsorbent, Srp/HAP (Li et al. 2021a, 2021b), whose F\(^-\), Fe\(^{2+}\), and Mn\(^{2+}\) removal rates reached 98.6%, 99.9%, and 99.8%, respectively. Although the removal effect of Csrp is slightly lower than that of Srp/HAP, the preparation process of Csrp is simple, and the preparation cost is low. The most important thing is that the quality of the effluent treated by Csrp meets the drinking water standards set by the World Health Organization. Therefore, Csrp is also an excellent adsorbent for removing fluoride and iron and manganese.

**Analysis of removal of F\(^-\), Fe\(^{2+}\) and Mn\(^{2+}\) by dealkalized Csrp**

It can be seen from Figure 3 that the removal rates of F\(^-\), Fe\(^{2+}\) and Mn\(^{2+}\) by dealkalized Csrp were lower than those by Csrp. This result may be due to the release of alkalinity by Csrp during the reaction, which caused some Fe\(^{2+}\) and Mn\(^{2+}\) to be removed by precipitation. The removal of Fe\(^{2+}\) and Mn\(^{2+}\) by dealkalized Csrp was due to adsorption. The removal rates of Fe\(^{2+}\) and Mn\(^{2+}\) reached 95.2% and 96.1% after 150 min, and these rates are only 3.8% and 2.8% lower than that of Csrp. It shows that the removal of Fe\(^{2+}\) and Mn\(^{2+}\) by Csrp mainly occurs via adsorption, and precipitation is only a small factor. The slight decrease in the F\(^-\) removal rate may be due to the decrease in the OH\(^-\) content in the dealkalized Csrp, which reduces the ion exchange between F\(^-\) and OH\(^-\).

**Kinetic analysis**

The Csrp dose was kept at 450 mg, the pH was 6, and the reaction temperature was 35 °C. Samples were taken at pre-set times to determine the concentrations of F\(^-\), Fe\(^{2+}\) and Mn\(^{2+}\) in the filtrate, and kinetic equation fitting was performed. The fitting curves are shown in Figure 4, and the fitting parameters are shown in Table 1.

It can be seen from the fitting curves in Figure 3 and the fitting results in Table 1 that the adsorption of F\(^-\), Fe\(^{2+}\) and Mn\(^{2+}\) by Csrp is more in line with the quasi-second-order kinetic equation. The correlation coefficients (R\(^2\)) of the quasi-second-order kinetics for all ions are greater than 0.99, and the theoretical equilibrium adsorption capacities are closer to the
Figure 4 | Kinetic equation fitting for (a) fluoride, (b) iron, and (c) manganese.

Table 1 | Quasi-first-order and quasi-second-order kinetic fitting results

| Ion type | Concentration mg/L | Quasi first-order dynamics | Quasi second-order dynamics |
|----------|---------------------|----------------------------|-----------------------------|
|          |                     | $q_e$ mg/g | $k_1$/min | $R^2$ | $q_e$ mg/g | $k_2$/min | $R^2$ |
| F$^-$    | 5                   | 0.7198     | 0.0158    | 0.9030 | 1.7198     | 0.0775    | 0.9986 |
|          | 10                  | 0.7807     | 0.0041    | 0.8519 | 3.0443     | 0.1184    | 0.9994 |
|          | 20                  | 0.6797     | 0.0154    | 0.9449 | 2.9202     | 0.1026    | 0.9993 |
| Fe$^{2+}$| 20                  | 1.4270     | 0.0179    | 0.8472 | 7.0827     | 0.0143    | 0.9986 |
|          | 30                  | 1.5342     | 0.0219    | 0.9256 | 5.7382     | 0.0135    | 0.9980 |
|          | 40                  | 1.1172     | 0.0069    | 0.8978 | 4.0426     | 0.0325    | 0.9991 |
| Mn$^{2+}$| 5                   | 1.2411     | 0.0327    | 0.9759 | 2.6714     | 0.0327    | 0.9980 |
|          | 10                  | 0.9807     | 0.0077    | 0.8583 | 2.3327     | 0.0377    | 0.9980 |
|          | 20                  | 0.8525     | 0.0136    | 0.9115 | 1.9884     | 0.0471    | 0.9988 |
The quasi-second-order kinetic equation assumes that the adsorption rate is constrained by chemisorption (Wang et al. 2021), indicating that the removal of $F^-$, $Fe^{2+}$ and $Mn^{2+}$ by Csrp is mainly by chemisorption.

**Adsorption isotherm**

The effects of different initial concentrations of $F^-$, $Fe^{2+}$ and $Mn^{2+}$ on the adsorption capacity of Csrp are shown in Figure 5 when the dose of Csrp was 450 mg, the pH was 6, and the reaction time was 150 min. Figure 5 shows that the adsorption capacities of $F^-$, $Fe^{2+}$ and $Mn^{2+}$ on Csrp increased with increasing reaction temperature and initial ion concentrations. With increasing initial ion concentrations, the active adsorption sites on the surface of the adsorbent gradually tend to be saturated, and thus, the adsorption capacity tends to plateau.

Table 2 shows the fitting results of the isothermal adsorption model. The correlation coefficient $R^2$ fitted by the Langmuir model for each ion is greater than 0.98, and the correlation coefficient $R^2$ fitted by the Freundlich model is greater than 0.96. The Langmuir isotherm model can better simulate the adsorption of $F^-$, $Fe^{2+}$ and $Mn^{2+}$ by Csrp, and the adsorption process of each ion conforms to monolayer adsorption. At 35 °C, the maximum monolayer saturated adsorption capacity $q_m$ values of Csrp for $F^-$, $Fe^{2+}$ and $Mn^{2+}$ were 6.6774 mg/g, 11.0473 mg/g and 9.9315 mg/g, respectively. Moreover, as seen from Table 3, Csrp has a higher adsorption capacity than most other adsorbents reported; thus, Csrp can be considered a potentially highly efficient adsorbent with the ability to synchronously remove $F^-$, $Fe^{2+}$ and $Mn^{2+}$ from aqueous solutions.

![Figure 5](http://iwaponline.com/ws/article-pdf/doi/10.2166/ws.2021.439/978806/ws2021439.pdf)
Analysis of adsorption regeneration

After 5 regeneration cycles, the removal rates of $F^-$, $Fe^{2+}$, and $Mn^{2+}$ by Csrp are shown in Figure 6. As shown in Figure 6, after five cycles of regeneration, the removal rates of $F^-$, $Fe^{2+}$, and $Mn^{2+}$ by Csrp decreased, which may be related to the incomplete elution of adsorbents. However, the removal rates of $F^-$, $Fe^{2+}$, and $Mn^{2+}$ remained above 83%, indicating that Csrp still

Table 2 | Fitting parameters of the adsorption thermodynamics

| Ion type | Temperature °C | Langmuir | | Freundlich |
|----------|----------------|----------|---|-------------|
|          |                | $q_m$ (mg/g) | $K_L$ | $R^2$ | $K_F$ | $1/n$ | $R^2$
| $F^-$    | 25             | 3.8001    | 0.9994 | 0.9988 | 2.2539 | 0.1519 | 0.9793 |
|          | 30             | 5.4212    | 0.4191 | 0.9859 | 2.5215 | 0.1958 | 0.9818 |
|          | 35             | 6.6774    | 0.6539 | 0.9945 | 3.0642 | 0.2302 | 0.9947 |
| $Fe^{2+}$| 25             | 9.4047    | 1.4628 | 0.9993 | 7.5058 | 0.0564 | 0.9858 |
|          | 30             | 10.6530   | 0.8059 | 0.9969 | 7.7244 | 0.0721 | 0.9663 |
|          | 35             | 11.0473   | 0.8264 | 0.9954 | 7.9446 | 0.0747 | 0.9635 |
| $Mn^{2+}$| 25             | 7.7453    | 0.7759 | 0.9963 | 4.3481 | 0.1585 | 0.9920 |
|          | 30             | 8.7352    | 0.6472 | 0.9927 | 4.6410 | 0.1685 | 0.9902 |
|          | 35             | 9.9315    | 0.6741 | 0.9907 | 5.1335 | 0.1797 | 0.9911 |

Table 3 | Comparison of the adsorption performance of different adsorbents for $F^-$, $Fe^{2+}$, and $Mn^{2+}$

| Adsorbents | $q_e$ of $F^-$ (mg/g) | $q_e$ of $Fe^{2+}$ (mg/g) | $q_e$ of $Mn^{2+}$ (mg/g) | References |
|------------|-----------------------|---------------------------|---------------------------|------------|
| Ti-zeolite | 1.511                 | –                         | –                         | Ma et al. (2018) |
| Carboxylated chitosan beads | 1.385               | –                         | –                         | Viswanathan et al. (2009) |
| Natural stilbite zeolite modified with Fe(III) | 0.540                 | –                         | –                         | Sun et al. (2011) |
| Granular activated carbon | –                    | 4.951                     | 0.791                     | Goher et al. (2015) |
| Amberlite IR-120H | –                    | 4.071                     | 0.967                     | Shavandi et al. (2012) |
| Slovakian natural zeolite | –                    | 1.157                     | 0.075                     | Present work |
| Csrp      | 1.572                 | 6.600                     | 1.648                     | Present work |

Figure 6 | Percentages of $F^-$, $Fe^{2+}$, and $Mn^{2+}$ removal by Csrp in different cycles.
had good reusability. Thus, Csrp can be used as an effective adsorption material for treating groundwater that contains F\(^-\), Fe\(^{2+}\) and Mn\(^{2+}\).

**Evaluating the cost of the treatment**

Both the effects of the treatment and the cost of the water treatment process should be considered. It can be seen from Table 4 that compared with membrane treatment and other adsorbent, Csrp water treatment has a lower cost, and its regeneration cost is reasonable.

**Microscopic characterization and adsorption mechanism analysis of Csrp**

**X-ray diffraction analysis**

Figure 7 shows the X-ray diffraction patterns of Srp and Csrp before and after adsorption. Figure 7 shows that Srp is mainly composed of Mg\(_3\)Si\(_2\)(OH)\(_4\)O\(_5\) and that there are 3 characteristic peaks at 2\(\theta\) values of 12.16°, 24.68°, and 35.56°. The diffraction peaks of Csrp were consistent with natural Srp, indicating that the Srp structure was almost unchanged after calcination at 500 °C. After adsorption, new characteristic peaks appeared in Csrp, which were analysed by XRD software as Fe\(_3\)Si\(_2\)(OH)\(_4\)O\(_5\), Mn\(_3\)Si\(_2\)(OH)\(_4\)O\(_5\) and MgSiF\(_6\)·6H\(_2\)O. It is speculated that F\(^-\) can exchange ions with OH\(^-\) and form organo-silicon bonds with unsaturated Si-O-Si bonds. Additionally, the ion-exchange reaction of Fe\(^{2+}\) and Mn\(^{2+}\) with Mg\(^{2+}\) occurred to form these three new substances (Li et al. 2003).

**SEM and EDS analysis**

As shown in Figure 8(a), the surface of Srp presents a porous curled structure, and flaky structures are superimposed on each other on the surface. There are obvious textures and concave-convex structures among the textures. This special structure increases the specific surface area of Srp and gives Srp a certain physical adsorption capacity. As shown in Figure 8(b),

| Material cost            | Water treatment cost (pound/m\(^3\)) | Regeneration cost (pound/kg) | References     |
|--------------------------|--------------------------------------|-----------------------------|----------------|
| ESPA4040 membrane (169.84 pound/piece) | 0.17                                 | —                           | Ma (2010)      |
| Modified zeolite (0.04 pound/kg)       | 0.10                                 | 0.022                       | Zuo et al. (2019) |
| Csrp (0.03 pound/kg)                     | 0.09                                 | 0.017                       | Present work   |

**Figure 7** | XRD patterns of Srp, Csrp and Csrp after reaction.
the surface structure of Srp calcined at 500 °C did not change significantly, indicating that the structure of Srp does not change significantly at a lower calcination temperature. Cao et al. (2019) used thermally activated Srp to adsorb Pb²⁺ and found that the structure of Srp did not change significantly at a lower thermal activation temperature (<550 °C). The XRD analysis results of Srp before and after calcination were confirmed. As shown in Figure 8(c), after the treatment of the test water sample, the pores on the surface of Csrp became significantly smaller, and the amount of fine flocculent crystals increased. It is speculated that F⁻, Fe²⁺, and Mn²⁺ may physically adsorb on the surface of Csrp or that a surface coordination reaction may have taken place.

Using an energy spectrometer to further determine the elements in the material, it can be seen from Figure 8(d) and 8(e) that Srp mainly contained O, Mg, and Si. After calcination, the content of O decreased, while the contents of magnesium and silicon increased, indicating that the dehydroxylation process occurred during the thermal activation of Srp. The EDS after adsorption (Figure 8(f)) showed F, Fe, and Mn, while the weight fraction of O decreased from 53.43% before adsorption to 46.70%, and the weight fraction of Mg decreased from 25.52% before adsorption to 17.53%. This further demonstrated that the ion-exchange reactions between F⁻ and OH⁻ and between Fe²⁺/Mn²⁺ and Mg²⁺ are in good agreement with the XRD analysis results.

**FTIR spectroscopy**

To understand the changes in the functional groups of Srp and Csrp before and after adsorption, FTIR spectroscopy was performed, and the results are shown in Figure 9. The infrared absorption peak of Csrp was very similar to that of natural Srp, indicating that the structure of serpentine did not change significantly after calcination and further confirming the XRD and SEM analysis results. The absorption peaks at 630.72 cm⁻¹ and 3,676.32 cm⁻¹ belonged to the Mg-OH stretching vibration. The absorption peaks of Csrp after adsorption were significantly weakened at these two points, indicating that the ion-exchange reactions between F⁻ and OH⁻ and between Fe²⁺/Mn²⁺ and Mg²⁺ occurred. In addition, the vibration peaks at 455.20 cm⁻¹ and 985.62 cm⁻¹ were attributed to Si-O bond stretching vibrations. After the reaction, the vibration peak of Csrp Si-O was weakened. This shows that F⁻, Fe²⁺, and Mn²⁺ may undergo surface coordination with the unsaturated Si-O-Si bond. The absorption peak at 1,452.4 cm⁻¹ was CO₃²⁻ (Selim et al. 2018), which may be because natural Srp absorbs
CO2 in the atmosphere and reacts to form carbonate groups. During the adsorption test, CO3\(^{2-}\) combined with H\(^+\) in the solution to produce CO\(_2\) gas that escaped; thus, the vibration peak of Srp at 1,452.4 cm\(^{-1}\) disappeared after the reaction.

**Analysis of the removal mechanism**

The removal of fluoride, iron and manganese by Csrp is mainly chemical adsorption, including ion exchange and surface coordination, and a small amount of metal ions are removed by precipitation. The specific analysis is as follows:

1. **Ion exchange:** At the beginning of the reaction, there was more H\(^+\) in the solution, which made the Csrp surface positively charged, and F\(^-\) could be adsorbed to the Csrp surface by electrostatic attraction. As the reaction went on, the pH of the solution increased, resulting in more OH\(^-\) in the solution, and Fe\(^{2+}\) and Mn\(^{2+}\) also accumulated on the Csrp surface due to electrostatic attraction. The Csrp then released an equivalent ion to exchange with it. The reaction equations are shown in (7) (8) and (9):

\[
\text{OH}^- + \text{Mg}^2+ + 2F^- \rightarrow F^- + \text{Mg}^2+ + 2\text{OH}^- \\
3\text{Fe}^{2+} + 2\text{Mg}_3\text{Si}_2(\text{OH})_4\text{O}_5 \rightarrow 2\text{Fe}_3\text{Si}_2(\text{OH})_4\text{O}_5 + 3\text{Mg}^{2+} \\
3\text{Mn}^{2+} + 2\text{Mg}_3\text{Si}_2(\text{OH})_4\text{O}_5 \rightarrow 2\text{Mn}_3\text{Si}_2(\text{OH})_4\text{O}_5 + 3\text{Mg}^{2+}
\]

2. **Surface coordination:** The unsaturated Si-O-Si bond has high chemical activity, can displace iron and manganese from the solution, and can adsorb fluoride to make it fixed on the surface. We found in FTIR analysis that the absorption peak of Si-O-Si was weakened, which further confirmed this speculation. The specific process is shown in Equations (10)–(12):

\[
\text{Si} - \text{O} - \text{Si} = + \text{NaF} \rightarrow \text{Si} - \text{O} - \text{Na} + = \text{Si} - \text{F} \\
\text{Si} - \text{O} - \text{Si} = + \text{Fe} - \text{OH} \rightarrow \text{Si} - \text{O} - \text{Fe} + = \text{Si} - \text{OH} \\
\text{Si} - \text{O} - \text{Si} = + \text{Mn} - \text{OH} \rightarrow \text{Si} - \text{O} - \text{Mn} + = \text{Si} - \text{OH}
\]

3. **Precipitation:** Some iron and manganese may have been removed by precipitation because Csrp releases alkalinity during the reaction, resulting in an increase in the pH of the solution system, which in turn induces heavy metal ions to precipitate. Guo & Yuan (2000) also obtained similar conclusions in the serpentine adsorption test for heavy metal ions.

The specific removal process is shown in Figure 10.
CONCLUSIONS

(1) Csrp has good performance in removing fluoride, iron and manganese. The best modification conditions were calcination at 500 °C for 120 min. The best conditions for Csrp to treat composite water samples with $F^-$, $Fe^{2+}$ and $Mn^{2+}$ at mass concentrations of 5 mg/L, 20 mg/L and 5 mg/L were as follows: a Csrp dose of 3 g/L, a pH of 6, a reaction temperature of 35 °C, and a reaction time of 150 min; the removal rates of $F^-$, $Fe^{2+}$ and $Mn^{2+}$ from the test water samples were 94.3%, 99.0%, and 98.9%, respectively. The quality of the treated water meets the drinking water standards set by the World Health Organization.

(2) The adsorption process of Csrp for the simultaneous removal of $F^-$, $Fe^{2+}$ and $Mn^{2+}$ was more in line with the quasi-second-order kinetic model and Langmuir model. This result indicated that Csrp not only physically adsorbed but also chemically adsorbed $F^-$, $Fe^{2+}$ and $Mn^{2+}$, and the adsorption process was single-layer adsorption.

(3) SEM, EDS, XRD, and FTIR spectroscopy were used to analyse Srp and Csrp before and after reaction. The results show that Srp underwent a dehydroxylation reaction during high-temperature calcination, which enhanced the ability of Srp to remove fluoride, iron and manganese. After reaction, new compounds, namely, $MgSiF_6 \cdot 6H_2O$, $Mn_3Si_2(OH)4O_5$, and $Fe_3Si_2(OH)4O_5$, were produced.

(4) After desorbing the adsorbed ions on Csrp, Csrp maintains good removal performance after 5 adsorption-desorption cycles. Csrp can be used as an excellent adsorbent for $F^-$, $Fe^{2+}$ and $Mn^{2+}$ in groundwater.

(5) At present, it is difficult to find adsorbents that can simultaneously remove fluoride, iron, and manganese. The adsorbents that we developed can achieve this effect. However, we are currently in the laboratory research stage, and other issues such as the amount of wastewater generated in the process of preparing future engineering applications need to be further studied.

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DATA AVAILABILITY STATEMENT

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