Initial fluoride concentration and loading capacity in defluoridation with bauxite, gypsum, magnesite and their composite
Bernard Thole

ABSTRACT

One of the parameters that impact on fluoride sorption capacities of materials in water defluoridation is initial concentration. Water from various sources will have different fluoride concentrations; as such the employment of a particular media in defluoridation requires information on how the media will perform in different concentrations. Consequently, research was carried out to determine how initial fluoride concentrations in raw water affect capacity in defluoridation with bauxite, gypsum, magnesite and their composite, and to investigate the possibility of predicting loading capacity of their composite filter through initial fluoride concentration to optimize their application in defluoridation. The results showed that sorption capacities increased with increase in initial concentrations. However, higher starting concentrations resulted in larger residual fluoride concentrations; as such the benefit of large sorption capacities obtained was overshadowed. Polynomial relations of capacity ($C_s$, mg/g) and initial concentration ($C_o$, mg/l), were obtained for bauxite and gypsum. Magnesite obtained a logarithmic relation for $C_s$ and $C_o$. A power relation was obtained between $C_s$ and $C_o$ for their composite, $C_s = 0.0328C_o^{1.2016}$. Approximation of capacities of this composite from initial fluoride concentrations was feasible. Water defluoridation has become important as a result of dental and skeletal fluorosis.

Key words | bauxite, defluoridation, fluorosis, gypsum, magnesite

INTRODUCTION

Removal of fluoride from water, water defluoridation, has been attempted with a variety of materials. Bone char, aluminium compounds, natural and synthetic oxy-hydroxides, clay and other media (Sujana et al. 2009; Wu et al. 2009; Maliyekkal et al. 2010; Smittakorn et al. 2010) Fluoride sorption with bauxite has been demonstrated to be feasible (Sajidu et al. 2008; Peter 2009; Shrivastava & Vani 2009). Gypsum, magnesite and a variety of other metallic oxides and hydroxides have been widely tried for the removal of fluoride from water (Singano 2000; Coetzee et al. 2003; Masamba et al. 2005). Magnesite, apophyllite, natrolite, stilbite, clinoptilolite, gibbsite, goethite, kaolinite, halloysite, bentonite, vermiculite, zeolite, serpentine, alkaline soil, acidic clay, kaolinitic clay, China clay, aiken soil, Fuller’s earth, diatomaceous earth and Ando soil are among the numerous naturally occurring minerals which have been studied and confirmed to adsorb fluoride from water (Fawell et al. 2006). Bauxite-containing clays have demonstrated the highest sorption capacities among the reported clays. A comparison of 25 South African clays, grouped as bauxite, laterite, polygorskite, bentonite and kaolinite, showed that the bauxite and lateritic samples obtained high adsorption and the lowest adsorption was recorded for kaolin samples (Coetzee et al. 2003). The fluoride sorption is known to be based on fluoride-hydroxyl ion exchange on the metallic lattice often represented as: $\text{M(OH)}_x + x\text{F}^- \rightarrow \text{MF}_x + x\text{OH}^-$, where M is the metal ion component of the hydroxyl compound and x is an integer. Limitations observed with bauxite are increase in residual aluminium and apparent colour (Masamba et al. 2005). Gypsum has been tested in defluoridation and has
demonstrated varied capacities with residual calcium sulphate in the treated water as the main challenge (Sajidu et al. 2008). Water deflouridation with magnesite also demonstrates feasible results except for residual magnesium and increase in pH to about 10 (Singano 2000). Clays in general are known to have low sorption capacities ranging from 0.05 to 5.5 mg F/g (Damte 2006; Fawell et al. 2006); however, they may still be considered for water deflouridation because they are readily available at low or no cost in many areas. Other disadvantages noted with clay are that the kinetics are slow and hygiene may be compromised (Feenstra et al. 2007). Clays, like other adsorbents, have varied capacities with respect to pH, initial fluoride concentrations, dose and temperature. The current research determined the effect of initial fluoride concentrations on loading capacities of bauxite, gypsum, magnesite and their composite, and the possibility of predicting sorption capacity of their composite from initial fluoride concentrations in raw water in an attempt to optimize their application in water deflouridation.

**METHODS**

**Media preparation**

Bauxite, gypsum and magnesite were locally sourced within Tanzania. Bauxite was obtained from Kwemashai, Usambara Mountains in Lushoto District. Gypsum was sourced from Makanya, Mwanga District and magnesite was obtained from Same District at Chambogo. The materials were characterized through X-ray fluorescence (XRF) to determine their composition. They were then crushed and sieved to obtain particles of diameter 1.2–1.4 mm. The three materials were then heat treated in an open air muffle furnace at 200 °C for 2 hours. The loading capacities of the materials were determined and a composite filter was prepared in the ratio of the means of the loading capacities that were 5.5:5.5:1.5 for bauxite, gypsum and magnesite, respectively. Raw water was characterized for pH, apparent colour, hardness and concentrations of F⁻, Cl⁻, SO₄²⁻, Fe³⁺, Al³⁺. The analyses were carried out as per standard methods described in Standard Methods (2005) and Water Analysis Handbook (2011). The raw water was diluted to fluoride concentrations of 6, 10, 14, 18 and 20 mg/l with deionised water. All experiments were carried out at room temperature that ranged from 18.5 to 24.5 °C during the experimental period.

**Loading capacity determinations**

Loading capacities were determined in batch. One gram of each material was placed in one litre of water. The medium was agitated at 125 rpm and fluoride was determined hourly until equilibrium concentrations were obtained. The loading capacities were calculated through a mass balance equation.

\[ q_e = \frac{(C_0 - C_e)V}{m}. \]  

In Equation (1) \( q_e \) is the amount of adsorbed fluoride at equilibrium (mg/g); \( V \) is the volume of the solution (l); \( C_0 \) and \( C_e \) are the initial fluoride concentration and fluoride concentration at equilibrium (mg/l), respectively. The term \( m \) is mass of adsorbent (g). Each experiment was replicated three times. Bauxite, gypsum and magnesite were then mixed in mass ratio of their respective loading capacities to formulate the composite. Loading capacities and residual fluoride concentrations were regressed with initial fluoride concentrations. The amount of adsorbent \( d \) required to obtain residual fluoride concentrations of 1.5 mg/l were calculated for each adsorbent and initial concentration through Equation (2) where \( d \) is optimal dose (g/l), \( C_o \) is initial concentration (mg/l), \( C_s \) is loading capacity (mg/g) and 1.5 mg/l is the upper World Health Organization (WHO) recommended limit for fluoride concentration in drinking water.

\[ d = \frac{C_o - 1.5}{C_s}. \]  

The optimal dose was regressed with initial fluoride concentration for each material.

**Prediction of sorption capacities of the composite filter**

Preliminary experiments were carried out with the composite to determine the relationship between its sorption capacity and initial fluoride concentration as described...
earlier, and the capacities were calculated through Equation (1). Sorption capacities were plotted against initial fluoride concentrations. An equation relating sorption capacity and initial concentration was obtained from the best fit curve. This equation was used to calculate capacities for arbitrary initial concentrations of 3.0, 4.5, 6.5, 7.5, 9.0, 10.5 and 12.5 mg/l. Experiments were carried out with water of the same fluoride concentrations, i.e. 3.0, 4.5, 6.5, 7.5, 9.0, 10.5 and 12.5 mg/l. Calculated capacities and capacities obtained from experimentation were compared statistically and graphically.

## RESULTS AND DISCUSSION

### Material and water quality

Table 1 presents the compositional properties of the three adsorbent materials as determined through XRF. The major components for the adsorbents were: Al$_2$O$_3$ (30.33%) for bauxite, CaO (28.09%) for gypsum and MgO (34.57%) for magnesite. Fluoride sorption was thus attributed to the oxides of the three cations Al$^{3+}$, Ca$^{2+}$, Mg$^{2+}$. The raw water quality parameters determined prior to defluoridation are presented in Table 2. The raw water was fairly soft and had a pH of 8.70.

The quality of the treated water as determined at equilibrium is presented in Table 3: water treated with bauxite failed in apparent colour and aluminium. Water treated with gypsum did not adhere to quality requirements for sulphates and water treated with magnesite failed in two quality parameters, pH and hardness. The results showed that water defluoridated with the composite filter adhered to the test quality parameters under the conditions of these experiments.

### Loading capacities, residual concentrations and optimal doses

Loading capacities, obtained at temperature 20 ± 3.5°C, increased with increase in initial fluoride concentration within the tested range of initial concentrations as depicted in Figure 1. This was attributed to higher fluoride ion to surface area ratio in higher concentrations shifting equilibrium.

### Table 1 | Composition of raw bauxite, gypsum and magnesite

<table>
<thead>
<tr>
<th>Material</th>
<th>MgO (%)</th>
<th>Al$_2$O$_3$ (%)</th>
<th>SiO$_2$ (%)</th>
<th>P$_2$O$_5$ (%)</th>
<th>K$_2$O (%)</th>
<th>CaO (%)</th>
<th>TiO$_2$ (%)</th>
<th>MnO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesite</td>
<td>34.57</td>
<td>0.51</td>
<td>19.3</td>
<td>0.77</td>
<td>0.04</td>
<td>1.89</td>
<td>0.03</td>
<td>0.02</td>
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<tr>
<td>Bauxite</td>
<td>0.56</td>
<td>30.33</td>
<td>15.0</td>
<td>0.18</td>
<td>0.02</td>
<td>0.76</td>
<td>1.57</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Gypsum</td>
<td>1.02</td>
<td>2.26</td>
<td>9.01</td>
<td>0.08</td>
<td>0.64</td>
<td>28.09</td>
<td>0.13</td>
<td>0.02</td>
</tr>
<tr>
<td>Material</td>
<td>TiO$_2$ (%)</td>
<td>Cl (%)</td>
<td>SO$_3$ (%)</td>
<td>SrO (%)</td>
<td>Fe$_2$O$_3$ (%)</td>
<td>Cr$_2$O$_3$ (%)</td>
<td>Na$_2$O (%)</td>
<td>LOI (%)</td>
</tr>
<tr>
<td>Magnesite</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>0.51</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>42.30</td>
</tr>
<tr>
<td>Bauxite</td>
<td>1.57</td>
<td>0.17</td>
<td>5.18</td>
<td>&lt;0.01</td>
<td>14.3</td>
<td>0.02</td>
<td>0.09</td>
<td>31.79</td>
</tr>
<tr>
<td>Gypsum</td>
<td>0.13</td>
<td>0.17</td>
<td>34.96</td>
<td>0.65</td>
<td>1.80</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>21.08</td>
</tr>
</tbody>
</table>

### Table 2 | Raw ground water quality

<table>
<thead>
<tr>
<th>Hardness as CaCO$_3$</th>
<th>F$^-$</th>
<th>Al$^{3+}$</th>
<th>Fe$^{2+}$</th>
<th>SO$_4^{2-}$</th>
<th>Cl$^-$</th>
<th>Phenol</th>
<th>OH$^-$</th>
<th>CO$_3^{2-}$</th>
<th>HCO$_3^{-}$</th>
<th>pH</th>
<th>Colour</th>
</tr>
</thead>
</table>
| 14.5                | 12.65| Bdl*   | 0.02    | 20        | 20   | 10    | 0     | 20        | 70        | 8.70 | Bdl (TCU)$^b$
| WHO recommended upper limits/range | 500  | 1.5    | 0.2     | 0.3      | 400  | 250   | 6.5–8.5 | 5–50  |

*Below detectable limit of method (1 for colour and 0.01 for Al).

$^b$True colour units.
towards the solid phase. The residual fluoride concentrations however increased with increase in initial fluoride concentrations as illustrated in Figure 2. This implied that the high loading capacities at large concentrations do not necessarily imply better performance at high concentrations. Equations (3) to (6) present relationships obtained between capacity ($C_s$, mg/g) and initial concentration ($C_o$, mg/l) for bauxite, gypsum, magnesite and the composite, respectively

$$C_s = 0.0776C_o - 0.001C_o^2 + 0.0106$$  \hspace{1cm} (3) \\
$$C_s = 0.1028C_o - 0.0026C_o^2 - 0.2793$$  \hspace{1cm} (4) \\
$$C_s = -0.4232 \ln C_o - 0.6884$$  \hspace{1cm} (5) \\
$$C_s = 0.043C_o^{1.2016}$$  \hspace{1cm} (6)

Figure 3 depicts a relationship between optimal dose of adsorbent ($d$) (that is, dose required to obtain residual concentrations of fluoride of 1.5 mg/l) and initial fluoride concentrations ($C_o$) for each adsorbent. Bauxite and gypsum had polynomial relations between the two parameters. No relation was discernible for magnesite and the composite with all correlations, logarithmic, linear, polynomial, exponential and power, obtaining coefficients

<table>
<thead>
<tr>
<th>Parameter</th>
<th>WHO limit</th>
<th>Bauxite</th>
<th>Gypsum</th>
<th>Magnesite</th>
<th>Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour (PtCo mg/l)</td>
<td>Desirable: 5 Maximum: 50</td>
<td>6</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Hardness (CaCO₃ mg/l)</td>
<td>500</td>
<td>87</td>
<td>350</td>
<td>775</td>
<td>142</td>
</tr>
<tr>
<td>pH</td>
<td>6.5–8.5</td>
<td>6.95</td>
<td>7.88</td>
<td>9.69</td>
<td>8.05</td>
</tr>
<tr>
<td>Cl⁻ (mg/l)</td>
<td>250</td>
<td>58.5</td>
<td>77.9</td>
<td>18.3</td>
<td>63.2</td>
</tr>
<tr>
<td>Al³⁺ (mg/l)</td>
<td>0.2</td>
<td>0.4</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe²⁺ (mg/l)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.1</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/l)</td>
<td>400</td>
<td>44</td>
<td>479</td>
<td>16</td>
<td>124</td>
</tr>
</tbody>
</table>

Figure 1 | Regression of loading capacity and initial fluoride concentration.

Figure 2 | Plot of residual concentrations against initial fluoride concentrations.

Figure 3 | Optimal dose regressed with initial fluoride concentration.
much lower than 0.5. The optimal dose – initial concentration relations for bauxite and gypsum are presented in Equations (7) and (8), respectively:

\[ d = 0.6533C_o - 0.0094C_o^2 + 6.74 \]  

\[ d = 0.0728C_o^2 - 1.4533C_o + 24.658 \]

Equation (9)

\[ C_s = 0.557e^{0.223C_o} \]

Employing Equation (9), capacities were calculated for initial concentrations of 3.0, 4.5, 6.5, 7.5, 9.0, 10.5 and 12.5 mg/l. The calculated and actual data obtained experimentally were plotted against initial concentration (Figure 5).

The experimental capacities were statistically similar to the projected capacities, \( p = 0.97 \). The results portray that loading capacities increase with increase in initial fluoride concentrations and that capacities may be approximated from initial fluoride concentrations for this system. Correlation between calculated and actual data was high, \( r^2 = 0.987 \), confirming that capacities increased in fluoride concentrations for each case, confirming results obtained elsewhere (Onyango et al. 2009).

### CONCLUSION

Water defluoridation with bauxite, gypsum, magnesite and their composite is plausible. Loading capacities increase with increase in initial fluoride concentrations; however,
such large starting concentrations result in high equilibrium residual fluoride concentrations. This results in large optimal doses being required for high concentrations. The optimal doses for the adsorbents under the operating conditions were 10–15 g/l (composite), 10–16 g/l (bauxite), 15–25 g/l (gypsum) and 25–35 g/l (magnesite) in the concentration range 6 to 20 mg/l. Quality of the treated water was within recommended limits for hardness, apparent colour, pH and concentrations of $\text{Cl}^-$, $\text{SO}_4^{2-}$, $\text{Fe}^{2+}$, $\text{Al}^{3+}$ for the composite filter but limitations of colour and aluminium (for bauxite), sulphates (gypsum), pH and hardness (for magnesite) were observed. The fluoride sorption capacity of the composite filter could be approximated from the knowledge of initial fluoride concentration. This information may be employed to determine the dose of the composite required with respect to the initial fluoride level and the desired volume of water to be treated. A composite filter of the three materials, prepared in the ratio of their loading capacities, is a promising solution to the challenges encountered in water quality during defluoridation with the three adsorbents separately.

REFERENCES


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