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DELIVERING WATER, SANITATION AND HYGIENE SERVICES IN AN UNCERTAIN ENVIRONMENT

Natural clay based adsorbent for defluoridation of groundwater: optimization of adsorption conditions

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Groundwater is the most appropriate and widely used source of drinking water for many rural communities in Sub-Saharan Africa. Studies reveal that in some of the boreholes, F^- concentration may be way beyond the recommended limits. This study evaluates the use of raw unprocessed bentonite clay and its Fe^{3+} modified form for fluoride adsorption. A series of batch adsorption experiments were carried out to evaluate parameters that influence the adsorption process. Fe^{3+}-bentonite exhibited $\approx 100 \% F^-$ removal as opposed to unprocessed bentonite < 5 % at initial concentration of 10 ppm F^-. The Fe^{3+} modified bentonite exhibited $\approx 100 \% F^-$ removal over the pH range 2-10 decreasing at pH > 10, while the unprocessed bentonite clay showed an increase in fluoride concentration over the same pH range. The results indicate that Fe^{3+}-modified bentonite is a candidate adsorbent for point of use water defluoridation systems for house hold use in rural areas

Introduction

Research into the techniques available to defluoridate groundwater identifies those methods based on the principals of sorption as the methods most suited for rural and remote locations. The systems are relatively simple, requiring a reactor vessel to contain the media (which could be a simple column), which once it is exhausted can be regenerated or replaced. The challenge is to come up with a cheap and reliable adsorbent that can be effectively and cheaply regenerated. Several studies have identified locally available materials as the most suitable for evaluation and application for defluoridation in most rural communities, these include natural clay used for making of bricks (Argaw et al., 2005), natural clay (Ahmedin, 2007), raw bauxite in Malawi (Sajidu, 2012) and natural lateritic geomaterials (Sarkar et al., 2007). Most of these studies have identified clay based materials obtained locally in rural areas affected by high fluoride in groundwater would be the most the most economically viable adsorbents. Moreover these materials could serve as good candidates for fabrication of point of entry or point of use water defluoridation systems that are suited for rural areas that are not connected to piped water supply.

Large specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), etc., have made some clays excellent adsorbent materials. Due to their great adsorptive properties, clays can be modified to create clay-based adsorbents for inorganic contaminants in water. This involves replacing the exchangeable cations such as Na^+, K^+. Ca^{2+} and Mg^{2+} with high ionic charge density ions like Fe^{3+}, Mn^{2+} or Al^{3+}. The modified clays have been observed to provide good abilities of adsorbing inorganic contaminants (Lothenbach et al. 1997). Onyango et al. (2009) observed a greater F^- adsorption capacity for Al^{3+} zeolite F9 modified zeolite compared to commercial adsorbents. Kemble et al. (2009) observed a higher F^- adsorption capacity for La, Mg and Mn^{2+} modified bentonite compared to the unmodified one. The objectives of this paper include:-1) Physicochemical and mineralogical characterization of the raw and modified bentonite clay, 2) Optimizing the loading of Fe^{3+} onto bentonite clay, 3) Optimization of the F^- adsorption capacity of the raw and modified bentonite clay, 4) Evaluate the F^- adsorption capacity of the raw and modified bentonite clay under optimized conditions.

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Experimental procedures

1. Preparation of clay, morphology, physicochemical and mineralogical Analysis

The raw bentonite samples were washed with ultra pure water and dried for 24 hours at 105°C and then crushed into a fine powder. Major and minor elemental analysis was done by a PAN analytical Axios X-ray fluorescence (XRF) spectrometer equipped with a 4 kW Rh tube at Council for Geoscience, South Africa and X-ray diffraction (XRD) analysis by a PANalytical X'Pert Pro powder diffractometer. Morphology was examined using a Hitachi X-650 scanning Electron Microanalyser equipped with a CDU- lead detector at 25kV.

2. Cation Exchange Capacity (CEC), determination of pH_{pzc} and BET Analysis

The CEC was determined using ammonium acetate method. Concentration of the exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) was determined by AAS (600 PerkinElmer). Results in ppm were then converted to meq/100g following the method of Radojevic and Bashkin (1999). pHpzc was determined using the solid addition method at 0.1M, 0.01M and 0.001M KCl. The surface area and pore size distribution was determined using the Brunnet- Emmett- Teller method of analysis using a Micromeritics Accelerated Surface Area and Porosimetry (ASAP) 2010 system (Brunauer, 1943).

3. Synthesis of Fe^{3+}modified bentonite clay

The Fe^{3+}modified bentonite for the defluoridation experiments was synthesized using the conditions optimized in previous experiments (Masindi, 2013).

4. Optimization of F^- Adsorption conditions

Adsorption of F^- with contact time was evaluated by use of 10 ppm F^- solution and 2g/100ml S/L ratio. Sample were agitated at 250 rpm using a table shaker. Samples were shaken for various time intervals ranging from 1-360 mins. Adsorption of F^- with adsorbent dosage was evaluated by use of 10 ppm F^- solution. The adsorbent dosage was varied as follows: 0.1, 0.3, 0.5, 1, 2, 3 and 4g. Samples were agitated for 30 mins at 250 rpm using a table shaker. Adsorption of F^- with adsorbate concentration was evaluated at 30 mins contact time and agitated at 250 rpm using a table shaker. A S/L ratio of 2g/100ml was used, adsorbate concentration was varied from 4-60 ppm. Adsorption of F^- as a function of pH was evaluated at 20 ppm F-concentration. Agitation was done for 30 mins contact time at 250 rpm using a table shaker. A S/L ratio of 2g/100ml was employed. Initial pH of the media was varied from 2-12. Samples were filtered through 0.45µm pore cellulose nitrate membranes. pH, EC and TDS were measured using crimson multimeter probe and F^- by crimson ion selective electrode. Reactions were conducted at room temperature.

Results and discussions

1. Morphology, physicochemical and mineralogical Analysis

SEM images of raw bentonite and Fe^{3+}-bentonite (fig1) were produced. No difference in morphology between bentonite and Fe^{3+}-modified bentonite was observed. The platy like features characteristic of clay minerals are clearly visible.
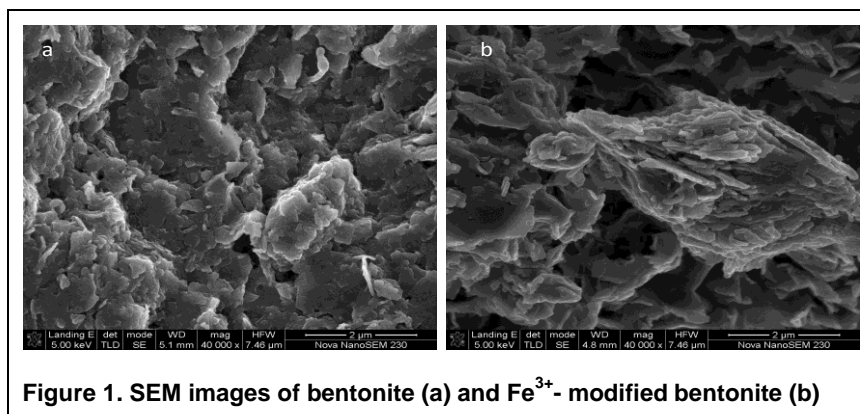

Figure 1. SEM images of bentonite (a) and Fe^{3+}- modified bentonite (b)

BET surface area increased from 16-49.9 m^2/g. external surface area from 11.08-37.42 m^2/g and micropore area from 4.93-12.53 m^2/g. An increase in the external surface area could be due to surface adsorption and surface precipitation of Fe^{3+} from solution. An increase in surface area makes the Fe^{3+}-modified bentonite clay a better adsorbent than the raw bentonite clay. Reaction of the bentonite with Fe^{3+} solution leads to a reduction of CEC indicating the main mechanism of Fe^{3+} uptake is by ion exchange. The CEC results also confirm that the main exchangeable cation is Na^+. CEC for bentonite was 262 meq/100g and for Fe^{3+}-modified bentonite was 188.9 meq/100g. Bentonite clay had pHpzc of 8.2 while Fe^{3+}-modified bentonite clay was 8.5. Modification of the raw bentonite clay with Fe^{3+} increases the pHpzc which extends the pH range for adsorption of anions meaning that the Fe^{3+}-modified bentonite clay will have high adsorption capacity for anions than the raw bentonite clay. XRF identified SiO_2 and Al_2O_3 as the main components confirming bentonite is an alumino-silicate material. Relatively high concentrations of MgO, Na_2O, CaO and K_2O indicates that Mg^{2+}, Na^+, Ca^{2+} and K^+ are the main exchangeable cations. This is confirmed by the subsequent decrease of the content of these chemical species in the Fe^{3+}-modified bentonite clay and subsequent increase in Fe in modified clay. Minor chemical species such as F^-, Sr, Ba, Zr and Cl^- were identified in both bentonite and the Fe^{3+}-modified bentonite that could be released in the reaction mixture during the adsorption process. XRD confirmed montmorillonite (74.76 %) as the major mineral phase with minor quantities of quartz (15.98 %), plagioclase (8.17 %) and muscovite (1.09 %) (Fig 2).
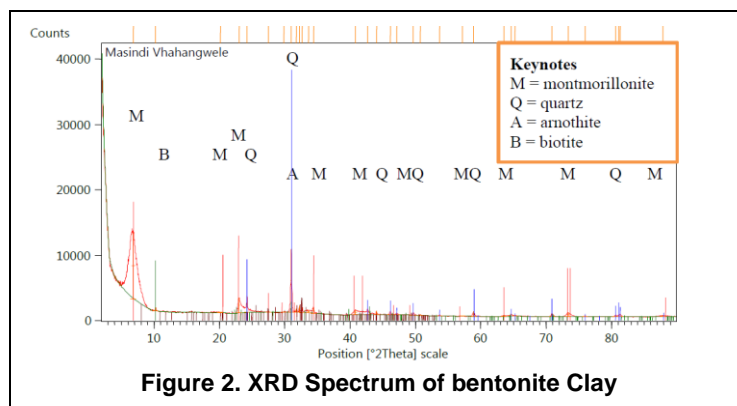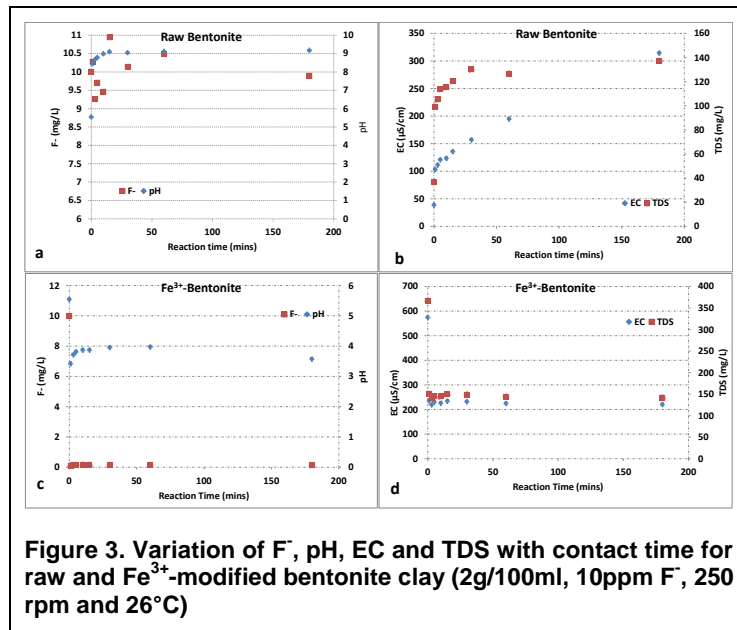

Figure 2. XRD Spectrum of bentonite Clay

2. Defluoridation of Water using the Raw and Fe^{3+}-modified Bentonite Clay: Optimization of F^- adsorption conditions

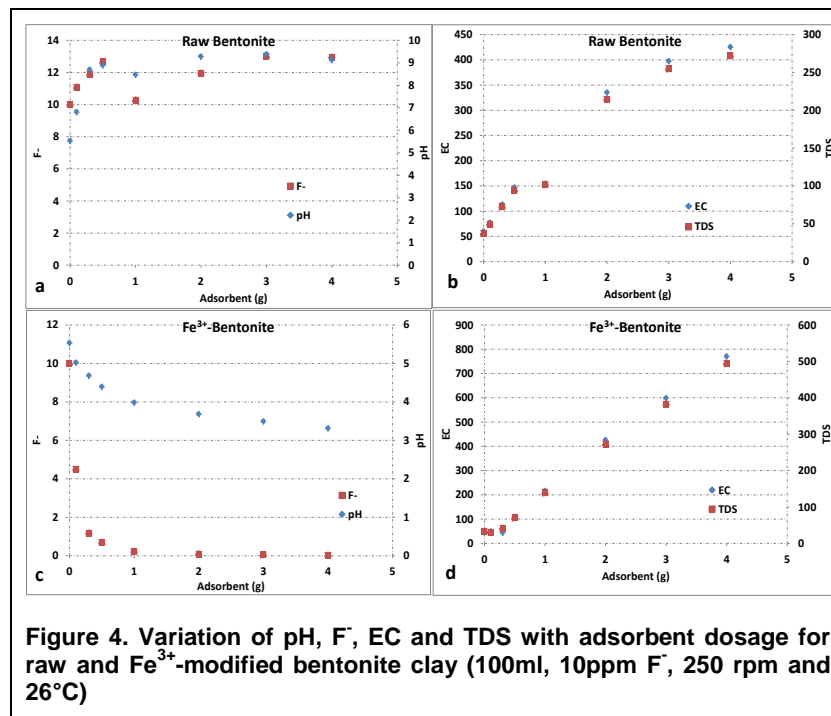*Fluoride removal as a function of contact time*

Figure 3 shows the variation of pH, F-, EC, TDS with time for raw and Fe3+-modified bentonite clay. The TDS and EC increased with contact time for bentonite (Fig 3b) indicating possible release of soluble chemical species in solution. Bentonite seems to increase the pH of the solution through possible dissolution of alkaline metal oxides (Fig 3a). In addition raw bentonite seems to release F^- into solution.

XRF results showed presence of F in the raw bentonite. Despite the initial decrease in EC and TDS for the Fe^{3+}-bentonite reaction mixture the EC and TDS stabilizes at the same level as raw bentonite for the entire contact time (Fig 3b and d). Fe^{3+}-bentonite reduces the F^- to below 1ppm within 1 minute of contact while the pH stabilizes at 8 (Fig 3c). This clearly indicates changes in the physicochemical and surface properties of the bentonite clay on introduction of Fe^{3+} ions.

Figure 3. Variation of F⁻, pH, EC and TDS with contact time for raw and Fe³⁺-modified bentonite clay (2g/100ml, 10ppm F⁻, 250 rpm and 26°C)

Fluoride removal as a function of adsorbent dosage

Figure 4 shows the variation of pH, F⁻, EC and TDS with adsorbent dosage for raw and Fe³⁺-modified bentonite clay. An observation of Fig 4a shows that raw bentonite actually releases F⁻ into solution, this is observed to increase with adsorbent dosage. pH also increases with adsorbent dosage confirming release of OH- in solution through possible dissolution of alkaline metal oxides (Fig 4a). On the contrary the Fe³⁺-modified bentonite clay decreases the F⁻ content to below 1 ppm at 1 g adsorbent dosage (Fig 4b). The pH decreases with increase of adsorbent dosage. The Fe³⁺-modified bentonite clay could be releasing H⁺ to compensate for the adsorbed F⁻ ions hence lowering pH (Fig 4b).

Figure 4. Variation of pH, F⁻, EC and TDS with adsorbent dosage for raw and Fe³⁺-modified bentonite clay (100ml, 10ppm F⁻, 250 rpm and 26°C)

Fluoride removal as a function of adsorbate concentration

Figure 5 shows the % F⁻ adsorption, final F⁻ concentration as a function of adsorbate concentration

Figure 5. Variation of % F⁻ adsorption, equilibrium F⁻ concentration as a function of adsorbate concentration (2g/100 ml, 250 rpm, Conc 4-60 ppm and 26°C)
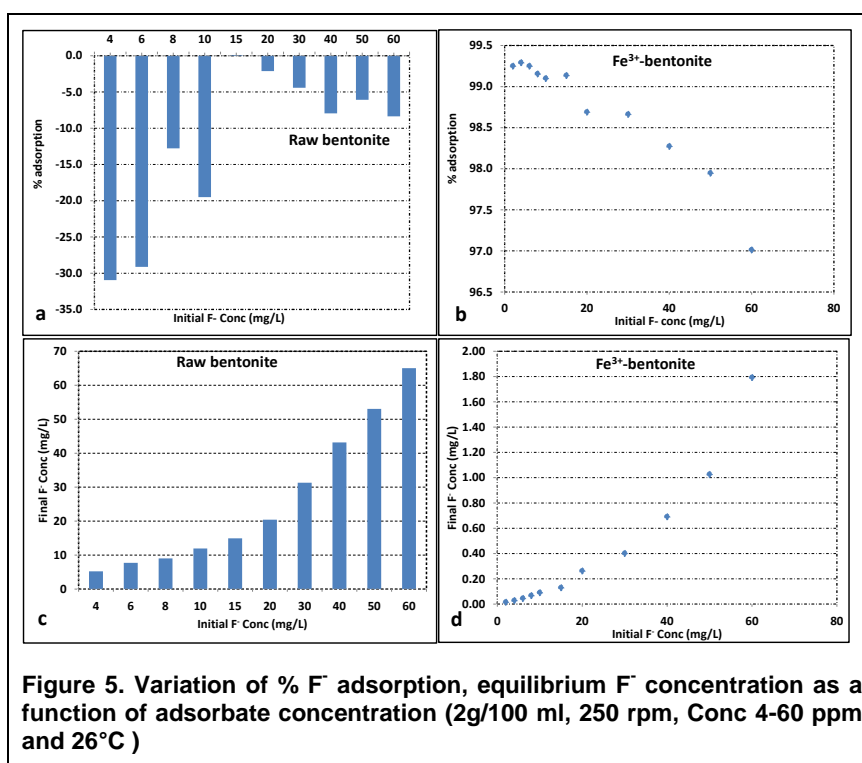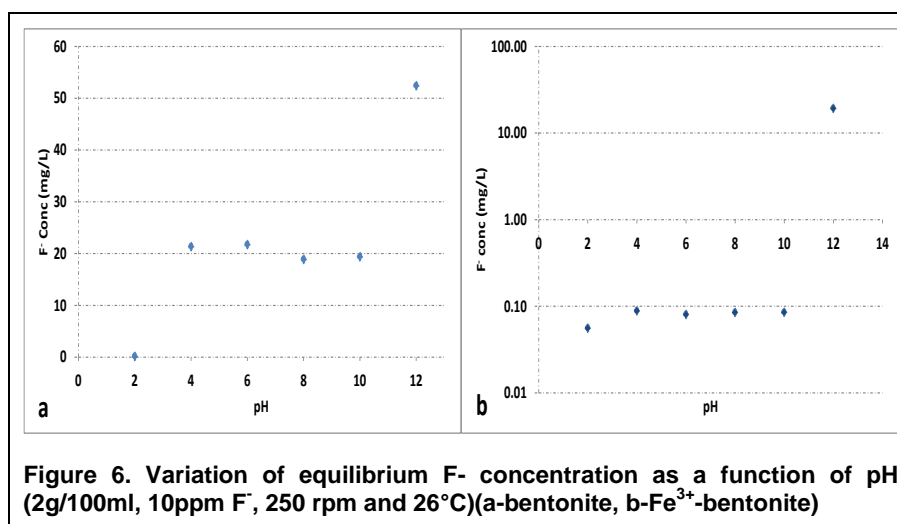
Figure 5a shows the % F- adsorption as a function of the adsorbate concentration for the raw bentonite. Raw bentonite is observed to release F- in the reaction mixture and this is observed to be high at lower adsorbate concentration (4-10 ppm) (Fig 5a and c). Fe3+-modified bentonite shows efficient adsorption, removing > 98 % of F⁻ even as the adsorbate concentrations increases to 60 ppm (Fig 5b and d).

Fluoride removal as a function of initial pH

Figure 6a and b shows the final concentration of F⁻ in the residual water as a function of the initial pH.

Figure 6. Variation of equilibrium F- concentration as a function of pH (2g/100ml, 10ppm F⁻, 250 rpm and 26°C)(a-bentonite, b-Fe³⁺-bentonite)

Both raw and Fe^{3+}-modified bentonite clay show high removal of F⁻ at low pH 2 (Fig 6a, b). Raw bentonite however shows no adsorption of F⁻ at pH 4-10 and at pH 12, it releases F⁻ into residual solution. Fe^{3+}-modified clay shows strong adsorption of F⁻ at pH range of 2-10 but at pH 12 the F⁻ remains largely in solution. The low adsorption at highly alkaline pH could be due to the competition of adsorption sites with OH^-.

Conclusions and recommendations

Raw bentonite was successfully modified by adsorption of Fe^{3+} from aqueous solution. Optimum loading was observed at 30 minutes of agitation using 100ppm Fe^{3+} solution. Fe^{3+}-bentonite was observed to be a suitable adsorbent for F^- from aqueous solution as compared to raw bentonite. The removal of F^- from aqueous solution was observed to strongly depend on the contact time, pH of the solution and amount of adsorbent. Raw bentonite was observed to be ineffective in the adsorption of F^- from the aqueous solution, it was observed to release F^- in the solution and this was more pronounced at alkaline pH > 10. The results reveal that Fe^{3+}-modified bentonite clay is a potential strong adsorbent for F^- removal in ground water. However pretreatment of the raw bentonite with alkaline media before modification should be investigated with a view to removing the residual fluoride in the clay matrix.

Acknowledgements

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