Intercalation of Mn²⁺ ions onto bentonite clay: implications in groundwater defluoridation

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Abstract

Fluorosis is a chronic disease caused by drinking water with a fluoride concentration greater than 1.5 mg/L for extended periods of time. The disease is manifested by tooth decay in dental fluorosis and deformation of bones in skeletal fluorosis. The World Health Organization (WHO) has set fluoride limits in drinking water at 1.5 mg/L. Most rural areas of South Africa depend on groundwater as a source of drinking water. However, groundwater in some of the boreholes has a concentration of fluoride above the permissible limit and will require defluoridation. The present work aims at evaluating the use of Mn²⁺ intercalated bentonite clay for defluoridation of groundwater. Clay was characterized for mineralogy using X-ray diffraction (XRD) and elemental composition using X-ray fluorescence (XRF) and morphology using scanning electron microscopy (SEM). Batch experiments were conducted to evaluate and optimize various operational parameters such as contact time, adsorbent dose, pH and initial adsorbate concentration. Optimum operation conditions for adsorption of fluoride were established to be 30 min contact time 1.0 g/100 mL adsorbent dosage, 3 mg/L adsorbate concentration and pH of 2. Maximum percentage F⁻ removal of 84.0% was achieved at optimized conditions. Mn²⁺ intercalated bentonite clay removed ≈ 55.89% of fluoride from field water. The study shows that Mn²⁺ intercalated bentonite clay has potential for application in defluoridation of groundwater.
Keywords: batch experiments, fluorosis, bentonite clay, defluoridation.

1   Introduction

Fluoride in drinking water may have beneficial or harmful effects on human health depending on its concentration. Optimal concentration of fluoride in drinking water set by the World Health Organization is at 1.5 mg/L [1]. A concentration higher than this can lead to fluorosis. The disease is manifested by mottled teeth in dental fluorosis and deformation of bones in skeletal fluorosis [2]. Groundwater in many regions contains fluoride concentration greater than 1.5 mg/L and will therefore require defluoridation. Various techniques such as precipitation, co-precipitation, ion exchange and adsorption for defluoridation of groundwater have been reviewed by Meenakshi and Maheshwari [3]. Among these techniques, adsorption is widely used because of its viability and sustainability since it uses locally available and cost effective materials. It involves the passage of high fluoride water through an adsorbent bed, where fluoride is removed by physical ion-exchange or surface chemical reaction with adsorbent. Various adsorbents have been tested for fluoride removal, including activated alumina [4], Cuttlefish bones [5], red mud [6] and clay soils [2]. Recently more studies are focusing on the use of clay soils for defluoridation due to their good adsorptive properties such as large specific surface area, chemical and mechanical stability, layered structure and high cation exchange capacity [7]. Bentonite clay belongs to the class of alumino-silicate clay group, which comprises of layers of alumino-silicate sheets. It exhibits a high cation exchange capacity and low permeability [8]. Bentonite has a permanent negative charge caused by the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer. These negative charges are balanced by the presence of exchangeable cations (Na^+, Ca^{2+} and K^+) in the lattice structure, which imparts high cationic exchange to the clay [9, 10]. Bentonite modified with high ionic density ions such as Fe^{3+}, Al^{3+} and Mg^{2+} has shown higher capacity for anion adsorption. The objectives of the present work are as follows: (1) Physicochemical characterization of raw and Mn^{2+} modified bentonite, (2) to optimize the loading of Mn^{2+} onto raw bentonite inter-layers, (3) to evaluate the effect of various operating parameters (contact time, adsorbent dosage, adsorbate concentration and pH) on the adsorption capacity of F^- by Mn^{2+} modified bentonite clay.

2   Material and methods

2.1 Sample collection

Bentonite clay used in this project was collected from ECCA Pty (Ltd) in Cape Town. Field water was collected from a community borehole in Siloam, Vhembe district in South Africa. All reagents and TISAB-III were obtained from Rochelle Chemicals & Lab Equipment CC, South Africa Ltd. A stock solution containing 1000 mg/L fluoride was prepared by dissolving 2.21 g Analytical grade sodium fluoride in 1 L of ultra-pure water (18.2 MΩ.cm^{-1}) and fluoride solutions for batch experiments were prepared from fresh stock fluoride solution by appropriate

dilution. Mn^{2+} stock solution containing 1000 mg/L was prepared by dissolving 2.29 g of analytical manganese chloride in 1 L of ultra-pure water.

2.2 Preparation and synthesis of Mn^{2+} modified bentonite clay

Raw bentonite clay was washed by mixing with ultra-pure water at a ratio of 1:5 in a 1000 mL beaker, the mixture was stirred for 5 min, and the procedure was repeated twice. After stirring, mixtures were agitated for 15 min using Stuart reciprocating shaker and then centrifuged for 10 min at 5 000 rpm. Samples were then dried in an oven for 12 hrs at 110°C. Clay samples were then milled to pass through <250 µm sieve. Optimum conditions (i.e., contact time, adsorbate concentration, adsorbent dosage, and pH) for modifying bentonite clay with Mn^{2+} ion were evaluated using batch experiments. The obtained conditions were: 60 min contact time, 4 g/100 mL adsorbent dosage, 50 mg/L Mn^{2+} adsorbate concentration and initial pH of 8. To synthesize Mn^{2+} modified bentonite, 200 mL of 50 mg/L Mn^{2+} solution was mixed with 8 g of raw bentonite to make up S/L ratio of 4 g/100 mL, the pH of the mixture was then adjusted to 8 using 0.1 M NaOH and 0.1 M HCl. The mixture was put on a 1 L Erlenmeyer flask in order to avoid spillage during agitation. The mixture was agitated for 60 min at 250 rpm on a table shaker and filtered. The solid residue left on the filter paper was dried for 12 hrs at a temperature of 105°C in the oven. The modified clay was then milled to pass through <250 µm sieve. The experiments were repeated five times to generate enough Mn^{2+} modified bentonite for subsequent experiments.

2.3 Physicochemical and mineralogical characterization

Mineralogical and chemical composition of Mn^{2+} bentonite clay was evaluated using XRD and XRF techniques respectively. Surface morphology was determined using Scanning electron microscopy (SEM) (Leo1450 SEM, at 10Kv, working distance 14mm). Properties were compared to those of raw bentonite clay soils.

2.4 Batch defluoridation experiments

Batch experiments were carried out to evaluate the effects of contact time, effect of adsorbent dosage, adsorbate initial concentration and the effect of pH on fluoride adsorption,. The fluoride concentration in the treated samples was measured using an ion selective electrode 9609 BNWP Orion (USA) attached to Thermo Scientific Orion Star ISE/pH/EC meter. Similar ion meter coupled with pH and EC electrode was used for measuring pH and EC of the treated samples. For residual fluoride, ion selective electrode was calibrated with four standards containing 1 mL of total ionic strength buffer (TISAB III) per 10 mL of solution. Same ratio was maintained for the sample. TISAB was added to decomplex F^- from Al^{3+}, Fe^{3+} and Si^{4+} fluorocomplexes and to maintain pH at between 5.2 and 5.5. All experiments were conducted in triplicate for better accuracy and the mean values were reported. Equations (1) and (2) were used to calculate the percentage removal and adsorption capacity respectively.

$$\% \ removal = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \tag{1}$$

where: C_o is initial fluoride ion concentration and C_e is equilibrium fluoride ion concentration.

$$Q = \left(\frac{C_o - C_e}{m}\right) \times v \tag{2}$$

where: C_i = initial F⁻ concentration (mg/L), C_e = F⁻ concentrations at equilibrium (mg/L), V = Volume of solution (L) and m = Weight of the adsorbent (g).

3   Results and discussion

3.1 Physicochemical characterization

3.1.1 X-ray diffraction analysis
X-ray diffraction spectra of raw and Mn^{2+} modified bentonite clay is presented in Figure 1. Analysis confirms the presence of montmorillonite and quartz as the major minerals and muscovite as one of the trace minerals of bentonite clay. No change in mineralogy of bentonite clay observed after modification with Mn^{2+} ions.
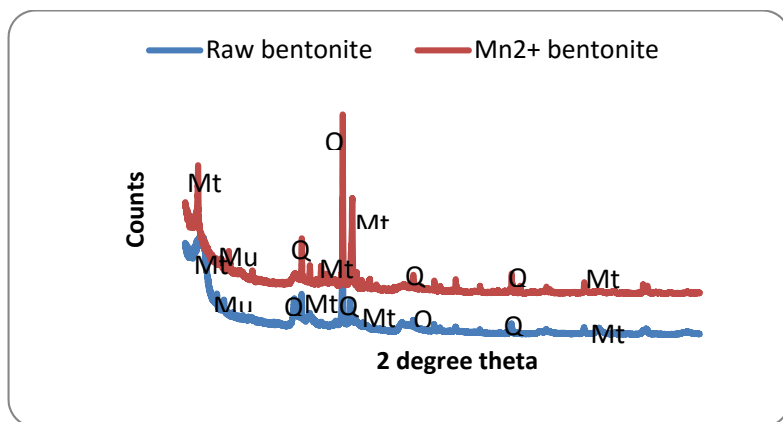

Figure 1:   X-ray diffraction spectra for raw and Mn^{2+} bentonite.

3.1.2 X-ray fluorescence analysis
The results for major chemical components are reported as percentage oxide in Table 1. The analysis reveals that silica (SiO_2) is the main component of bentonite clay while Al_2O_3 is the main minor component. High concentration of SiO_2 and Al_2O_3 reveal that bentonite clay is an alumino-silicate material. Manganese oxide is higher in Mn^{2+} bentonite (0.29%) than in raw bentonite (0.09%). The relatively high concentrations of MgO, Na_2O, CaO, and K_2O indicates that Mg^{2+}, Na^+, Ca^{2+}, and K^+ are the main exchangeable cations and main charge balancing cations in the clay interlayers. This is confirmed by the subsequent decrease of the content of these chemical species in the Mn^{2+} modified bentonite clay.

Table 1:   Chemical composition of raw and Mn^{2+} modified bentonite clay.

Oxide	Raw bentonite (W/W%)	Mn^{2+} bentonite (W/W%)
Al_2O_3	15.30	15.84
CaO	0.88	1.50
Cr_2O_3	0.01	0.00
Fe_2O_3	3.41	3.18
K_2O	0.98	0.39
MgO	3.20	3.06
MnO	0.06	0.29
Na_2O	2.12	0.94
P_2O_5	0.09	0.04
SiO_2	66.88	62.48
TiO_2	0.46	0.12
L.O.I.	6.45	11.65
Sum of Conc.	99.89	99.49

3.1.3 Scanning electron microscopy (SEM) analysis

SEM analysis was conducted to assess the effect of modification on the surface morphology of the bentonite clay. Figure 2 shows the surface morphology of raw and Mn^{2+} bentonite clay at 20,000x and 40,000x magnification. The analysis reveals that raw bentonite has flat and spongy like material. After the modification
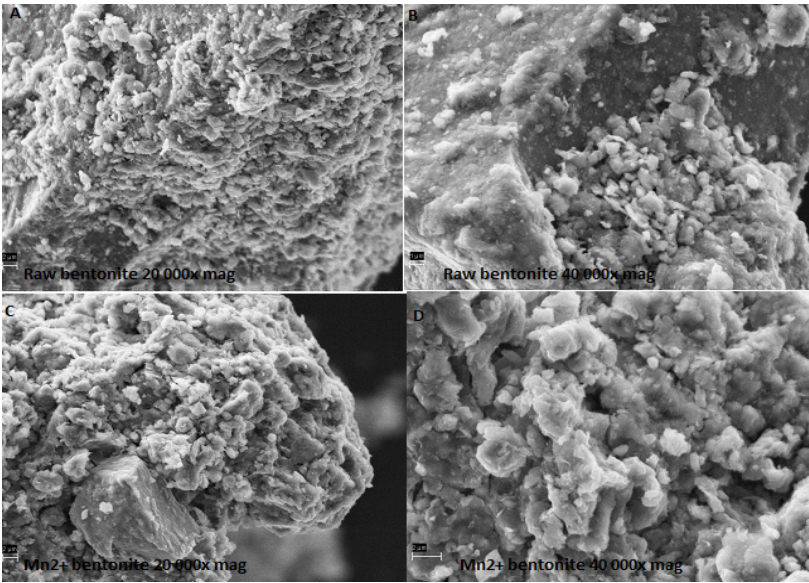

Figure 2:   Surficial morphology of raw and Mn^{2+} modified bentonite.

of bentonite, the analysis reveals the formation of larger agglomerate and specs on the surface on the surface of clay platelets. This could be due to swelling during the treatment by Mn^{2+} ions and formation of manganese hydroxides precipitates on the clay surface.

3.2 Batch experiments

3.2.1 Effects of contact time
The effect of contact time on the adsorption of F^- onto Mn^{2+} bentonite clay was evaluated by varying contact time from 5 to 270 min at various adsorbent dosages (0.1, 0.3, 0.5 g/100 mL), 3 mg/L initial F^- concentration, pH 5.54 ± 0.5 and 250 rpm shaking speed. The results are represented in Figure 3.

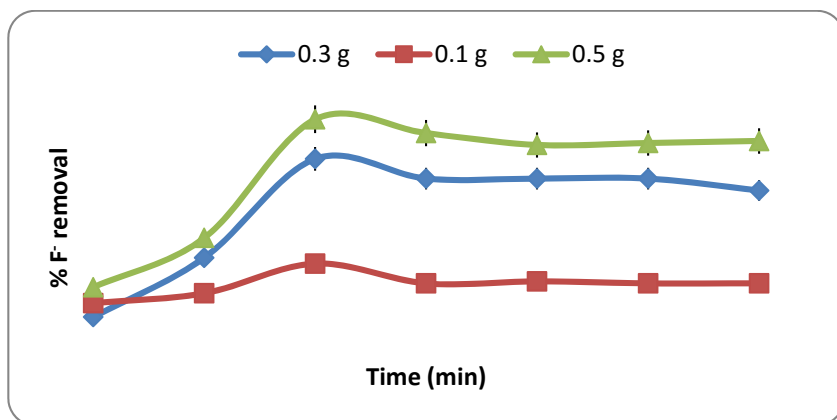
Figure 3:   Effect of contact time on %F^- removal.

From the results in fig. 3 it is observed that F^- removal was rapid during the first 30 min of the experiment where optimum uptake of F^- was achieved and thereafter decreased gradually up to 60 min thereafter no significant change in percentage F^- removal was observed indicating that equilibrium was reached within 30 min. The increase in fluoride removal may be attributed to the availability of sorption sites in the adsorbent and the decrease may be due to the saturation of the adsorbent surface with time. The same trend was observed at other adsorbent dosages. The percentage F^- removal was also observed to be increase with increase in adsorbent dosage. Contact time of 30 min was taken as the optimum time and was applied in subsequent experiments.

3.2.2 Effect of adsorbent dosage
The effect of adsorbent dosage on the adsorption of F^- onto Mn^{2+} bentonite clay was evaluated at 30 min contact time at shaking speed of 250 rpm, 3 mg/L initial concentration of F^- and pH of 5.54 ± 0.5. The adsorbent dosage was varied from 0.1 g/100 mL to 2 g/100 mL. The plot of percentage fluoride removal and adsorption capacity against adsorbent dosage is presented in Figure 4.
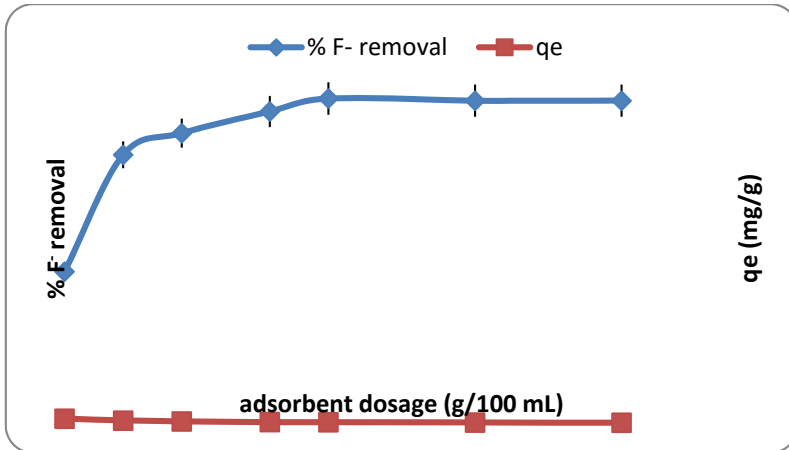
Figure 4:   Effect of adsorbent dosage on %F⁻ removal.

Figure 4 shows the relationship between percentage fluoride removal, adsorption capacity and adsorbent dosage. It is observed that percentage fluoride removal onto Mn^{2+} modified bentonite clay increased with an increase in the adsorbent dosage from 0.1 up to 1 g/100 mL were optimum uptake occurred. This may be attributed to the increase in the sorption sites for fluoride ions as the adsorbent dosage increases. No significant change observed after 1 g/100 mL adsorbent dosage this may be attributed to too many sites are available for limited quantity of adsorbate. The adsorption capacity on the other hand decreased with increase in adsorbent dosage. At the dosage of 1 g/100 mL, about 50% of fluoride was removed and this dosage was taken as the optimum and was used in subsequent experiments.

3.2.3 Effect of adsorbate concentration

The effect of initial concentration in the adsorption of F⁻ onto Mn^{2+} bentonite clay was evaluated at various contact times (30, 60 and 120 min), at 250 rpm shaking speed, 1.0 g/100 mL adsorbent dosage and pH of 5.54±0.5. The initial concentration was varied from 3 mg/L to 25 mg/L. Plot of percentage removal with adsorbate concentration is presented in Figure 5.

Figure 5 shows the effect of adsorbate concentration on the percentage fluoride removal at various contact times, it is observed that the percentage removal decreased with an increase in the initial concentration, the same trend was observed at other contact times. This is due to availability of more fluoride ions in solution at higher concentration and the adsorption sites become the limiting factor in the adsorption process. At contact times > 30 min the adsorption capacity was lower, this was earlier observed in the contact time experiments where maximum absorption was at 30 min. Initial adsorbate of 3 mg/L was taken as the optimum concentration for subsequent experiments.
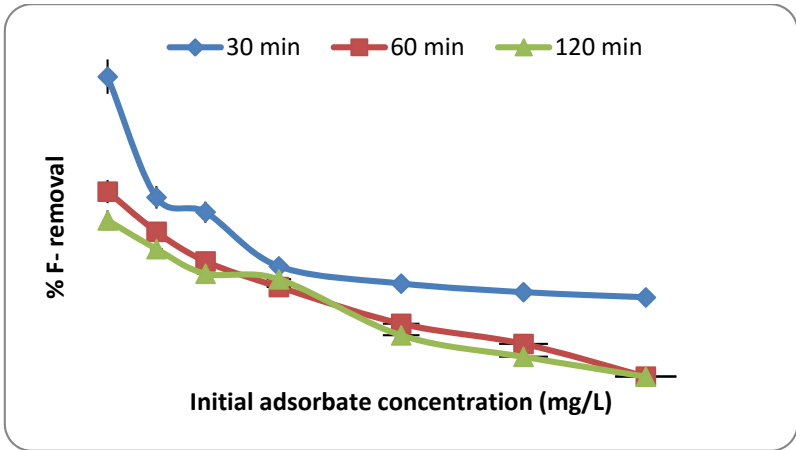
Figure 5:   Effect of adsorbate concentration of %F⁻ removal.

3.2.4 Effects of pH

To study the effects of pH in the adsorption of F⁻ onto Mn^{2+} bentonite clay, the initial pH was adjusted from 2 to 12 using 0.1 M NaOH and 0.1 M HCl. The effect of pH was evaluated under the condition of 30 min contact time at 250 rpm, 1.0 g/100 mL adsorbent dosage, 3 mg/L initial concentration. The plot of pH with percentage F⁻ removal is shown in Figure 6.
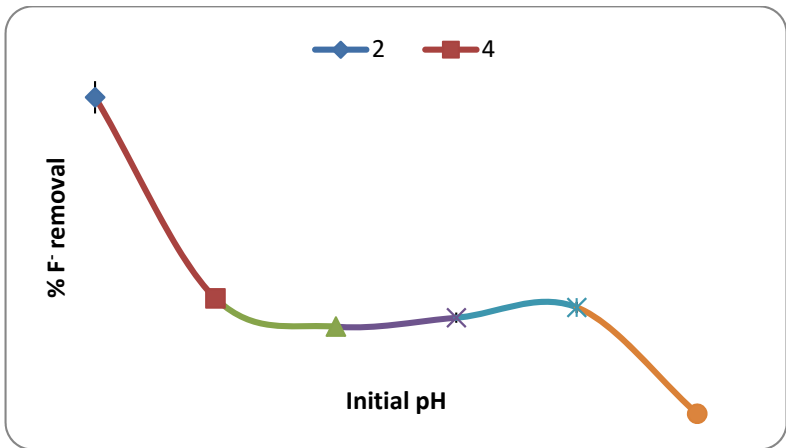

Figure 6:   Effect of pH on %F⁻ removal.

pH of the medium is the most important parameter that influences the fluoride removal and helps in elucidating fluoride uptake mechanisms of the adsorbent. From the results in Figure 6, it is observed that % fluoride removal decreases with an increase in initial pH, from 84% removal at pH 2 to 24.33% at pH 6, thereafter

a slight increase was observed up to 30% at pH 10. The drastic decrease in F$^-$ removal was observed at pH beyond 10. This may be due to the abundance of OH$^-$ ions in alkaline pH that compete with F$^-$ for adsorption sites. Fluoride adsorption onto Mn^{2+} bentonite occurred via ligand exchange at lower pH and ion exchange at higher pH.

4   Defluoridation of field water

The effectiveness of Mn^{2+} bentonite clay in fluoride removal was tested on field water from Siloam community borehole containing 5.4 mg/L fluoride ion concentration. Field water was treated at its natural pH, adsorbent dosage 1.0 g/100 mL and the mixture was agitated for 30 min at 250 rpm shaking speed. Results are presented in Table 2.

Table 2:   Physicochemical parameters of field water before and after treatment.

Parameters	Before treatment	After treatment (initial pH adjusted to 2)
pH	8.62	3.2
Conductivity (μS/cm)	338	402
Total dissolved solids (mg/L)	203	84.1
F$^-$ (mg/L)	5.4	2.7
Cl$^-$ (mg/L)	31.59	37.15
SO$_4^{2-}$ (mg/L)	11.89	11.89
NO$_3^-$ (mg/L)	1.13	2.07
Br$^-$ (mg/L)	2.08	ND
PO$_4^{3-}$ (mg/L)	2.67	ND

ND=Not detected.

Percentage F$^-$ removal of 55.89% was achieved from field water at optimized conditions this is lower than the percentage F$^-$ removal achieved at the same conditions from the synthetic F$^-$ solution (84.0%) (Fig. 6). This may be attributed to the competition for adsorbent surface between co-existing anion and F$^-$ ion. From Table 2 it is noticed that there was reduction in Br$^-$ and PO$_4^{3-}$ ions after defluoridation indicating that they were also adsorbed during the process. The results indicate that the fabricated adsorbent would be suitable for treatment of groundwater with F$^-$ concentration $\leq$ 3 mg/L to achieve the recommended concentration of 1.5 mg/L.

5   Conclusions

Bentonite clay was successfully modified by intercalation of Mn^{2+} in the interlayers through ion exchange. Mineralogical characterization revealed main mineral phase in raw and Mn^{2+} bentonite is montmorillonite. Elemental characterization showed that silica and alumina are the main components in bentonite clay. Optimum conditions for adsorption of F^- were established to be 30 min contact time, 1.0 g/100 mL adsorbent dosage, 3 mg/L adsorbate concentration and pH of 2. A maximum F^- removal of 84.0% was achieved at the optimized batch conditions. When applied to field water, Mn^{2+} bentonite removed 55.89% F^- at field pH which was lower as compared 84.0% achieved at pH 2.

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