Application of cryptocrystalline magnesite-bentonite clay hybrid for defluoridation of underground water resources: implication for point of use treatment

V. Masindi

ABSTRACT

A new synthesis method was established to fabricate a nanocomposite material comprising of cryptocrystalline magnesite and bentonite clay that has high adsorption capacity for ionic pollutants. To synthesize the composite at 1:1 weight (g): weight (g) ratio, a vibratory ball mill was used. Batch adsorption experiments were carried out to determine optimum conditions for fluoride adsorption. Parameters optimized included: time, dosage, concentration and pH. Optimum conditions for defluoridation were found to be 30 min of agitation, 0.5 g of dosage, 0.5:100 solid to liquid (S/L) ratios and 25 mg L⁻¹ of initial fluoride ions. Fluoride removal was independent of pH. The adsorption kinetics and isotherms were well fitted by pseudo-second-order and Langmuir models, respectively, indicating chemical and monolayer adsorption. Findings illustrated that the newly synthesized adsorbent was a promising adsorbent for the environmental pollution clean-up of excess fluoride in underground water and it can be used as a point source treatment technology in rural areas of South Africa and other developing countries.

INTRODUCTION

Fluorosis has become a chronic peril endangering the health of the majority of the population worldwide, especially those living in rural areas (Ayoob & Gupta 2006; Mohapatra et al. 2009; Bhatnagar et al. 2011; Gitari et al. 2013; Zulfiqar et al. 2014). In a number of African countries, including Kenya, Tanzania and South Africa, very high levels of fluoride in groundwater (as high as 30 mg L⁻¹) have been reported. Excessive fluoride in drinking water causes the development of dental and skeletal fluorosis in affected populations who source drinking water from untreated groundwater (Gitari et al. 2013; Masindi et al. 2014c).

Considering the dangers that come with consuming high fluoride waters, a maximum permissible limit of 1.5 mg L⁻¹ has been recommended for consumption in potable water (Ayoob & Gupta 2006; Mohapatra et al. 2009; Bhatnagar et al. 2011; Miretzky & Cirelli 2011; Jagtap et al. 2012; Gitari et al. 2013; Masindi et al. 2014c; Zulfiqar et al. 2014). Compared to underground water, surface waters do not always contain fluoride beyond this level. Due to the presence of fluoride-rich minerals as well as hydrogeological conditions of the place the water is sourced, underground water contains this excess fluoride (Gitari et al. 2013; Masindi et al. 2014c). With fluorosis being a serious health issue, it follows that defluoridation of drinking water has to be practised on those waters that have excessive fluoride levels beyond the recommended limit (Gitari et al. 2013; Masindi et al. 2014c).

Methods practised for removal of excess fluoride include adsorption (Zhou et al. 2004; Tor 2006; Zhu et al. 2009; Thakre et al. 2010a; Viswanathan & Meenakshi 2010;
Zulfiqar et al. 2014; Yu et al. 2015), precipitation (Turner et al. 2005; Onyango & Matsuda 2006; Zhang et al. 2014), coagulation (Khatibikamal et al. 2010; Emamjomeh et al. 2011; Vasudevan et al. 2011; Gong et al. 2012; Sandoval et al. 2014), filtration (Kettunen & Keskitalo 2000; Mohapatra et al. 2009; Maliyekkal et al. 2010; Wang et al. 2010; Dolar et al. 2011), reverse osmosis (Mohapatra et al. 2009; Shen & Schäfer 2014; Trikha & Sharma 2014), ion exchange (Ruixia et al. 2002; Luo & Inoue 2004; MeenaPesh & Viswanathan 2007; Mohapatra et al. 2009) and distillation (Hou et al. 2010). Limitations of these methods include the daily addition of chemicals; large volumes of sludge production; and some of these methods have been reported as being ineffective with water sources having high total dissolved solids (TDS) (Ayoob & Gupta 2006; Onyango & Matsuda 2006; Mohapatra et al. 2009; Bhatnagar et al. 2011; Miretzky & Cirelli 2011; Zulfiqar et al. 2014).

However, adsorption is one of the techniques, which is comparatively more useful and economical at low pollutant concentration (Onyango & Matsuda 2006; Zulfiqar et al. 2014). To that end, it is the defluoridation method that is now widely used in rural areas (Masindi et al. 2014c). Many types of low-cost and effective materials have been used as adsorbents in defluoridation which include different clays, tree bark, charcoal, saw dust, alum sludge and red tea waste (Srimurali et al. 1998; Çengeloglu et al. 2002; Mohapatra et al. 2009; Bhatnagar et al. 2011; Jagtap et al. 2012; Gitari et al. 2013; Masindi et al. 2014c; Zulfiqar et al. 2014).

Due to their versatility, high surface area, swelling capabilities, cation exchange capacity and abundance, clays and clay minerals have received paramount attention in depollution science (Bhattacharyya & Gupta 2008; Masindi et al. 2015a). However, their inorganic species retention capabilities are dependent on pH and species concentrations (Masindi et al. 2015a). To respond to those limitations and to minimize the use of virgin materials, clays can be blended with metal oxides and carbonates to improve their adsorption ability for inorganic contaminants (Gitari et al. 2013; Masindi et al. 2014c, 2015a; Masindi & Gitari 2016). The aim of the present study was to develop a cryptocrystalline magnesite-bentonite clay nanocomposite as a novel technology and evaluate the feasibility of using the fabricated composite for the defluoridation of surface and underground water for use in households.

**MATERIALS AND METHODS**

**Sampling**

Fluoride-rich water collected from a community borehole in Siloam village Limpopo Province, South Africa was used to evaluate the effectiveness of the prepared composite adsorbent in the treatment of field water. Raw magnesite rocks from the Folovhodwe Magnesite Mine in Limpopo Province, South Africa, were collected without any prior processing. Bentonite clay was supplied by ECCA Holdings (Pty) Ltd Cape Bentonite mine (Cape Town, South Africa).

**Adsorbent preparation**

To prepare the material for adsorption processes, the magnesite rock samples were milled into a powder using a Retsch RS 200 mill and afterwards passed through a sieve to obtain 32 μm particle sizes. The raw bentonite was washed by soaking in ultra-pure water for 10 min and thereafter draining the wash. The level of the ultrapure water used was such that it covered the entire sample in the beaker and was allowed to overflow. The procedure was repeated four times. The washed bentonite was dried in an oven (24 h at 105 °C). The dried samples were milled into a fine powder (Retsch RS 200 mill) and sieved (32 μm particle size sieves).

**Synthesis of mechanochemical activated composite**

The composite adsorbent was synthesized via a mechanochemical method using the following procedure. A vibratory ball mill was used for making the magnesite-bentonite clay composite. Powdered bentonite (500 g) and magnesite (500 g) were mixed on a 1:1 wt% mass ratio. The mixture was crushed and homogenized by pulverizing into a fine powder (Retsch RS 200 mill) for 30 min at 800 rpm. After sieving <32 μm sized particles were obtained and the prepared material was kept in sealed zip-lock plastic bags. The conditions for milling were previously determined as optimal milling parameters for mechanochemical modification of bentonite clay-cryptocrystalline magnesite composite by Masindi (Masindi et al. 2014a, 2015a; Masindi & Gitari 2016).
Preparation of working solution

For all the experiments, the accuracy of the analysis was monitored by analysis of National Institute of Standards and Technology (NIST) water standards. Simulated fluoride-rich water was synthesized using sodium fluoride salt. A standard stock solution of fluoride (1,000 mg L\(^{-1}\) F\(^{-}\)) was prepared by dissolving 0.221 g sodium fluoride into 100 mL deionized water from a Milli-Q water system. Fluoride-bearing solutions were prepared by diluting the stock solution to desired concentrations with ultra-pure water.

Determination of fluoride concentration

Fluoride concentrations were measured by a fluoride ion selective electrode (Thermo Scientific Orion Star A215 pH/Conductivity Benchtop Meter (USA) coupled to an 8157BNUMD Orion ROSS Ultra Triode pH/ATC electrode). Before fluoride determination, a total ionic strength adjusting buffer (TISAB III) was added to the solutions in a ratio of 10:1 in order to maintain ionic strength and pH, and eliminate the interference effect of F-ion complexing with metal cations.

Microstructural characterisation

Mineralogical composition of the composite and resulting solid residues was determined using X-ray diffraction (XRD). They were analysed using a PANalytical X'Pert Pro powder diffractometer in \(\theta-\theta\) configuration with an X'Celerator detector and variable divergence, and fixed receiving slits with Fe filtered Co-K\(\alpha\) radiation (\(\lambda = 1.789 \text{ Å}\)). The phases were identified using X'Pert Highscore plus software at University of Pretoria, South Africa. Morphology was determined using scanning electron microscopy-electron dispersion spectrometry (SEM-EDS) (JOEL JSM – 840, Hitachi, Tokyo, Japan).

Optimization of adsorption conditions

Optimization experiments were done in batch experimental procedures. Parameters optimized include time, dosage, concentration and pH. All experiments were done in triplicate. Samples of 100 mL of 50 mg L\(^{-1}\) F\(^{-}\) solution were pipetted into nine, 250 mL high-density polyethylene plastic bottles and 1 g of the composite added. The mixtures were agitated for varying contact times. The mixtures were then filtered through a 0.45 \(\mu\)m pore nitrate cellulose filter membrane. pH, electrical conductivity (EC) and TDS were measured using a CRISOM MM40 multimeter probe. The samples were refrigerated at 4 \(^{\circ}\)C until analysis by fluoride meter.

Eight, 100 mL solutions of 50 mg L\(^{-1}\) F\(^{-}\) were pipetted into eight, 250 mL bottles and varying masses of the composite added. The mixtures were agitated for an optimum time of 30 min at 250 rpm using the Stuart reciprocating shaker. The filtered samples were treated as discussed previously.

Six, 100 mL solutions were pipetted into six, 250 mL bottles with 0.5 g of the composite and 100 mL of the stock solution with different concentrations of fluoride were added into each container. The mixtures were agitated for an optimum time of 30 min at 250 rpm using the Stuart reciprocating shaker. The filtered samples were treated as discussed previously.

Six, 100 mL solutions of 25 mg L\(^{-1}\) F\(^{-}\) were pipetted into eight, 250 mL bottles with 0.5 g of the composite and the pH was adjusted from 2 to 12 using NaOH and nitric acid. The mixtures were agitated for an optimum time of 30 min at 250 rpm using the Stuart reciprocating shaker. The filtered samples were treated as discussed previously.

The synthetic and fluoride-rich underground water were treated under optimized conditions.

Calculation of the extent of fluoride removal and adsorption capacity

The percentage removals of fluoride by the composite were computed by the expression:

\[
\% \text{ Removal} = \left( \frac{C_i - C_e}{C_i} \right) \times 100
\]

where \(C_i\) = initial concentration and \(C_e\) = equilibrium ion concentration, respectively.

The amounts of fluoride adsorbed by the composite were determined by the expression:

\[
q = \frac{(C_i - C_e)V}{m}
\]

where \(C_i\) = initial ions concentration (mg L\(^{-1}\)), \(C_e\) = ions
concentration at equilibrium (mg L\(^{-1}\)), \(V\) = volume of ions solution (L) and \(m\) = weight of the composite in grams.

**RESULTS AND DISCUSSION**

**Microstructural characterizations**

**X-ray diffraction analysis**

The mineralogical composition of magnesite, bentonite clay and magnesite-bentonite clay composite are shown in Figure 1.

XRD analysis showed that magnesite consists of periclase, brucite and forsterite as the main mineral phase. The low intensity peaks indicate that the material is enriched with amorphous phases. Bentonite clay was observed to contain smectite, quartz, plagioclase, calcite and muscovite. Common between the magnesite and bentonite clay is the quartz which also tends to form the highest peaks. XRD pattern of the product synthesized shows one intense diffraction peak around about 2\(\theta\) = 27.2\(^\circ\) which is due to quartz. The composite was determined to contain smectite, periclase, quartz, gibbsite and muscovite which are the main components of magnesite and bentonite clay. The presence of gibbsite and quartz substantiates that the material is still an alumino-silicate. Broad peaks indicate that the synthesized composite has amorphous phases thus proving that ball milling can result in amorphization of the material (Kumrić et al. 2015a; Dukić et al. 2015a, 2015b).

**Transmission electron microscopy-electron dispersion spectrometry**

Transmission electron microscopy (TEM) images and spectra of magnesite, bentonite clay, magnesite-bentonite clay composite and fluoride reacted composite are shown in Figure 3(a)–3(d).

Figure 3(a) displays a cloudy background with sheet-like structures on the cryptocrystalline magnesite. This shows that the material contains amorphous and crystalline phases. The EDS revealed that Mg, C and O are the major components verifying that the material under study is magnesium carbonate. Traces of Ca and Fe were also observed to be present. Such metals also aid in removal of fluoride from wastewaters. The availability of Cu is due to the use of a copper grid.

Figure 3(b) reveals the presence of rod and sheet identical structures. EDS revealed that Al, O and Si are the predominant species. This is indicative of the material being an alumino-silicate. Fe and Mg were also observed to be present hence proving that these are the exchangeable cations which can also aid in the removal of fluoride from underground water.

Figure 3(c) shows the availability of tube- and rod-like structures with a background which is cloudy. This indicates that the material is a blend of magnesite and bentonite clay. Moreover, this shows that the fabricated material contains crystalline and amorphous phases. The EDS disclosed that there is a notable amount of C, O, Si, Mg, and Al thus proving that the material is a blend of magnesite and bentonite clay.
Figure 3(d), like Figure 3(c), shows the availability of tube- and rod-like structures with a cloudy background. EDS proved the addition of fluoride on the composite matrices hence proving that the composite is a sink of fluoride from aqueous solution.

**Optimization experiments**

Batch experiments were carried out to evaluate the effects of shaking time, dosage, fluoride concentration and pH on removal of fluoride from aqueous solution.

**Effect of shaking time**

The effect of shaking time on the removal of fluoride from aqueous solution is shown in Figure 4.

As shown in Figure 4, there was a rapid increase in percentage removal of fluoride with an increase in contact time from the first minute of contact time to about 30 min. From 1 to 30 mins, the composite managed to remove >99% of fluoride from the aqueous solution. Thereafter, no significant uptake of fluoride was observed indicating that the reaction kinetics had reached an equilibrium.
state. A possible explanation of this trend is that the composite provided more surfaces sufficient to remove all the fluorides that were in aqueous solution in the first 30 min. This study showed shorter contact time for removal of fluoride as compared to a study by Thakre et al. (2010b) that required 12 h of equilibration for removal of fluoride using magnesium modified bentonite clay. On this basis 30 min was selected as the optimum equilibration time for further optimization experiments.

Effects of dosage

The effect of dosage on the removal of fluoride from aqueous solution is shown in Figure 5.

As shown in Figure 5, the percentage removal of fluoride was observed to increase with an increase in dosage. The percentage removal of fluoride increased rapidly, as the dosage was increased from 0.1 to 0.5 g. The composite managed to remove >99% of fluoride from the aqueous solution. After which, no significant increase in adsorption was observed. High percentage removal is attributed to more surface suitable for adsorption becoming available as the dosage increases. As such, it was concluded that 0.5 g is the optimum dosage for adsorption of 10 mg L\(^{-1}\) of fluoride from aqueous solution and it will be used for the following experiments.

Effect of initial fluoride concentration

The effect of initial fluoride concentration on the removal of fluoride from aqueous solution is shown in Figure 6.

The uptake of fluoride by the composite was studied by varying the initial concentration of fluoride from 2 to 50 mg L\(^{-1}\). As shown in Figure 6, there was a high percentage removal of fluoride at low concentrations but as the concentration of fluoride increased the percentage removal
Figure 3 | TEM images and spectra of magnesite (a), bentonite clay (b), magnesite-bentonite clay composite (c) and fluoride-reacted composite (d).
decreased. High percentage removal at low concentration is attributed to more adsorption sites being available at initial stages, but when the concentration increases more fluoride ion species become available to occupy the vacant surfaces on the composite. However, it was observed that the composite removed >99% of fluoride in the range of 2–25 mg L$^{-1}$. Based on the observed results, 25 mg L$^{-1}$ of fluoride concentration was taken as the optimum concentration for subsequent experiments.

**Effect of supernatant pH**

The effect of pH on the removal of fluoride from aqueous solution is shown in Figure 7.

The effect of pH on removal of fluoride from aqueous solution was evaluated from pH 2 to 12. Removal of fluoride by the composite at varying pH was observed to be high over a wide range of pH values (Figure 7). From pH 2 to 12, the removal efficiency was greater than 99%. High adsorption of
the composite may be attributed to a high pH at point of zero charge (pH\text{pzc}) of 10. As such at pH < 10, the system is removing anions from the aqueous solution as the adsorbent is positively charged attracting anions. On the basis of this, pH of 2–10 was taken to be the optimum pH range for the subsequent experiments.

Modelling of experimental results

Adsorption kinetics

The effect of contact time on removal of fluoride from aqueous solution was evaluated using different kinetic models to reveal the nature of the adsorption process and the rate limiting processes. A Lagergren pseudo-first-order kinetic model is a well-known model that is used to describe mechanisms of adsorption by different adsorbents. It can be written as follows (Shou et al. 2015):

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

where \(k_1\) (min\(^{-1}\)) is the pseudo-first-order adsorption rate coefficient and \(q_e\) and \(q_t\) are the values of the amount adsorbed per unit mass at equilibrium and at time \(t\), respectively. The experimental data were fitted using the pseudo-first-order kinetic model by plotting \(\ln(q_e - q_t)\) vs. \(t\), and
the results are shown in Table 1. The pseudo-first-order was applied and it was found to fairly converge with the experimental data. Moreover, the calculated amount of fluoride ions adsorbed by the composite \(q_{e, \text{calc}} \text{ (mg g}^{-1}\) was less than the experimental values \(q_{e, \text{exp}} \text{ (mg g}^{-1}\) (Table 1). The findings indicated that the Lagergren pseudo-first-order kinetic model is inappropriate to describe the adsorption of fluoride ions from aqueous system by the composite.

The pseudo-second-order kinetic model is another kinetic model that is widely used to describe the adsorption process from an aqueous solution. The linearized form of the pseudo-second-order rate equation is given as follows:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]  

(4)

where \(k_2 \text{ [g(mg min}^{-1}\)] is the pseudo-second-order adsorption rate coefficient and \(q_e\) and \(q_t\) are the values of the amount adsorbed per unit mass at equilibrium and at time \(t\), respectively. An application of the pseudo-second-order rate equation for adsorption of fluoride to the composite matrices portrayed a good fit with the experimental data (Figure 8 and Table 1). The obtained results confirm that the pseudo-second-order model is the most suitable kinetic model to describe adsorption of fluoride ions by the composite from the aqueous system. Moreover, this also confirms that the mechanism of fluoride removal from aqueous solution is chemisorption. To be noted is that the theoretical adsorption capacity is close to the experimental adsorption capacity further confirming that this model describes the adsorption data.

The overall kinetics of the adsorption process may be governed by diffusional processes as well as by the kinetics of the surface chemical reaction. In diffusion studies, the rate is often expressed in terms of the square root of time.

\[
q_t = k_{id}t^{1/2} + C_i
\]

(5)

### Table 1 | Different kinetic model parameters for adsorption of fluoride ions on the composite

<table>
<thead>
<tr>
<th>Adsorption kinetics</th>
<th>Parameters</th>
<th>(q_{e, \text{exp}} \text{ (mg g}^{-1})</th>
<th>(q_{e, \text{calc}} \text{ (mg g}^{-1})</th>
<th>(k_1 \text{ (min}^{-1})</th>
<th>(R^2)</th>
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<td>(k_1 \text{ (min}^{-1})</td>
<td>(R^2)</td>
<td></td>
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<tr>
<td>Pseudo-second-order</td>
<td>Parameters</td>
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<td>2.6</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(q_{e, \text{exp}} \text{ (mg g}^{-1})</td>
<td>(C_i \text{ (mg g}^{-1})</td>
<td>(k_{id} \text{ (mg g}^{-1} \text{ min}^{-1/2})</td>
<td>(R^2)</td>
<td></td>
</tr>
<tr>
<td>Intra-particle-diffusion</td>
<td>Parameters</td>
<td>9.9</td>
<td>9.0</td>
<td>0.17</td>
<td>0.7</td>
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</tbody>
</table>

**Figure 8** | Pseudo-second-order plot for fluoride adsorption by the composite adsorbent.
where $k_{id}$ (mg g$^{-1}$ min$^{-1/2}$) is the intra-particle diffusion coefficient (slope of the plot of $q_t$ vs. $t^{1/2}$) and $C_i$ is the intra-particle diffusion rate constant. The results show that the intra-particle diffusion model was not applicable for the present process due to the lower correlation coefficients as shown in Table 1. Different kinetic model parameters for the adsorption of fluoride ions onto the composite are shown in Table 1.

Pseudo-second-order plot for fluoride removal by the composite is shown in Figure 8.

**Adsorption isotherms**

The relationship between the amount of ions adsorbed and the ion concentration remaining in solution can be described by adsorption isotherms. The two most common isotherm types for describing this type of system are Langmuir and Freundlich adsorption isotherms. These models describe adsorption processes on a homogenous (monolayer) or heterogeneous (multilayer) surface, respectively.

The most important model of monolayer adsorption came from Langmuir. This isotherm is given as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_mb} + \frac{C_e}{Q_m}$$  \hspace{1cm} (6)

The essential characteristics of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, $R_L$, which is defined as:

$$R_L = \frac{1}{1 + bC_o}$$  \hspace{1cm} (7)

$R_L > 1$ means unfavourable reaction, $R_L = 1$ means linear fit, $0 < R_L < 1$ means favourable reaction and $R_L = 0$ means irreversible reaction.

Where $C_e = \text{equilibrium concentration (mg L}^{-1})$, $Q_e = \text{amount adsorbed at equilibrium (mg g}^{-1})$, $Q_m = \text{Langmuir constants related to adsorption capacity (mg g}^{-1})$ and $b = \text{Langmuir constants related to energy of adsorption (L mg}^{-1})$. A plot of $C_e$ versus $C_e/Q_e$ should be linear if the data are described by the Langmuir isotherm. The value of $Q_m$ is determined from the slope and the intercept of the plot. It is used to derive the maximum adsorption capacity and $b$ is determined from the original equation and it represents the intensity of adsorption. The Langmuir adsorption isotherm plot is shown in Figure 9.

The Freundlich adsorption isotherm describes the heterogeneous surface energy by multilayer adsorption. The Freundlich isotherm can be formulated as follows:

$$\log q_e = \frac{1}{n} \log C_e + \log K$$  \hspace{1cm} (8)

where $C_e = \text{equilibrium concentration (mg L}^{-1})$, $q_e = \text{amount adsorbed at equilibrium (mg g}^{-1})$, $K = \text{partition coefficient (mg g}^{-1})$ and $n = \text{intensity of adsorption}$. The linear plot of $\log C_e$ versus $\log q_e$ indicates if the data are described...
by the Freundlich isotherm. The value of $K$ implies that the energy of adsorption on a homogeneous surface is independent of surface coverage and $n$ is an adsorption constant which reveals the rate at which adsorption is taking place. These two constants are determined from the slope and intercept of the plot of each isotherm. The plot of Freundlich adsorption isotherm is shown in Figure 10.

The parameters of Langmuir and Freundlich adsorption isotherms are shown in Table 2.

As tabulated, the Langmuir isotherm showed a high correlation coefficient ($R^2 > 0.99$) (Figure 9). $R_L$ shows that the reaction of fluoride and the composite was favourable. The $Q_m$ and $b$ show that the adsorption of fluoride by the composite takes place at high energy with high intensity of adsorption. The Freundlich adsorption isotherm also showed a good regression coefficient ($R^2 > 0.90$) (Figure 10). The $n$ value between 0 and 10 shows that the reaction is beneficial and the $K_f$ value shows that it has high adsorption capacity. This indicates a good agreement between the experimental values and isotherm parameters. The data fitted better to the Langmuir adsorption isotherm than the Freundlich adsorption isotherm thus depicting a monolayer adsorption mode.

### Removal of fluoride under optimized conditions

Results for the removal of fluoride on raw water under optimized conditions are shown in Table 3. The physiochemical conditions of borehole water before and after deflouridation are also tabulated in Table 4. The fluoride-rich ground water was observed to be slightly alkaline with a pH of 9. The composite was observed to remove fluoride from groundwater to below 0.01 mg L$^{-1}$. This shows that the composite is an effective material that can be used for the removal of fluoride in groundwater.

### Adsorption capacity of the composite as compared to other adsorbents

A comparison of the adsorption capacity of the composite and other adsorbents that have been reported to remove fluoride is shown in Table 4.

Table 4 compares the different adsorption capacities of various adsorbents of fluoride reported in different

<table>
<thead>
<tr>
<th>Type of water Parameter</th>
<th>Synthetic water</th>
<th>Field water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw</td>
<td>Treated</td>
</tr>
<tr>
<td>pH</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>EC ($\mu$S cm$^{-1}$)</td>
<td>145</td>
<td>41.2</td>
</tr>
<tr>
<td>TDS (mg L$^{-1}$)</td>
<td>73</td>
<td>27.3</td>
</tr>
<tr>
<td>F$^-$ (mg L$^{-1}$)</td>
<td>50</td>
<td>0.01</td>
</tr>
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</table>

Figure 10 | Freundlich adsorption plot for fluoride adsorption onto the composite adsorbent.
literature. Even though the adsorption capacities were obtained at different experimental conditions, they offer a useful criterion to compare the different adsorption capacities. From the table, it is clear that the composite has a higher adsorption capacity as compared to the other adsorbents. Therefore, the composite can be effectively applied for deflouridation of groundwater because of its ability to adsorb fluoride.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity (mg g⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesite/bentonite composite</td>
<td>10</td>
<td>Present study</td>
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<tr>
<td>Cryptocrystalline magnesite</td>
<td>9.2</td>
<td>Masindi et al. (2013b)</td>
</tr>
<tr>
<td>Alum-bent</td>
<td>5.7</td>
<td>Masindi et al. (2014c)</td>
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<td>Al-oxide origin alumina</td>
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<td>Kamble et al. (2010)</td>
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<td>Mg²⁺ bentonite</td>
<td>2.3</td>
<td>Thakre et al. (200a)</td>
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<td>Polymer/bio-polymer composites</td>
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<td>Karthikeyan et al. (2011)</td>
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<td>Activated alumina</td>
<td>1.1</td>
<td>Maliyekkale et al. (2006)</td>
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<td>La impregnated silica gel</td>
<td>3.8</td>
<td>Zhou et al. (2004)</td>
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<td>Fe³⁺ modified bentonite clay</td>
<td>2.9</td>
<td>Giti et al. (2013)</td>
</tr>
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</table>

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