Synthesis, characterization, and potential application of Mn^{2+} -intercalated bentonite in fluoride removal: adsorption modeling and mechanism evaluation

Rabelani Mudzielwana¹ · Wilson M. Gitari¹ · Segun A. Akinyemi¹ · Titus A. M. Msagati²

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Abstract The study synthesizes a low-cost adsorbent made from Mn^{2+} -modified bentonite clay for groundwater defluoridation. The clays were characterized using X-ray diffraction, X-ray fluorescence, scanning electron microscopy, and Fourier transform infrared techniques. The fluoride adsorption capacity of the modified clay was evaluated using batch experiments. The adsorption kinetics results showed that the optimum fluoride (F^-) uptake was achieved within the 30 min' contact time. The data fitted well to pseudo-second-order of reaction kinetics indicating that adsorption of F^- occurred via chemisorption. In addition, the adsorption isotherm data fitted well to Langmuir isotherm model indicating that adsorption occurred on a mono-layered surface. Maximum F^- removal of 57% was achieved from groundwater with an initial F^- concentration of 5.4 mg L^{-1} and natural pH of 8.6 using adsorbent dosage of $1 \text{ g}/100 \text{ mL}$. Fluoride adsorption occurred through ligands and ion exchange mechanisms. The synthesized adsorbent was successfully regenerated for up to five times. The study shows that Mn^{2+} -intercalated

bentonite clay has potential for application in defluoridation of groundwater.

Keywords Adsorption · Batch experiment · Characterization · Kinetics · Mechanism · Toxicity

Introduction

The presence of fluoride in groundwater has attracted world-wide attention due to its considerable impact on human physiology. The ingestion of fluoride into human body at concentration below 1.0 mg L^{-1} enhances bone development and prevents dental caries. Conversely, assimilation of water containing fluoride concentration beyond World Health Organization (WHO) permissible limits of 1.5 mg L^{-1} would give rise to teeth mottling and deformation of bones (Ncube and Schutte 2005; WHO 2011; Rajkumar et al. 2015).

Groundwater containing fluoride concentration greater than 1.5 mg L^{-1} will, therefore, require defluoridation. Several authors have reviewed various techniques such as precipitation, co-precipitation, ion exchange and adsorption for defluoridation of groundwater (Mohapatra et al. 2009; Velazquez-Jimenez et al. 2015). Among these techniques, adsorption is widely used because of its viability and sustainability since it uses locally available and cost effective materials. Numerous adsorbents have been developed and tested for fluoride removal which includes cow dung (Rajkumar et al. 2015), clay soils (Coetzee et al. 2003), activated alumina (Maliyekaal et al. 2006), cuttlefish bones (Nasr et al. 2011) and bimetal oxide (Tang and Zhang 2016). Out of the tested adsorbents, the activated alumina is the most widely used because of its low-cost advantage and availability. However, activated alumina has difficulty for operation and poor sustainability due to frequent regeneration and low adsorption capacity (Chen et al.

✉ Rabelani Mudzielwana
mudzrabe@gmail.com

¹ Environmental Remediation and Water Pollution Chemistry Research Group, Department of Ecology and Resources Management, School of Environmental Sciences, University of Venda, Private Bag X5050, Thohoyandou, Limpopo 0950, South Africa

² College of Science Engineering and Technology, University of South Africa, The Science Campus, Florida Park, Roodepoort, Florida, Private Bag X6, Johannesburg 1710, South Africa

2010). Vinati et al. (2015) reviewed the potential application of clay and clay minerals in defluoridation and concluded that clays exhibit immense potential for fluoride adsorption due to large specific surface area, chemical and mechanical stability, layered structure, and high cation exchange capacity. Bentonite is an aluminosilicate clay group which comprises of layers of aluminosilicate sheets and exhibits a high cation exchange capacity and low permeability (Agnello 2005). The permanent negative charges in the bentonite clay are stabilized by available exchangeable cations. This enhances the ability to remove contaminants by cationic exchange (Ma et al. 2012; Bradley and Weils 2004). Bentonite modified with high ionic density cations has shown higher capacity for anion adsorption. Thakre et al. (2010) documented that the Mg^{2+} -incorporated bentonite works effectively over a wide range of pH and showed a maximum fluoride removal capacity of 2.26 mg g^{-1} at an initial fluoride concentration of 5 mg L^{-1} , which was much better than the raw bentonite. Gitari et al. (2013) in their study show that Fe^{3+} -modified bentonite exhibits $\approx 100\%$ of fluoride removal from drinking water over a pH range of 2–10, while the raw bentonite clay showed release of fluoride over the same range of pH. The main objective of the study was to synthesize a low-cost adsorbent by increasing surface charge density with introduction of Mn^{2+} ions onto bentonite interlayers. The specific objectives were as follows: (1) to evaluate physicochemical properties of raw and modified bentonite, (2) to optimize the loading of Mn^{2+} onto raw bentonite and lastly, (3) to evaluate F^{-} adsorption capacity of the modified bentonite clay.

Materials and methods

Sample preparation

Bentonite clay was collected from ECCA Pty (Ltd) in Cape Town, South Africa. Field water was collected from a community borehole in Siloam, Vhembe District in South Africa. All reagents and Total Ionic Solution Buffer (TISAB-III) were of analytical grade. They were purchased from Rochelle Chemicals & Lab Equipment CC, South Africa Ltd. A stock solution containing 1000 mg L^{-1} of fluoride was prepared by dissolving 2.21 g of NaF in 1 L of Milli-Q water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$). Mn^{2+} stock solution containing 1000 mg L^{-1} was prepared by dissolving 2.29 g of $MnCl_2$ in 1 L of Milli-Q water. Fluoride solutions for batch experiments were prepared from stock solution by appropriate dilutions.

Sample preparation, modification, and synthesis of Mn^{2+} bentonite clay

Raw bentonite clay was washed with Milli-Q 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 5000 rpm . Samples were then dried in an oven for 12 h at $110 \text{ }^{\circ}\text{C}$. Clay samples were homogenised by milling and pass through less than $250 \mu\text{m}$ sieve. Optimum conditions (i.e., contact time, adsorbate concentration, adsorbent dosage, and pH) for modifying bentonite clay with Mn^{2+} ion was evaluated using batch experiments. The obtained conditions were: 60 min contact time, $4 \text{ g}/100 \text{ mL}$ of adsorbent dosage, 50 mg L^{-1} Mn^{2+} of adsorbate concentration and initial pH of 8. To synthesize Mn^{2+} -modified bentonite, 200 mL of 50 mg L^{-1} Mn^{2+} solution was mixed with 8 g of raw bentonite to make up S/L ratio of $4 \text{ g}/100 \text{ mL}$, the pH of the mixture was then adjusted to 8 using 0.1 M of NaOH and 0.1 M of HCl. The mixture was put on a 1 L Erlenmeyer flask 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 h at a temperature of $105 \text{ }^{\circ}\text{C}$ in the oven. The modified clay was then milled to pass through $<250 \mu\text{m}$ sieve. The experiments were repeated five times to generate enough Mn^{2+} -modified bentonite for subsequent experiments.

Physicochemical characterization of Mn^{2+} -modified bentonite

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 10 kV , working distance 14 mm). Functional groups were evaluated using FTIR. Properties were compared to those of raw bentonite clay soils.

Batch defluoridation experiments

Batch experiments were used to examine fluoride adsorption kinetics at various adsorbent dosages, adsorption isotherms, the effect of pH and adsorbent stability as well as the effect of co-existing anions. To evaluate the fluoride adsorption kinetics, initial F^{-} concentration of 3 mg L^{-1} was used and adsorbent dosage varying from 0.1 to $0.5 \text{ g}/100 \text{ mL}$ with the initial pH of 5.54 ± 0.5 . Mixtures were agitated at different contact time such as $5, 15, 30, 60, 120, 180$ and 270 min using table shaker. After agitation, samples were filtered through $0.45 \mu\text{m}$ pore membrane. The residual fluoride concentration in the treated samples was measured using an ion-selective electrode (model: 9609 BNWP Orion, USA) attached to Thermo Scientific Orion Star ISE/pH/EC meter. pH measurements were also recorded. For residual fluoride, ion-selective electrode was

calibrated with four standards containing 1 mL of TISAB-III per 10 mL of solution. Same ratio was maintained for the sample. To evaluate the adsorption isotherms, initial concentration was varied for 3–25 mg L⁻¹ and the adsorbent dosage of 1 g/100 mL and mixtures were equilibrated for 30 min. To evaluate the effect of pH, the initial F⁻ concentration of 3 mg L⁻¹ and the adsorbent dosage of 1.0 g/100 mL were used. The initial pH was adjusted from 2 to 12 using 0.1 M of NaOH and 0.1 M of HCl and agitated for 30 min. After agitation, the concentration of cationic species were analyzed using NexION[®] 350D Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). To evaluate the effect of co-existing ions, 5 mg L⁻¹ of SO₄²⁻, Cl⁻, CO₃²⁻ and NO₃⁻ were prepared separately at initial fluoride of 3 mg L⁻¹. Blank experiment was done for control with initial F⁻ concentration of 3 mg L⁻¹. The adsorbent dosage of 1.0 g/100 mL was used and the mixtures were agitated for 30 min. The 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;

$$\% \text{removal} = \left(\frac{C_0 - C_e}{C_0} \right) \times 100, \quad (1)$$

where C_0 is initial fluoride ion concentration and C_e is equilibrium fluoride ion concentration.

$$Q = \left(\frac{C_0 - C_e}{m} \right) \times v, \quad (2)$$

where C_i = initial F⁻ concentration (mg L⁻¹), C_e = F⁻ concentrations at equilibrium (mg L⁻¹), V = volume of solution (L) and m = weight of the adsorbent (g).

Regeneration of adsorbent

1.0 g of fluoride-loaded clay was agitated with 100 mL of 0.1 M NaOH for 30 min. After agitation, the adsorbent was

filtered through 0.45 µm pore membrane and the filtrate was diluted to 100 mL and then analyzed for desorbed fluoride. The collected adsorbent on filter paper was washed with Milli-Q water and then dried at 110 °C for 3 h. Regenerated adsorbent was then re-used for defluoridation for up to five times.

Results and discussion

Physicochemical parameter evaluation

X-ray diffraction analysis

Figure 1 shows the X-ray diffraction spectra of raw and Mn²⁺-modified bentonite clay. Montmorillonite and quartz are the major minerals, while muscovite is present in minor quantities. No change in bentonite clay mineralogy was observed after modification with Mn²⁺ ions.

X-ray fluorescence analysis

Major chemical components of raw and Mn²⁺-modified bentonite is reported as percentage oxides in Table 1. SiO₂ is the main component of bentonite clay followed by Al₂O₃-indicating aluminosilicate material. Manganese oxide is relatively higher in Mn²⁺-modified bentonite (3.9%) than in raw bentonite (0.1%). This is attributed to precipitation of Mn²⁺ onto the clay interlayers during intercalation. The relatively high concentrations of MgO, Na₂O, CaO, and K₂O in the raw bentonite indicates that Mg²⁺, Na⁺, Ca²⁺, and K⁺ are the main exchangeable cations in the clay interlayers (Table 1). This is corroborated by the subsequent decrease in the content of these chemical species in the Mn²⁺-modified bentonite clay.

Fig. 1 X-ray diffraction spectra for raw and Mn²⁺-modified bentonite

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	15.8
CaO	1.50	0.88
Fe_2O_3	3.41	3.18
K_2O	0.98	0.4
MgO	3.20	3.06
MnO	0.1	3.9
Na_2O	2.12	0.9
SiO_2	65	62.5
TiO_2	0.46	0.12
L.O.I.	6.45	11.6
Sum of Conc.	99.89	99.4

L.O.I loss on ignition

Scanning electron microscopy

Figure 2a–d shows the surface morphology of raw and Mn^{2+} -modified bentonite clay at 2500 $\times$ and 25,000 $\times$ magnification. Bentonite morphological surface is

characterized by flat and sponge-like material. Whereas, the modified bentonite reveals the formation of larger agglomerate and spicules on the surface of clay platelets (Fig. 2). This could be attributed to swelling during the treatment by Mn^{2+} ions and formation of manganese hydroxides precipitates on the clay surface.

FTIR analysis

Figure 3 shows the FTIR spectra of raw bentonite, Mn^{2+} -modified bentonite and F^- -loaded Mn^{2+} -modified bentonite clay. According to Toor et al. (2014), three main absorption regions of bentonite clay are 3000–3800, 1300–1800 and 500–1200 cm^{-1} and notable difference can be observed in each region of raw, Mn^{2+} -modified and F^- -loaded bentonite clay. The absorption band between 3619.12 and 3623.81 cm^{-1} could be ascribed to stretching vibrations of structural OH^- groups of montmorillonite and water. At lower frequency (i.e. 999.10 cm^{-1}), bentonite showed a strong broadband this could be due to the stretching and vibration of Si–OH group. Band at 914.93 and 795 cm^{-1} could be attributed to Al–OH–Al group and

Fig. 2 Surficial morphology of **a, b** raw bentonite and **c, d** Mn^{2+} -modified bentonite

Fig. 3 FTIR spectrum of raw bentonite, Mn^{2+} bentonite and the F^- -loaded Mn^{2+} bentonite clay

Al–O and Si–O vibration, respectively, which indicates presence of quartz. Increase absorbance intensity was observed in Mn^{2+} -modified bentonite at these peaks indicating the formation of new bonds such as; Mn–O, Mn–OH and Mn– H_2O . Reduction in the absorption intensities of F^- -loaded Mn^{2+} -modified bentonite was recorded. This could be attributed to the fact that structural hydroxide groups and water molecules contributed to F^- adsorption process through the exchange of OH^- in Mn, Al, Si oxides for F^- .

Batch experiments

Effect of contact time and adsorption kinetics

Figure 4 depicts the relationship between contact time and % F^- removal. It is evident that F^- removal was rapid during the first 30 min of the experiment. The optimum

uptake of F^- was achieved within 30 min and decreased gradually up to 60 min. Thereafter, no significant change in percentage F^- removal was observed. The increase in fluoride removal could be attributed to the availability of sorption sites in the adsorbent. Whereas, the decrease could be due to the saturation of the adsorbent surface over time. Similar trend was observed at other adsorbent dosages. Therefore, contact time of 30 min was taken as the optimum time and was applied in subsequent experiments.

The adsorption kinetics were employed to determine the rate-limiting steps of fluoride adsorption onto Mn^{2+} -modified bentonite as well as the potential rate-controlling steps. Pseudo-first- and second-order models of reaction kinetics were used to explain the adsorption data and the adsorption mechanism.

The pseudo-first-order is shown in Eq. (3) and it is used to describe liquid–solid phase adsorption systems, and it is the earliest known kinetic model describing the adsorption

Fig. 4 Variation of % F^- removal as a function of contact time for various adsorbent dosages ($3 \text{ mg L}^{-1} \text{ F}^-$, pH 5.54 ± 0.5 and 250 rpm shaking speed)

Fig. 5 Pseudo-first-order plot at various adsorbent doses (3 mg L⁻¹ F⁻, pH 5.54 and shaking speed of 250 rpm)

rate based on the adsorption capacity (Oladoja and Helmreich 2014):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_{ad}t}{2.303}, \quad (3)$$

Pseudo-second-order is shown in the linear Eq. (4) and it is used to describe chemisorption, as well as cation exchange reactions.

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

where q_e and q_t (both in mg g⁻¹) are the amount adsorbed per unit mass at a time, t (in min), K_{ad} and K_{2ads} are first- and second-order rate constant (g mg⁻¹ min⁻¹).

The value of K_{ad} is determined from the slope and intercepts of $\log(q_e - q_t)$ vs t (min) and the value of K_{2ads} is determined from the slope and intercepts of t/q_t vs q_e .

Plot of $\log(q_e - q_t)$ values against time is shown in Fig. 5. Adsorption of fluoride ion onto Mn²⁺ bentonite did

not follow the pseudo-first-order process since it did not yield a straight line.

Figure 6 shows the plot of t/q with time which indicates high correlation coefficient at both adsorbent doses. This implies that fluoride sorption onto Mn²⁺-modified bentonite clay followed pseudo-second-order and chemisorption. The constant values of pseudo-first- and second-order are presented in Table 2.

Effect of adsorbent dosage

Figure 7 shows the effect of adsorbent dosage in percentage fluoride removal. Increase in the percentage fluoride removal with corresponding increase in adsorbent dosage was observed from 0.1 to 1 g/100 mL. The optimum uptake of F⁻ is considered to take place at 1 g/100 mL. This observed trend could be attributed to the increase in the sorption sites for fluoride ions as the adsorbent dosage increases (Kamble et al. 2009). No significant change was observed after 1 g/100 mL

Fig. 6 Pseudo-second-order plot at various adsorbent doses (3 mg L⁻¹ F⁻, pH 5.54 and shaking speed of 250 rpm)

Table 2 Pseudo-first- and second-order kinetics constant values

	Pseudo-first-order		Pseudo-second-order		
	K_{ad} (min^{-1})	R^2	q_e (mg g^{-1})	K_{2a} ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
0.1 g/100 mL	2.1×10^{-2}	0.47	0.56	2.73	0.99
0.3 g/100 mL	5.06×10^{-3}	0.35	0.33	1.36	0.99
0.5 g/100 mL	4.6×10^{-3}	0.05	2.4	0.52	0.99

Fig. 7 Variation % F^- removal and adsorption capacity by Mn^{2+} bentonite clay as a function of adsorbent dosage (contact time of 30 min, adsorbent dosage, $3 \text{ mg L}^{-1} \text{F}^-$, pH of 5.54 ± 0.5 and shaking speed of 250 rpm)

which indicates that the system has reached equilibrium. 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 adsorbent dosage required.

Effect of initial concentration and adsorption isotherms

Figure 8 shows the effect of adsorbate concentration on the percentage fluoride removal at various contact times. It is

observed that the percentage F^- removal decreased with an increase in the initial concentration. Similar trend was observed at all the contact times. This could be due to availability of more fluoride ions in the solution at higher adsorbate concentration. Besides, it could also indicate that fluoride binding sites of the adsorbent was getting exhausted.

Langmuir and Freundlich are widely used adsorption isotherm models. Langmuir isotherm model is applicable to homogeneous adsorption where adsorption process has

Fig. 8 Variation of % F^- removal by Mn^{2+} bentonite clay as a function of adsorbate concentration at various contact times (adsorbent dosage 1.0 g/100 mL, pH of 5.24 and shaking speed of 250 rpm)

Table 3 Constant values for Langmuir and Freundlich isotherm

	Langmuir isotherm			Freundlich isotherm		
	q_m (mg g ⁻¹)	b (L mg ⁻¹)	R^2	K_f (mg g ⁻¹)	$1/n$	R^2
30 min	0.14	0.88	0.99	0.08	0.45	0.93
60 min	0.17	0.55	0.96	0.07	0.26	0.64
120 min	0.19	0.10	0.87	0.06	0.27	0.63

equal activation energy. It is assumed that the adsorbent surface is uniform, i.e. all the adsorption sites are equivalent and adsorption molecules do not interact (Zhang et al. 2011; Ghosh et al. 2015). The linear equation for Langmuir isotherm model is expressed in Eq. (5):

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}, \quad (5)$$

where C_e is the equilibrium concentration (mg L⁻¹), Q_e is the adsorption capacity (mg L⁻¹).

Q_m is theoretical maximum adsorption capacity (mg g⁻¹), b is the Langmuir constant related to enthalpy of adsorption (L mg⁻¹), Q_m and b are determined from the slope and intercept of the plot of $\frac{C_e}{Q_e}$ Vs C_e .

Calculated Langmuir constants are presented in Table 3 and the Langmuir plots are shown in Fig. 9.

Furthermore, to reveal the feasibility of Langmuir adsorption isotherm, the dimensionless parameter of the equilibrium or adsorption intensity (R_L) was used for further analysis of Langmuir equation. The values of R_L were calculated using Eq. (6):

$$R_L = \frac{1}{1 + bC_0}, \quad (6)$$

where C_0 is the initial concentration, b is the Langmuir constant.

The value of R_L less than 1 generally indicates favorable adsorption, while greater than 1 indicates unfavorable adsorption. Figure 10 shows calculated R_L values which ranged between 0 and 1 indicating adsorption process was favorable at room temperature for all the adsorbate concentrations tested.

Freundlich isotherm model on the other hand describes the adsorption process on heterogeneous surfaces and it is used to model multilayer adsorption processes (Sun et al. 2011; Yi et al. 2014). The linear Eq. (7) describes the Freundlich isotherm model:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e, \quad (7)$$

where C_e is the equilibrium concentration (mg L⁻¹), Q_e is the amount adsorbed at equilibrium (mg g⁻¹), K_f is the Freundlich constant related to adsorption capacity, $1/n$ is the adsorption intensity.

The value of K_f and $1/n$ are obtained from the slope and intercepts of linear plot of $\log Q_e$ vs $\log C_e$ and calculated values are shown in Table 3. The value of adsorption intensity indicates the type of isotherm. The adsorption is favorable when $0 < 1/n < 1$ while irreversible when $1/n = 1$. The adsorption is unfavorable when $1/n > 1$. Figure 11 shows Freundlich isotherm plots for fluoride adsorption onto Mn²⁺-intercalated bentonite clay.

Fig. 9 Langmuir isotherm plot for fluoride removal onto Mn²⁺-incorporated bentonite clay at 30, 60 and 120 min contact time 250 rpm shaking speed, pH 5.54 ± 0.5 and adsorbent dosage of 1 g/100 mL

Fig. 10 R_L values for adsorption of F^- onto Mn^{2+} -intercalated bentonite clay

Fig. 11 Freundlich isotherm plot for fluoride removal onto Mn^{2+} -incorporated bentonite clay at 30, 60 and 120 min contact time, 250 rpm shaking speed, pH 5.54)

Based on the correlation coefficient values (R^2), the experimental data fitted well to Langmuir isotherm model and adsorption of fluoride occurred on a monolayer surface. The value of dimensionless equilibrium parameter (R_L) and the value of adsorption intensity ($1/n$) were between 0 and 1. This indicates that the adsorption of F^- onto Mn^{2+} -modified bentonite was favorable.

Effect of pH

Figure 12a shows the effect of pH on percentage F^- removal. The F^- removal decreases from 84 to 24% at pH 2 and 6, respectively. Thereafter, a slight increase was observed up to 30% at pH 10. The significant decrease in percentage F^- removal was observed at pH greater than 10. This could be due to the abundance of OH^- ions in alkaline pH that compete with F^- for adsorption sites. Therefore, pH 2 was considered as an optimum for F^- removal in this

study. From the change in pH during F^- adsorption trend as indicated in Fig. 12b, it is observed that at pH below 8.8, the final pH increased which lead to positive pH change ($+\Delta pH$). At pH above 8.8, final pH decreased during adsorption of pH leading to negative pH change ($-\Delta pH$). Nur et al. (2014) observed the same ΔpH trend for F^- adsorption onto hydrous ferric oxide. The increase in final pH at low initial pH values was attributed to the release of OH^- from the adsorbent during adsorption by ligand exchange process. At pH above 8.8, the final pH decreased from the initial pH probably due to the release of H^+ from the surface of the adsorbent.

Effect of co-existing anions

Figure 13 shows the effect of co-existing ions on percentage F^- removal. It was observed that fluoride removal is slightly affected due to the presence of co-existing

Fig. 12 a Variation of % F^- removal by Mn^{2+} bentonite clay as a function of pH and b ΔpH during F^- adsorption (contact time 30 min, adsorbent dosage 1.0 g/100 mL, $3 \text{ mg L}^{-1} F^-$ and shaking speed of 250 rpm)

anions in groundwater. The presence of CO_3^{2-} decreased fluoride removal by up to 18%. This could be due to increased equilibrium pH which promotes competition for adsorption sites. This observation agreed with the work done by Chen et al. (2011) and Yi et al. (2014). The order of increase of effect of co-existing anion on fluoride removal is as follows: $NO_3^- > Cl^- > SO_4^{2-} > CO_3^{2-}$.

Regeneration potential evaluation

Figure 14 shows that percentage fluoride removal decreases with increasing cycles of reuse. However, a very slight decrease was observed up to the second cycle and a drastic decrease by 20% was observed at fifth cycle. The decrease in F^- removal ratio could be due to dissolution of metals in the clay surface during regeneration. Jia et al. (2015) reported the same trend and attributed it to inadequate regeneration of the adsorbent.

Field water defluoridation

The effectiveness of Mn^{2+} bentonite clay in fluoride removal was tested on field water from Siloam community borehole containing 5.4 mg L^{-1} of fluoride ion concentration. Field water was treated at the optimized pH of 2 and at its natural pH of 8.6. Optimum adsorbent dosage of 1 g/100 mL was added and the mixture was agitated for 30 min at 250 rpm shaking speed. Results are presented in Table 4. The maximum F^- removal of 57% was achieved from field water at natural pH, while 67% fluoride removal was achieved at optimized pH. This is lower than the 84% F^- removal achieved at the same conditions from the synthetic F^- solution (Fig. 12a). This could be attributed to the competition for adsorbent surface between co-existing anions and F^- ion. Table 4 further shows reduction in Br^- and PO_4^{3-} ions after defluoridation which indicate that they were also adsorbed during the process. The results

Fig. 13 Effects of co-existing anions on fluoride removal and pH by Mn^{2+} -modified bentonite clay soils ($3 \text{ mg L}^{-1} \text{ F}^{-}$, 1.0 g/100 mL adsorbent dosage, 30 min contact time at 250 rpm and pH of 6.5)

Fig. 14 % Fluoride removal onto Mn^{2+} -modified bentonite clay in successive regeneration cycles (3 mg L^{-1} , 30 min contact time at 250 rpm and pH 5.54)

Table 4 Physicochemical parameters of field water before and after treatment

Parameters	Natural condition of Siloam borehole water	After treatment at natural pH	After treatment at optimized pH
pH	8.6	7.89	3.2
Conductivity ($\mu\text{S cm}^{-1}$)	338	168.4	402
Total dissolved solids (mg L^{-1})	203	154.7	84.1
F^{-} (mg L^{-1})	5.4	2.3	1.8
Cl^{-} (mg L^{-1})	31.6	31	37.15
SO_4^{2-} (mg L^{-1})	12	9.2	12
NO_3^{-} (mg L^{-1})	1.13	1	2.1
Br^{-} (mg L^{-1})	2.1	ND	ND
PO_4^{3-} (mg L^{-1})	2.7	ND	ND

ND not detected

indicated that the fabricated adsorbent would be suitable for treatment of groundwater contaminated with F^{-} less than 3 mg L^{-1} . This is to achieve the WHO-recommended concentration of 1.5 mg L^{-1} .

Fluoride adsorption mechanism

Ma et al. (2012) reported that fluoride adsorption depends on the number of hydroxyl sites. Figure 3 shows FTIR spectra of Mn^{2+} -modified bentonite which depicted

structure that has highly accessible hydroxyl groups located on the layers which favors F^- adsorption. Effective removal of fluoride corresponds with decrease in intensity of transmittance which indicates exchange of OH^- from the surface of the adsorbent for F^- ion during adsorption. At pH below 8.8, the surface of the clay is positively charged (Eq. 8) and therefore F^- ions will be electrostatically adsorbed to the clay surface (Eqs. 9, 10). Loganathan et al. (2013) suggested that at low pH adsorption of fluoride follows the ligand exchange mechanism. This could be due to stronger attractive force between fluoride, the adsorbent surface, and the presence of more hydroxylated sites for exchange of F^- . At moderate pH, fluoride adsorption occurs via ion exchange (Eq. 11). At alkaline pH, F^- adsorption also occurs via ion exchange (Eq. 12):

where $\equiv M$ represent metal in the adsorbent surface (Mn, Si, and Al).

Conclusion

A successful attempt for removal of fluoride from groundwater was made by modified Mn^{2+} bentonite. Optimum conditions for F^- adsorption were established to be 30 min. Contact time, 1 g/100 mL of adsorbent dosage and 3 mg L^{-1} of adsorbate concentration at pH 2. The presence of co-existing anions was found to decrease the efficiency of fluoride removal. The study reveals that Mn^{2+} -modified bentonite can be successfully regenerated with 0.1 M of NaOH. The adsorption isotherm data fitted well to Langmuir model indicating the adsorption was monolayer. The kinetic data adequately described by the pseudo-second-order model indicating that the adsorption was chemisorption. Fluoride adsorption onto Mn^{2+} -modified bentonite occurred through ligand exchange and ion exchange adsorption mechanisms. Moreover, the optimal adsorption capacity was observed at pH 2 and this would limit its application for defluoridation of groundwater in rural areas. This study recommends further research to improve its adsorption capacity at a wide pH range.

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