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Efficient Defluoridation of Water by Monetite Nanorods

Junjie Shen^{1,2*}, Marina Franchi Evangelista¹, Godfrey Mkongo³, Haibao Wen⁴, Richard Langford⁵, Georgina Rosair¹, Martin R.S. McCoustra¹, Valeria Arrighi^{1*}

¹ School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom

² Centre for Advanced Separations Engineering, Department of Chemical Engineering, University of Bath, Bath, BA2 7AY, United Kingdom

³ Ngurdoto Defluoridation Research Station, P.O.Box 482, Usa River, Tanzania

⁴ Department of Economics, University of Bath, Bath, BA2 7AY, United Kingdom

⁵ Cavendish Laboratory, Department of Physics, University of Cambridge, Cambridge, CB3 0HE, United Kingdom

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*Corresponding authors: Junjie Shen, Email: j.shen@bath.ac.uk, +44 745 979 3330; Valeria Arrighi, Email: v.arrighi@hw.ac.uk, +44 131 451 3108

Abstract

Novel Monetite nanorods were successfully prepared for fluoride removal for the first time. The fluoride adsorption on the Monetite nanorods was studied by the batch adsorption technique. The Monetite nanorods were characterized by transmission electron microscope (TEM), X-ray powder diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR), and the point of zero charge (pH_{PZC}) measurement. The results revealed that the Monetite nanorods transformed to fluorapatite after adsorbing fluoride. The adsorption kinetics followed the pseudo-second-order model, and the adsorption isotherms could be well described by the Sips model. The maximum adsorption capacity was 222.88 mg g^{-1} at pH 7, 328 K when the initial fluoride concentration was 300 mg L^{-1} and the Monetite dose was 1 g L^{-1} . The thermodynamic parameters revealed that the adsorption of fluoride onto Monetite nanorods was spontaneous and endothermic. The effects of different parameters including adsorbent dosage, pH, initial fluoride concentration and co-existing anions were investigated to understand the adsorption behaviour of Monetite nanorods under various conditions. Their adsorption capacities decreased with the increase of adsorbent dosage, and also decreased with the increase of pH. Electrostatic attraction and ion exchange were found to be the major mechanisms governing the adsorption of fluoride onto Monetite nanorods. Furthermore, a field study was conducted with the water from a fluoride endemic area in Tanzania. This study demonstrated that the synthesized Monetite nanorods were very effective adsorbents for defluoridation applications.

Keywords: Monetite, nanorods, fluoride, adsorption, drinking water

1. Introduction

Fluoride (F^-), as the simplest anion of fluorine, is found in all natural water sources at some concentration (Fawell et al. 2006). Although small amounts of fluoride intake help prevent dental caries among children, prolonged ingestion of fluoride at excessive levels is linked to various diseases, such as dental and skeletal fluorosis, masculine infertility, thyroid disorder, and brain damage (Fawell et al. 2006). The World Health Organization (WHO) recommends that the drinking water guideline for F^- is 1.5 mg L^{-1} (World Health Organization 2017). The fluoride contents in many regions of the world, including East Africa, Middle East, India, and China, greatly exceed the WHO guideline (Amini et al. 2008).

Many technologies have been developed for fluoride removal from drinking water, such as coagulation (Gong et al. 2012), precipitation (Turner et al. 2005), ion exchange (Ku et al. 2002), electrocoagulation

(Vasudevan et al. 2011), membrane techniques (Shen and Schäfer 2015), and adsorption (Bhatnagar et al. 2011). Among these technologies, adsorption has been demonstrated as the best method in balancing defluoridation capacity and economic feasibility.

Several types of adsorbents have been used for defluoridation, including (1) aluminium based materials (Ghorai and Pant 2005), (2) calcium based materials (Nath and Dutta 2015), (3) rare earth based materials (Raichur and Jyoti Basu 2001), (4) carbon based materials (Osei et al. 2015; Vinati et al. 2015), and (5) biopolymer based materials (Sairam Sundaram et al. 2009a; Viswanathan and Meenakshi 2010). Aluminium and rare earth based materials have very high adsorption capacity because of the high affinity between metal and fluoride ions. However, the presence of toxic metal ions in water is a major disadvantage for use of these adsorbents (Jagtap et al. 2012). Besides, the increasing price of rare earth seems problematic for the poverty-stricken regions. Carbon and biopolymer based materials are relatively poor adsorbents for fluoride because their surfaces lack anionic exchange sites, and any surface modification will incur additional cost (Loganathan et al. 2013). Calcium based materials are non-toxic, inexpensive, and more importantly, highly effective for fluoride adsorption (Nath and Dutta 2015). As a result, calcium based materials are very attractive adsorbents for defluoridation of drinking water, particularly in small communities and rural areas of developing countries (Ayoob et al. 2008).

Most of the research on calcium based materials for defluoridation has been focused on hydroxyapatite (HAP). HAP interacts with fluoride ions to form the more insoluble fluorapatite (FAP) (Johnsson and Nancollas 1992). However, HAP suffers from low solubility itself, which restricts the penetration of fluoride into the interior crystal (Chow and Brown 1973). As a result, the conversion of HAP into FAP proceeds slowly and its adsorption capacity is thus compromised. It is believed that an acid calcium phosphate with higher solubility may exhibit higher adsorption capacity for fluoride. There are various known calcium phosphate (CaP) materials, with different calcium-to-phosphate molar ratios and solubilities (Table 1). Despite that HAP has been extensively studied for fluoride removal, very little is known about the defluoridation properties of other CaP materials, especially the more soluble species.

The present study aimed to extend our knowledge of CaP-based materials from HAP to the more soluble Monetite. The Monetite nanorods as adsorbents for fluoride removal were prepared for the first time. Their adsorption capacities, adsorption kinetics and thermodynamic for fluoride were investigated in a systematic manner. The effects of adsorbent dosage, pH, initial fluoride concentration and co-existing anions were examined. Furthermore, a field study was conducted with the water

sample collected from a fluoride endemic area in Tanzania to assess the applicability of the Monetite nanorods in practical drinking water treatment.

Table 1: Major calcium phosphate (CaP) materials

Name	Abbreviation	Chemical formula	Ca/P	log K_{sp} at 298 K (Tung 1998)
Monocalcium phosphate monohydrate	MCPM	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	0.5	Highly soluble
Monocalcium phosphate anhydrous	MCPA	$\text{Ca}(\text{H}_2\text{PO}_4)_2$	0.5	Highly soluble
Brushite/dicalcium phosphate dehydrate	DCPD	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	1.0	-6.59
Monetite/dicalcium phosphate anhydrous	DCPA	CaHPO_4	1.0	-6.90
Octacalcium phosphate	OCP	$\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$	1.33	-96.6
Tricalcium phosphate	TCP	$\text{Ca}_3(\text{PO}_4)_2$	1.5	-25.5
Amorphous calcium phosphate	ACP	$\text{Ca}_x(\text{PO}_4)_y \cdot n\text{H}_2\text{O}$	1.2–2.2	-28.9
Hydroxyapatite	HAP	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	1.67	-58.4
Fluorapatite	FAP	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	1.67	-60.5

2. Materials and Methods

2.1. Chemicals

Chemicals including calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), dibasic ammonium phosphate ($(\text{NH}_4)_2\text{HPO}_4$), sodium fluoride (NaF), sodium hydroxide (NaOH), sodium nitrate (NaNO_3), sodium sulfate (Na_2SO_4), sodium chloride (NaCl), sodium bicarbonate (NaHCO_3), potassium chloride (KCl), potassium hydroxide (KOH), and ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$) were purchased from Sigma-Aldrich, UK. All the chemicals were of analytical grade and used directly without further purification. Aqueous solutions were made by dissolving appropriate quantities in de-ionized water.

2.2. Synthesis of Monetite

Monetite was synthesized by a precipitation method using $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ as starting materials. An appropriate amount of phosphate solution was added dropwise to the calcium solution at a Ca/P ratio of 1.0 consistent with the stoichiometry of Monetite. The pH of the mixture was left

unaltered. The mixture was continuously stirred at 300 rpm and heated at 90 °C under nitrogen atmosphere for 2 h. The milky suspension produced by this procedure was aged at room temperature for 24 h and then filtered. The product was washed several times with distilled water to neutralize the pH and remove residual impurities. The resultant gel-like paste was oven-dried at 100 °C for 24 h to yield a white powder.

2.3. Characterization methods

The microstructure and morphology of Monetite were characterized using a FEI Philips TECNAI-20 transmission electron microscope (TEM). To prepare TEM samples, a small amount of Monetite was dispersed in ethanol and sonicated for 15 min. One drop of the suspension was placed onto 400 mesh copper grids and then air dried. The X-ray powder diffraction (XRD) patterns of Monetite were measured on a Bruker D8 Advance diffractometer equipped with a Ge-monochromated Cu $K\alpha$ radiation source in reflectance mode using a LynxEye detector between 5 and 85 degrees in 2θ . Each scan was carried out for one hour. The Fourier transform infrared (FTIR) spectra of Monetite were measured on a Thermo Scientific Nicolet IS5 FTIR spectrometer in the wavenumber region 400-4000 cm^{-1} . All IR measurements were carried out at room temperature using the KBr pellet technique.

The pH at the point of zero charge (pH_{PZC}) was determined using the batch equilibration technique (Smičiklas et al. 2000). KCl was selected as an inert electrolyte to keep the ionic strength constant. The initial pH values of 0.1 M KCl solutions were adjusted between 4 and 12 by adding 0.1 M HCl or 0.1 M KOH. Nitrogen was bubbled into the solutions to remove dissolved carbon dioxide. 20 mg of Monetite was added to 20 mL of the KCl solution. The suspensions were stirred at 298 K for 24 h until the pH stabilized. The suspensions were then centrifuged, and the pH of the supernatant was measured. The plot of the equilibrium pH versus the initial pH was used to determine pH_{PZC} where the initial pH and the equilibrium pH values were equal.

2.4. Adsorption experiments

Adsorption experiments were performed by the batch adsorption technique. Briefly, a solution containing F^- of known concentration was mixed with a given mass of Monetite for a given period of time. The above suspension was withdrawn at appropriate time intervals and the supernatant liquid was separated from Monetite by centrifugation. The F^- concentration in the supernatant was determined by a fluoride ion selective electrode connected to a Mettler Toledo SevenCompact pH/ion

meter) using equal amounts of sample and total ionic strength adjustment buffer. The limit of detection of the electrode was $0.02 \text{ mg L}^{-1} \text{ F}^{-}$, and the limit of quantification was $0.1 \text{ mg L}^{-1} \text{ F}^{-}$. Precision of fluoride determination was represented as reproducibility, which was $\pm 2\%$ in this case. Accuracy of fluoride determination was higher than 95% compared to values of certified fluoride standard solution. A fluoride stock solution of $1000 \text{ mg L}^{-1} \text{ F}^{-}$ was prepared by dissolving 2.21 g NaF in 1 L distilled water. The working solutions for adsorption experiments were prepared by appropriate dilution of the stock solution to 100 mL and were kept in polypropylene flasks.

The adsorption kinetic experiments were performed by using $100 \text{ mg L}^{-1} \text{ F}^{-}$ solutions with 1 g L^{-1} Monetite at pH 7. The suspensions were stirred at 300 rpm for 24 h at 298 K. After 24 h, the solid phases were filtered, washed with distilled water, and dried at $80 \text{ }^{\circ}\text{C}$ for further examination.

The adsorption isotherms experiments were carried out with a series of different initial F^{-} concentrations (50, 100, 150, 200, 250, 300 $\text{mg L}^{-1} \text{ F}^{-}$) and a fixed Monetite dose of 1 g L^{-1} at pH 7. The suspensions were stirred at 300 rpm for 24 h at 298, 308, 318 and 328 K, respectively.

The effects of adsorbent dosage, initial pH and co-existing anions on fluoride adsorption were investigated by changing only one parameter at a time while keeping the other parameters constant. Specifically, the effect of adsorbent dosage was studied by adding different amounts of Monetite (0.5, 1, 1.5, 2, 2.5, 3 g L^{-1}) into the $100 \text{ mg L}^{-1} \text{ F}^{-}$ solutions at pH 7. The effect of initial pH was studied by adjusting the initial solution pH to the desired value (from 4 to 12) using 0.1 M HCl or 0.1 M NaOH solution, with $100 \text{ mg L}^{-1} \text{ F}^{-}$ and 1 g L^{-1} Monetite. The effect of co-existing anions was investigated by preparing a solution containing $100 \text{ mg L}^{-1} \text{ F}^{-}$ and 100 mg L^{-1} of a co-existing anion (HCO_3^{-} , NO_3^{-} , Cl^{-} , or SO_4^{2-}). The Monetite dose was 1 g L^{-1} and the pH was 7. The suspensions were stirred at 300 rpm for 24 h at 298 K.

The prepared Monetite was further tested by treating a natural water sample from the Maji ya Chai River in Tanzania. The river is a major water body in the rural area of the Arusha region, but its high fluoride concentration prevents local people from drinking it. 1 L of the water was airfreighted to Scotland within 3 days after collection and was stored at $4 \text{ }^{\circ}\text{C}$ in darkness after arrival. Table S1 (Supplementary Material) displays the compositions of the natural water sample. The water sample was pre-filtered by centrifugal ultrafiltration (2000 Da, Vivaspin 15R, Sartorius) to remove large particles before the adsorption experiment. Adsorption experiments of the natural water sample were performed by adding 1 g L^{-1} Monetite into 100 mL of the natural water. The suspensions were stirred at 300 rpm for 24 h at 298 K.

All of the experiments were conducted in triplicate and the average values of the results were used for data analysis. The adsorption capacity at equilibrium and the percentage of fluoride ions removed from aqueous solution were calculated using the following equations:

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

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

where q_e is the amount of fluoride adsorbed per unit mass of adsorbent at equilibrium (mg g^{-1}); R is the percent removal of fluoride from aqueous solution (%), c_0 and c_e are the initial and equilibrium F^- concentrations (mg L^{-1}); V is the solution volume (L); and m is the mass of adsorbent (g).

3. Results and Discussion

3.1. Characterization of Monetite

Fig 1 a shows the general TEM view of the prepared Monetite, revealing that the Monetite nanostructures were in rod-like shapes. The nanorods had varied sizes with widths ranging from 20 to 80 nm and lengths from 200 to 600 nm. The rod-like structures were due to preferred orientation growth along the c -axis of Monetite crystals (Lin et al. 2014). The Monetite nanorods were well crystallized with clear lattice stripes, as shown in **Fig 1** b. The interplanar distance is estimated to be 0.295 nm, which corresponds to the $(-1\ 2\ 0)$ plane of Monetite (Shen et al. 2016).

Fig 1 TEM images of Monetite nanorods at different magnifications

Fig 2 depicts the XRD patterns of Monetite before and after fluoride adsorption, respectively. The XRD pattern of Monetite before adsorption is a good visual match with the reference Monetite (JCPDS 01-070-0359) (**Fig 2 a, b**). The peaks with considerable intensities at 13.09° , 26.35° , 30.24° and 32.46° can be assigned to $(0\ 0\ 1)$, $(0\ 0\ 2)$, $(-1\ 2\ 0)$, and $(2\ 0\ 1)$ planes of Monetite, respectively. These peaks represent the triclinic structure of Monetite (Wang and Nancollas 2008). No peaks can be attributed to

tricalcium phosphate, calcium oxide or any other secondary product. After 24 h of reaction with fluoride, the XRD pattern of the remaining solids was obtained to identify the crystal phases. The characteristic peaks of Monetite completely disappeared, and new diffraction peaks showed up, which can be well-indexed to FAP (JCPDS 01-084-1997) (**Fig 2 c, d**). The peaks appearing at 25.89° , 31.85° , 32.99° , and 39.92° , correspond to (0 0 2), (1 2 1), (3 0 0), and (3 1 0) planes of FAP, respectively. These peaks are characteristic of the hexagonal crystal structure of FAP (Wei et al. 2003). Compared to the XRD pattern of a commercial HAP powder (**Fig S1**), the peaks of Monetite after fluoride adsorption are narrower and more separated. This indicates that fluoride adsorption improved crystallinity and increased crystallite size, which is due to the high affinity of F^- towards the apatite crystal growth.

Fig 2 XRD patterns of Monetite nanorods (a) before adsorption and (c) after adsorption. Also shown are the JCPDS reference patterns of (b) Monetite and (d) FAP.

The FTIR spectra of Monetite before and after fluoride adsorption are shown in **Fig 3**. In the spectrum of Monetite before adsorption, the peak at 526 cm^{-1} is assigned to the HO- PO_3 bending vibration originating from the HPO_4 groups, and the peak at 874 cm^{-1} is attributed to the P-OH stretching vibration in HPO_4 . The peak at 577 cm^{-1} is due to the P-O bending vibration, and the peaks at 987, 1063 and 1133 cm^{-1} are due to P-O stretching vibrations in the HPO_4 and PO_4 groups (Mandel and Tas 2010; Mourabet et al. 2011). The weak bands at 1380 cm^{-1} are attributed to NO_3^- which is from the synthesis residue.

As shown in **Fig 3**, the FTIR spectrum of Monetite changed significantly after adsorption. The characteristic peaks of the HPO_4 groups disappear while new peaks appear at 567, 606, 1035 and 1099 cm^{-1} . The strong peaks at 1099 and 1035 cm^{-1} are attributed to the asymmetric stretching vibration of PO_4 , and peaks at 606 and 567 cm^{-1} are associated with the symmetric and asymmetric deformation of PO_4 (Berzina-Cimdina and Borodajenko 2012). The spectrum is similar to the spectrum of HAP (**Fig S2**), except for the absence of the two OH peaks which exist in HAP. This confirms that Monetite predominately transformed to FAP instead of HAP. For both spectra, the weak absorption bands between 1630 and 1640 cm^{-1} identify the presence of CO_3^{2-} , which was due to dissolution of atmospheric CO_2 . The weak band at 3440 cm^{-1} is attributed to adsorbed water.

Fig 3 FTIR absorbance spectra of Monetite nanorods (a) before adsorption and (b) after adsorption

3.2. Adsorption kinetics

Measurements of adsorption kinetics make it possible to determine the adsorption rate and the time necessary to achieve equilibrium. The adsorption kinetics data of fluoride ions on Monetite are shown in **Fig 4**. The adsorption rate was fast in the first 4 h, and then decreased gradually until equilibrium was reached in 22 h. The adsorption equilibrium was reported to be dependent on external conditions (*e.g.* temperature, F^- concentration, adsorbent dose) and the physical and chemical properties of adsorbent (Liang et al. 2011; Zhang et al. 2012). At neutral pH and room temperature, the equilibrium adsorption capacity of 1 g L^{-1} Monetite for $100 \text{ mg L}^{-1} F^-$ is 56.60 mg g^{-1} . For comparison, the fluoride adsorption capacities of various CaP-based materials were listed in Table 2. Caution should be taken when comparing these materials because they were tested under very different conditions (*e.g.*, initial fluoride concentration, pH, adsorbent dosage). Therefore, the values reported for fluoride removal capacity have only a relative meaning. Nevertheless, it can be seen that the Monetite nanorods synthesised in this work have much higher adsorption capacities than other CaP materials, which suggests their promising applications for defluoridation of drinking water.

Table 2: Comparison of the fluoride adsorption capacities of various CaP materials

Adsorbent	Initial F^- (mg L^{-1})	pH	Adsorbent dosage (g L^{-1})	Adsorption capacity (mg g^{-1})	Reference
HAP	5	5.0	20	0.23	(Gao et al. 2009)
	20	7.5	0.4	4.70	(Jiménez-Reyes and Solache-Ríos 2010)
	50	3.0	8	3.44	(Wang et al. 2011)
	95	7.3	2	11.02	(Sternitzke et al. 2012)
	200	7.0	0.5	40.70	(He et al. 2016)
DCPD	50	6.8	8	6.59	(Mourabet et al. 2011)
	50	7.0	2.3	20.71	(Yang et al. 2012)
OCP	50	7.0	1.8	22.89	(Yang et al. 2012)
TCP	60	4.0	5.8	8.52	(Mourabet et al. 2012)
Monetite	100	7.0	1	56.60	Present study

Two types of models were used to represent the adsorption kinetic data. The first type is a reaction-based model, which assumes that the adsorption process is controlled by reactions at the liquid/solid interface in the adsorbent system (Simonin 2016). The most commonly used reaction-based models are the pseudo-first-order and the pseudo-second-order ones, which can be expressed as below (Zhang et al. 2012):

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

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

where q_t and q_e are the adsorption capacity (mg g^{-1}) of adsorbent at time t and at equilibrium, k_1 is the equilibrium rate constant of pseudo-first-order adsorption (h^{-1}), and k_2 is the equilibrium rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{h}^{-1}$).

The second type of model corresponds to a diffusion-controlled process (diffusion-based model). One of these, the intraparticle diffusion model, can be represented mathematically as follows:

$$q_t = k_d t^{0.5} + C \quad (5)$$

where k_d is the intraparticle diffusion rate parameter ($\text{mg g}^{-1} \text{h}^{-0.5}$), and C is a constant indicating the thickness of boundary layer.

Fits to the experimental data using the reaction-based models are reported in **Fig 4**. It is clear that the pseudo-first-order model is applicable to the initial data (three hours) but does not describe the entire range. The pseudo-second-order model fits better the experimental data, especially at longer adsorption times. The correlation coefficients R^2 of the pseudo-second-order model (0.998) is higher than that of the pseudo-first-order model (0.965) (Table S2). The applicability of the pseudo-second-order model suggests that the overall rate of the adsorption process is controlled by chemisorption which involves valency forces through sharing or exchange of electrons between sorbent and sorbate (Ho and McKay 1999).

The experimental data were also compared with the intraparticle diffusion model (**Fig 5**). The distinct stages of the adsorption process indicate that the adsorption rate was initially faster and then slowed down when the time increased. Stage 1 is attributed to rapid external surface adsorption, which is due to the boundary layer diffusion of fluoride ions; Stage 2 is the intraparticle diffusion stage, where the transportation of fluoride ions within the nanoparticles is rate determining; Stage 3 is the final equilibrium stage where intraparticle diffusion begins to slow down due to extremely low fluoride concentrations in the solution (Zhang et al. 2012). It is understood that if the plot of q_t versus $t^{0.5}$ passes through the origin, then the rate limiting process is only due to the intraparticle diffusion. Otherwise, some other mechanism along with intraparticle diffusion is also involved (Tan et al. 2009). As can be seen from **Fig 5**, the curves of Stage 2 and Stage 3 do not pass through the origin, suggesting that intraparticle diffusion is not the only rate-limiting mechanism in the adsorption process. Results from reaction-based and diffusion-based models indicate that chemisorption and intraparticle diffusion are two rate-limiting steps for adsorption of fluoride onto Monetite.

Fig 4 Plot of pseudo-first-order and pseudo-second-order models for adsorption of fluoride onto Monetite nanorods (100 mg L⁻¹ F⁻, 1 g L⁻¹ Monetite, pH 7, 298 K)

Fig 5 Plot of intraparticle diffusion model for adsorption of fluoride onto Monetite nanorods (100 mg L⁻¹ F⁻, 1 g L⁻¹ Monetite, pH 7, 298 K)

3.3. Adsorption isotherms

Adsorption isotherms provide information on the equilibrium between adsorbent and adsorbate at constant temperature, and are therefore important for the optimization of the adsorption process. In this study, the adsorption isotherms of fluoride on Monetite were obtained at four different temperatures. As shown by data in **Fig 6**, the adsorption capacity of Monetite increased with increasing temperature and fluoride concentration at equilibrium.

The experimental data were fitted to three models: Langmuir, Freundlich and Sips models. The Langmuir model assumes monolayer adsorption onto a homogenous surface (Langmuir 1918). The non-linear form of the Langmuir isotherm is given by:

$$q_e = q_m \frac{K_L c_e}{1 + K_L c_e} \quad (6)$$

where q_e is the adsorption capacity of Monetite at equilibrium (mg g^{-1}), c_e is the fluoride concentration at equilibrium (mg L^{-1}), q_m is the maximum adsorption capacity of Monetite (mg g^{-1}), and K_L is the Langmuir constant that relates to the energy of adsorption (L mg^{-1}).

Unlike the Langmuir model, the Freundlich equation is empirical and can be used for non-ideal adsorption processes involving heterogeneous surfaces or multilayers (Yang 1998):

$$q_e = K_F c_e^{1/n} \quad (7)$$

where K_F is the Freundlich constant representing the adsorption capacity ($\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$), and n is a constant related to the adsorption intensity (dimensionless). The magnitude of n indicates the favourability of adsorption. Values of n in the range 2-10 represent good, 1-2 moderately difficult, and less than 1 poor adsorption characteristics (Mourabet et al. 2011).

The Sips (also known as Langmuir-Freundlich) model is a combination of the Langmuir and Freundlich equations and can be used to model both homogeneous and heterogeneous surfaces (Umpleby et al. 2001). The Sips model is given in the following general form:

$$q_e = q_m \frac{K_S c_e^{1/n}}{1 + K_S c_e^{1/n}} \quad (8)$$

where K_S is the Sips constant (L mg^{-1}).

Fig 6 Adsorption isotherms of fluoride on Monetite nanorods at various temperatures (1 g L^{-1} Monetite, pH 7) and comparison with fits using equation (6), (7) and (8)

As shown in **Fig 6** and R^2 reported in Table 3, the Freundlich and Sips models give much better fits to the experimental data than the Langmuir model. In particular, the Sips model has the highest R^2 (>0.99) at all temperatures investigated. This suggests that the F^- adsorption process occurs on a heterogeneous surface and involves multimolecular layers of coverage (Zhang et al. 2012). Values of n lie between 2 and 5 for different temperatures, which also suggests that Monetite nanorods favour fluoride adsorption under the experimental conditions. The maximum adsorption capacity based on the Sips model is 222.88 mg g^{-1} , when the Monetite dose is 1 g L^{-1} and temperature is 328 K . To our knowledge, this is the highest fluoride adsorption capacity ever reported for CaP materials.

Table 3: Isotherm parameters of Monetite nanorods obtained at different temperatures

<i>Model</i>	<i>Parameters</i>	<i>298 K</i>	<i>308 K</i>	<i>318 K</i>	<i>328 K</i>
Langmuir	$q_m \text{ (mg g}^{-1}\text{)}$	80.15	85.39	91.63	96.45
	$K_L \text{ (L mg}^{-1}\text{)}$	0.06	0.10	0.15	0.42
	R^2	0.950	0.929	0.914	0.837
Freundlich	$K_F \text{ (mg}^{1-(1/n)} \text{ L}^{1/n} \text{ g}^{-1}\text{)}$	22.43	28.88	34.41	44.34
	n	4.27	4.85	5.21	6.15
	R^2	0.986	0.986	0.985	0.994
Sips	$q_m \text{ (mg g}^{-1}\text{)}$	119.92	133.01	142.02	222.88
	$K_S \text{ (L mg}^{-1}\text{)}$	0.15	0.20	0.24	0.23
	n	2.11	2.42	2.55	4.01
	R^2	0.996	0.994	0.996	0.998

To conclude whether this adsorption process is spontaneous or not, the following thermodynamic parameters were calculated, and results are listed in Table 4:

$$\Delta G^\circ = -RT \ln K_0 \quad (9)$$

$$\ln K_0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

where ΔG° is the standard free energy change (kJ mol^{-1}), T is the temperature in Kelvin, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), K_0 is the adsorption equilibrium constant, ΔH° is the standard enthalpy change (kJ mol^{-1}), and ΔS° is the standard entropy change ($\text{kJ mol}^{-1} \text{ K}^{-1}$). K_0 was determined by plotting $\ln(q_e/c_e)$ versus c_e at different temperatures and extrapolating c_e to zero (the intercept value corresponds to $\ln K_0$) (Khan and Singh 1987). The values of ΔH° and ΔS° were computed from the slope and intercept of the linear plot of $\ln K_0$ versus $1/T$, respectively.

ΔG° indicates the feasibility and spontaneity of a chemical reaction (Saha and Chowdhury 2011). The negative values of ΔG° measured at all temperatures are indicative of the spontaneous nature of the fluoride adsorption process by Monetite (Sairam Sundaram et al. 2009b). ΔG° becomes more negative with increasing temperature, which suggests that the adsorption is more favourable at higher temperatures. The positive value of ΔH° confirms the endothermic nature of the adsorption process. The positive value of ΔS° shows an increased randomness at the solid/solution interface during adsorption, which reflects a good affinity of Monetite surface towards fluoride ions (Zhang et al. 2012).

Table 4: Thermodynamic parameters of the fluoride adsorption on Monetite nanorods

ΔG° (kJ mol^{-1})				ΔH° (kJ mol^{-1})	ΔS° ($\text{kJ mol}^{-1} \text{ K}^{-1}$)
298 K	308 K	318 K	328 K		
-2.07	-3.03	-3.94	-5.64	32.38	0.12

3.4. Effect of adsorbent dosage

The effect of Monetite dosage on the adsorption capacity and fluoride removal was studied at pH 7, 298 K and for a contact time of 24 h with an initial F^- concentration of 100 mg L^{-1} . An increase in adsorbent dosage from 0.5 to 3 g L^{-1} resulted in the increase of fluoride removal efficiency from 36.4 to 91.3% (**Fig 7**). This phenomenon can be explained by the increased surface area and adsorption sites that are caused by the increased Monetite dosage (Gao et al. 2009). Further addition of Monetite can therefore approach nearly 100% fluoride removal. However, the adsorption capacity decreased with increasing Monetite dosage (**Fig 7**). This is mainly attributed to unsaturation of the active sites during the adsorption process, which leads to inefficient use of Monetite. Similar phenomena were reported by others (Gao et al. 2009; Liang et al. 2011). Therefore, the amount of Monetite should be carefully chosen to achieve its effective utilization. Factors to consider include the raw water quality, water volume and treatment requirements (*e.g.* drinking water guidelines).

Fig 7 Effect of adsorbent dosage on fluoride adsorption capacity and fluoride removal by Monetite nanorods ($100 \text{ mg L}^{-1} \text{ F}^{-}$, pH 7, 298 K)

3.5. *Effect of initial pH*

The solution pH plays a critical role in adsorption at the water-adsorbent interface, because it controls ionization of functional groups of the adsorbent and speciation of the solutes (Sairam Sundaram et al. 2008). The effect of initial pH on the adsorption capacity of Monetite is shown in **Fig 8a**. The adsorption capacity decreased gradually from pH 4 to 10, kept relatively stable in the neutral pH range, and then fell sharply beyond pH 10. The maximum adsorption capacity (74.4 mg g^{-1}) was reached at pH 4 and the minimum adsorption capacity (8.3 mg g^{-1}) was at pH 12. Similar trends were observed in other CaP materials such as HAP and Brushite (Sairam Sundaram et al. 2008; Zhang et al. 2012; Liang et al. 2011; Mourabet et al. 2011).

The notable change of adsorption capacity with pH can be explained in terms of electrostatic attraction and ion exchange mechanisms (Zhang et al. 2012; Shen et al. 2016). As **Fig 8b** shows, the pH_{PZC} value of Monetite is 8.12. Below pH 8.12, the surface of Monetite acquires a positive charge and preferably attracts negatively charged fluoride ions via electrostatic attraction. In addition, the acidic medium destroys the embedding calcium triangles structure, which induces the protonation at the surface of Monetite and therefore creates substantial amounts of active sites on the surface (Zhang et al. 2012). Above pH 8.12, the surface of Monetite becomes negatively charged by deprotonation, thus hindering the diffusion of fluoride ions towards Monetite via charge repulsion. Besides, substantial amounts of OH^{-} ions in alkaline medium compete with F^{-} ions for decreased adsorption sites via ion exchange, which further lowers the adsorption capacity of Monetite.

Fig 8 Effect of initial pH on (a) fluoride adsorption capacity ($100 \text{ mg L}^{-1} \text{ F}^{-}$, 1 g L^{-1} Monetite, 298 K) and (b) equilibrium pH of Monetite nanorods (0.1 M KCl , 1 g L^{-1} Monetite, 298 K)

3.6. *Effect of co-existing anions*

Natural waters contain many co-existing anions which may compete with F^{-} ions for available adsorption sites. Thus, it is necessary to assess the effect of common co-existing anions on the fluoride

adsorption capacity of Monetite. HCO_3^- , NO_3^- , Cl^- , and SO_4^{2-} are common anions found in natural and treated waters (Crompton 2003). As shown in **Fig 9**, NO_3^- , Cl^- , and SO_4^{2-} have no significant effect on fluoride adsorption, while HCO_3^- anions cause a 13.4% reduction in fluoride adsorption capacity. The relative affinity of Monetite for fluoride compared to co-existing anions can be related to the ionic radii. The order of the ionic radii is F^- (0.133 nm) < OH^- (0.137 nm) < HCO_3^- (0.163 nm) < NO_3^- (0.179 nm) < Cl^- (0.181 nm) < SO_4^{2-} (0.230 nm) (Marcus 1991). Due to its smaller ionic radii, F^- ion fits into the crystal lattice of Monetite better than other anions which are too large to be easily accommodated (Sternitzke et al. 2012; Yu et al. 2013; Shen et al. 2016). The presence of HCO_3^- increases the pH and consequently reduces the adsorption capacity, as discussed above.

Fig 9 Effect of co-existing anions on fluoride adsorption capacity of Monetite nanorods (100 mg L⁻¹ F⁻, 100 mg L⁻¹ co-existing anion, 1 g L⁻¹ Monetite, 298 K)

3.7. Field study

The feasibility of using Monetite nanorods under real-world conditions was further evaluated using the natural water sample collected from a fluoride-endemic region in Tanzania. As shown in Table 5, the fluoride concentration in the natural water samples was reduced from 17.8 mg L⁻¹ to 0.2 mg L⁻¹ after the treatment, which completely meets the WHO drinking water guideline for fluoride (<1.5 mg L⁻¹). Meanwhile there was insignificant change in pH and electrical conductivity after treatment, which suggests that the overall water quality kept unchanged except for the removal of fluoride. This preliminary result implies that the Monetite nanorods can be effectively used as a defluoridation adsorbent in practical drinking water treatment. However, in the future when conducting on-site experiments, a wide range of water quality parameters (e.g., nitrate, phosphate, bacteria) should be monitored after the adsorption process to meet every aspect of drinking water standards.

Table 5: Field study results of Monetite nanorods

Water quality parameter	Before treatment	After treatment
F ⁻ (mg L ⁻¹)	17.8	0.2
pH	8.40	7.92
Conductivity (μS cm ⁻¹)	1075	946

4. Conclusions

Monetite nanorods were successfully synthesized by a simple wet chemical route for fluoride removal from water for the first time. These Monetite nanorods showed much higher fluoride adsorption capacities than other CaP materials reported in the literature. XRD and FTIR results for the Monetite nanorods before and after adsorption experiments revealed that Monetite transformed to fluorapatite after adsorbing fluoride. The adsorption process reached equilibrium in 22 h. The adsorption kinetics were modelled using the pseudo-first-order, pseudo-second-order and intraparticle diffusion models, respectively. It was shown that the pseudo-second-order model best described the adsorption kinetics. The adsorption isotherms followed both the Freundlich and Sips models, but better fitted to the Sips model. The maximum adsorption capacity was 222.88 mg g^{-1} at 328 K and pH 7 when $300 \text{ mg L}^{-1} \text{ F}^{-}$ and 1 g L^{-1} Monetite were used. The thermodynamic parameters suggested that the adsorption process of fluoride on the Monetite nanorods was spontaneous and endothermic in nature. The adsorption capacities of Monetite nanorods were significantly influenced by the adsorbent dosage and the initial pH. There was no considerable influence of other co-existing anions except for bicarbonate ions. The fluoride removal mechanisms involved both electrostatic attraction and ion exchange. A field study demonstrated that the Monetite nanorods could be used as an efficient and cost-effective adsorbent for fluoride removal from natural water. This study has expanded the possibility of developing novel CaP materials in addressing drinking water decontamination.

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