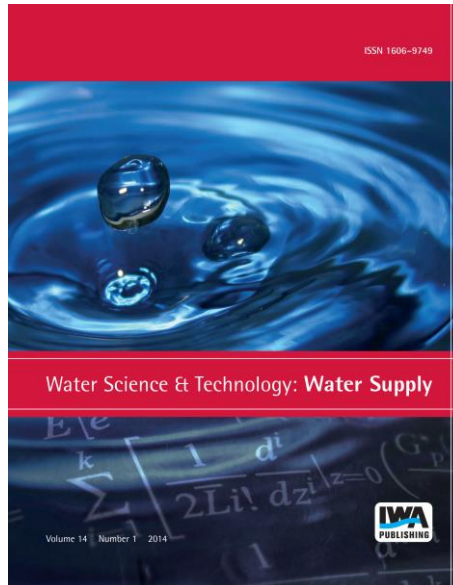


ELECTRONIC OFFPRINT

Use of this pdf is subject to the terms described below



This paper was originally published by IWA Publishing. The author's right to reuse and post their work published by IWA Publishing is defined by IWA Publishing's copyright policy.

If the copyright has been transferred to IWA Publishing, the publisher recognizes the retention of the right by the author(s) to photocopy or make single electronic copies of the paper for their own personal use, including for their own classroom use, or the personal use of colleagues, provided the copies are not offered for sale and are not distributed in a systematic way outside of their employing institution. **Please note that you are not permitted to post the IWA Publishing PDF version of your paper on your own website or your institution's website or repository.**

If the paper has been published "Open Access", the terms of its use and distribution are defined by the Creative Commons licence selected by the author.

Full details can be found here: <http://iwaponline.com/content/rights-permissions>

Please direct any queries regarding use or permissions to ws@iwap.co.uk

Effects of calcination temperature and solution pH on the defluoridation potential of Al/Fe oxide-modified diatomaceous earth: metal leaching and sorbent reuse

Anthony A. Izuagie, Wilson M. Gitari and Jabulani R. Gumbo

ABSTRACT

An evaluation of the effects of calcination temperature and solution pH on the fluoride removal capacity of Al/Fe oxide-modified diatomaceous earth was carried out. The sorbent was observed to be most effective and stable within the pH range 6.70–8.12, where the lowest concentrations of Al and Fe (<1 mg/L) in treated water were recorded. Thus, sorbent loss was minimal at that pH range. It was observed that the sorbent lost its efficiency and stability at calcination temperatures above 600 °C. Inductively coupled plasma-mass spectrometer analysis of metals in supernatants and thermogravimetric analysis of the sorbent showed that there was substantive loss of Al and Fe from the sorbent at temperatures above 600 °C because of evaporation. K₂SO₄ solution proved to be the best regenerant for spent sorbent compared to NaOH and Na₂CO₃, which caused sorbent loss owing to high solution pH. The CO₃²⁻ from Na₂CO₃ bound to regenerated sorbent so much that it could not be displaced by fluoride during subsequent defluoridation experiments. Sorbent regenerated with 0.1 M K₂SO₄ solution could reduce 10 mg/L fluoride in artificial water at a dosage of 0.8 g/100 mL by 81.8% and 67.2% at the second and third cycles, respectively.

Key words | calcination, defluoridation, diatomaceous earth, metal leaching, reuse, solution pH

Anthony A. Izuagie (corresponding author)

Wilson M. Gitari

Department of Ecology and Resource
Management,
University of Venda,
Thohoyandou,
South Africa
E-mail: aaizuagie@gmail.com

Jabulani R. Gumbo

Department of Hydrology and Water Resources,
University of Venda,
Thohoyandou,
South Africa

Anthony A. Izuagie

Wilson M. Gitari

Jabulani R. Gumbo

Environmental Remediation and Pollution
Chemistry Research Group, School of
Environmental Sciences,
University of Venda,
Thohoyandou,
South Africa

INTRODUCTION

Groundwater serves as source of drinking-water in many rural communities where there is no pipe-borne water. But long-term ingestion of groundwater containing fluoride in excess of the WHO guideline of 1.5 mg/L causes dental fluorosis. Skeletal fluorosis occurs as a result of long-term ingestion of water containing 3–6 mg/L fluoride (WHO 2011). However, a minimum fluoride concentration of 0.5 mg/L is required in drinking-water to prevent dental caries in children and adults (WHO 2011). Where there is no appropriate alternative drinking-water besides high-fluoride groundwater, it is crucial to reduce the fluoride content to a safe limit.

This study was premised on the use of the adsorption technique as the most suitable method for groundwater defluoridation in households in rural communities with

Al/Fe oxide-modified diatomaceous earth (DE) as an adsorbent. DE is an earthy, very finely porous, siliceous sedimentary rock. It is chemically inert in most liquids and gases and has low thermal conductivity (Antonides 1998; Mohamedbaker 2010). Among many uses of DE, the natural material has been used as filtration medium for beer and wine because of its very fine pores (Antonides 1998). DE is not toxic, based on the report of the elemental analysis of treated water using raw DE (Izuagie *et al.* 2015). The chemical formula of DE is SiO₂·2H₂O. Not being organic, the material does not have the tendency of undergoing putrefaction to foul water.

A study by Yuan *et al.* (2004) showed that DE has hydroxyl groups in its chemical structure (SiO₂·nH₂O) which could exchange for electronegative fluoride. It has

been reported that the fluoride uptake capacity of raw DE is very poor, even at the most favourable solution pH of 2 (Izuagie *et al.* 2015). Hence, surface modification of DE with high fluoride affinity metal oxides has become expedient to achieve high fluoride removal from water. The metal oxide modification occurred through the coating of the pores of DE with Al/Fe oxide.

Adsorbent is the key focus in adsorption technology. The cost and the processes involved in the development of a high-performance adsorbent cannot be overemphasized. It is therefore necessary to understand the chemical state and characteristics of an adsorbent at different calcination temperatures and solution pH; not only to achieve a maximum contaminant uptake from water but also considering the reusability of the exhausted sorbent.

The pH of solution plays a principal role in determining the amount of fluoride adsorbed from solution (Kagne *et al.* 2009; Manna *et al.* 2015; Saha *et al.* 2015; Xu *et al.* 2015). However, the most suitable solution pH for the removal of a contaminant may correspond to the pH at which the highest leaching of an active metal component in the sorbent occurs. A pH range of 3 to 6 was reported for the highest adsorption of phosphate from contaminated water using Fe–Mg–La tri-metal composite sorbent (Yu & Chen 2015). While the pH range appeared most appropriate for phosphate removal from water, a high dissolution of lanthanum from the sorbent was observed at pH < 5. Hence, loss of sorbent was most pronounced at pH < 5. Sakhare *et al.* (2012) reported the use of calcium aluminate material for defluoridation of water where significant amounts of calcium and aluminium were released from the sorbent under acidic and alkaline conditions, thereby resulting in sorbent loss. However, at a neutral pH, the amount of aluminium leached from the calcium aluminate material was within the acceptable limit of 0.2 mg/L. The loss of adsorbent as a result of unfavourable solution pH undermines the reusability of sorbent for subsequent contaminant removal from water.

Calcination of sorbents at different temperatures is usually intended to improve their adsorption capacity (Wang *et al.* 2015). Calcination above a temperature limit may affect the phase and chemical composition of some sorbents. An example is the case of the change of phase of bauxite calcined at 400 °C and 500 °C (Sadju *et al.* 2008).

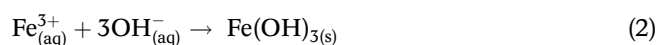
Bauxite calcined at 200 °C was reported to have a better adsorption capacity than at any other higher temperature. The thermogram showed that at 400 °C, gibbsite (Al(OH)₃) had started to transform to boehmite (AlOOH), while the kaolinite structure was completely destroyed at 500 °C, resulting in a highly amorphous phase that could be ascribed to different activated aluminas (Sadju *et al.* 2008).

DE is available in large deposits around the world (Lemonas 1997). Perhaps for this reason not much is reported about the reusability of its modified species. Being an amorphous material the modified form may be considered to be less apt to withstand the reaction rigours of the crystalline sorbents (Volzone & Garrido 2008; Ma *et al.* 2011; Tomar *et al.* 2013). This study therefore was undertaken to evaluate the effect of calcination temperature and solution pH on the defluoridation potential of Al/Fe oxide-modified DE and also to find an appropriate reagent for regenerating the spent sorbent for subsequent fluoride removal from water.

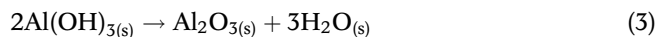
MATERIALS AND METHODS

Sorbent preparation

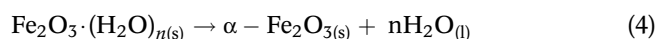
Al/Fe oxide-modified DE with metal ratio 1:1 was prepared by adding 15 g of DE, 50 mL each of 0.5 M Al³⁺ and 0.5 M Fe³⁺ solutions, prepared from aluminium tetraoxosulphate(IV) octadecahydrate (Al₂(SO₄)₃·18H₂O) and iron(III) hydrate (Fe₂(SO₄)₃·xH₂O), respectively. The hydroxides of the two metals were co-precipitated on DE by adjusting the pH of the mixture to 8.2 with 2 M NaOH with vigorous stirring. The formation of aluminium and iron(III) hydroxides from solution is illustrated by Equations (1) and (2), respectively. Further mixing was done for 50 min at 100 rpm followed by centrifuging. The solid was washed with 500 mL of Milli-Q water and separated from the supernatant by centrifuging. The solid was dried in the oven at 110 °C for 8 h, cooled in the desiccator, crushed and sieved through a 250 μm test sieve. The dry sorbent was stored in a corked plastic bottle.



Water would be eliminated from $\text{Al}(\text{OH})_3$ to form Al_2O_3 on heating at $1,050^\circ\text{C}$ (Seecharran 2010) according to Equation (3):



The hydrous oxide $\text{Fe}_2\text{O}_3(\text{H}_2\text{O})_n$, part of which contains $\text{FeO}\cdot\text{OH}$, is converted to $\alpha\text{-Fe}_2\text{O}_3$ on heating at 200°C (Lee 2007) according to Equation (4):



Effect of contact time and sorbent dosage on fluoride removal

The effect of contact time on adsorption of fluoride on Al/Fe oxide-modified DE was evaluated by contacting 0.1 g of the sorbent with aliquots of 100 mL of 10 mg/L fluoride solution at 200 rpm for 5, 10, 20, 30, 40, 50, 60 and 70 min. The experiment was repeated using sorbent dosages of 0.2 g and 0.3 g. Fluoride analysis of the centrifuged mixtures showed that the highest fluoride removal occurred at the 50 min contact time. The results of fluoride in supernatants obtained when mixtures of sorbent dosages of 0.1 to 1 g and aliquots of 100 mL of 10 mg/L fluoride solution were equilibrated showed that the optimum fluoride removal was achieved with a dosage of 0.6 g. The use of dosages above 0.6 g would amount to a waste of material as no appreciable increase in fluoride removal occurred at higher dosages.

Morphological analysis and energy dispersion X-ray spectroscopy

The surface structures of the raw and calcined samples of Al/Fe oxide-modified DE were analysed by carrying out the scan using a JEOL JSM-7500F Scanning Electron Microscope (SEM). The elemental analysis of the raw and Al/Fe oxide-modified DE was carried by coupling the energy dispersion X-ray spectroscope (EDX) on the JEOL JSM-7500F Scanning Electron Microscope. Both SEM and EDX analyses of samples were carried out at the University of Cape Town, South Africa.

Metals leaching assessment of the sorbent

The pH of mixtures containing 0.6 g of Al/Fe oxide-modified DE and 90 mL of 12.5 mg/L fluoride was adjusted to different values (2 to 12) using 0.1 M HCl and 0.1 M NaOH solutions. In each mixture, the final volume of 100 mL of solution was attained by adding an appropriate volume of Milli-Q water. The mixtures were equilibrated for 50 min, followed by centrifuging to obtain clear supernatants. The stability of the sorbent in the different mixtures was evaluated by analysis of Al and Fe in the supernatants. Aliquots of 10 mL of the supernatants were measured into 15 mL centrifuge tubes and acidified with 2 mL of 3 M HNO_3 . The tubes were corked and shaken thoroughly before carrying out Al and Fe analyses of the supernatants using an inductively coupled plasma-mass spectrometer (ICP-MS).

Sorbent calcination

A mass of 1.5 g of Al/Fe oxide-modified DE was weighed into six porcelain crucibles and calcined respectively in a muffle furnace at 200, 400, 600, 700, 800 and 900°C for 60 min. Each sample was removed from the furnace after calcination, cooled in air for some time and finally left to cool to room temperature in the desiccator. Further analyses were carried out using the calcined samples.

Effect of calcination on composite metals

A mass of 0.5 g of each of the calcined samples and the sample originally dried at 110°C was weighed into 50 mL of 3 M HNO_3 solutions contained in 250 mL plastic bottles. The bottles were corked and left to stand for 3 h to bring the Al and Fe into solution. The dissolution was further enhanced by heating the mixtures at a temperature of 60°C for 30 min. The mixtures and the analysis blank were passed through $0.45\ \mu\text{m}$ polypropylene membrane filters in a filter flask assemblage aided by a vacuum pump. The filtrates were then analysed for dissolved metals by ICP-MS.

Batch defluoridation experiment using calcined sorbent

The calcined samples were used in defluoridation of artificial fluoride water to evaluate the stability temperatures of the

calcined sorbent. The procedure involved contacting the optimum dosage of 0.6 g of each sample, including the original sample dried at 110 °C, with 100 mL of 10 mg/L fluoride solution for 50 min (the optimum contact time) in a reciprocating water bath at a shaking speed of 200 rpm. The mixtures were filtered using 0.45 µm polypropylene membrane filters. One millilitre of Total Ionic Strength Adjustment Buffer (TISAB III) was added to aliquots of 10 mL of each filtrate, stirred and left for 40 min for complete decomplexation of metal-fluoride complexes. The fluoride was analysed with a fluoride ion-selective electrode (Orion VERSA STAR advanced electrochemistry meter fluoride ion-selective electrode) calibrated with four fluoride standards in which TISAB III was added at the volume ratio of 1:10.

The per cent fluoride removal was calculated using the following equation:

$$\%F^- \text{ removal} = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (5)$$

where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of fluoride.

Thermogravimetric analysis of sorbent

Thermogravimetric analysis was used to evaluate the change in weight of Al/Fe oxide-modified DE with temperature. Using the thermogravimetry instrument, TGA Q500 V20.13 Build 39, the thermogravimetry of the sorbent was run along with that of the pure Al/Fe oxide for comparison. In the analysis, 9.4101 mg of Al/Fe oxide and 8.3161 mg of Al/Fe oxide-modified DE were heated in the furnace at increasing temperature until a maximum temperature of 900 °C was attained. The per cent weight of each sample at each temperature was plotted against the corresponding temperature.

Sorbent regeneration and reuse

A sorbent regeneration study was carried out to evaluate the reusability of the recycled spent sorbent. The reagents used for regenerating the spent sorbent included 0.01 M NaOH, 0.01 M Na₂CO₃ and 0.1 M K₂SO₄ solutions. In each case, the first process involved defluoridation of 100 mL of 10 mg/L fluoride solution using 0.8 g of Al/Fe oxide-modified DE. The mixtures were centrifuged and analysis of supernatant for residual fluoride was done as described above. The separated

solid was then washed with Milli-Q water, dried in the oven at 110 °C for 8 h and then cooled in the desiccator. The dry solid was crushed and sieved with a 250 µm test sieve.

The sieved, spent sorbent was weighed and equilibrated with 100 mL of each of the evaluated regenerants for 50 min to desorb fluoride. Centrifuging, washing of solids, measurement of desorbed fluoride and drying of solids were done as in previous cases. A known mass of dry, crushed and sieved sorbent was again contacted with 100 mL of 10 mg/L fluoride solution. The regeneration of spent sorbent and defluoridation with the regenerated sorbent continued until the third or fourth cycles of defluoridation depending on the observed trend of fluoride removal.

Solubility of DE

The solubility of DE, which is basically a siliceous material (Antonides 1998), was evaluated at different solution pH. The procedure involved equilibration of a mixture of 0.4 g of DE and 50 mL of 8 mg/L fluoride solutions of different pH for 30 min. The supernatants obtained after centrifuging the mixtures were acidified with 3 M HNO₃ and analysed for Si among other elements using ICP-MS and ICP-atomic emission spectroscopy (ICP-AES). The concentrations of Si determined in the various supernatants give the estimate of the dissolved silica.

RESULTS AND DISCUSSION

Scanning electron microscopy

The images of the scanning electron microscopy of calcined samples of Al/Fe oxide-modified DE at a particle-size image magnification of 10,000 are presented in Figure 1. The pores of Al/Fe oxide-modified DE in images (a), (b) and (c) for Al/Fe oxide-modified DE calcined at 200, 400 and 600 °C, respectively, were more pronounced than those in image (d). At 900 °C, the DE structural framework had become very fragile perhaps partly because of loss of some silica to evaporation and possibly as a result of Si-O bond rupture. So the pores were thinning out. Ibrahim & Selim (2012) reported a similar result of the gradual disappearance of pores of DE from a temperature of 900 °C.

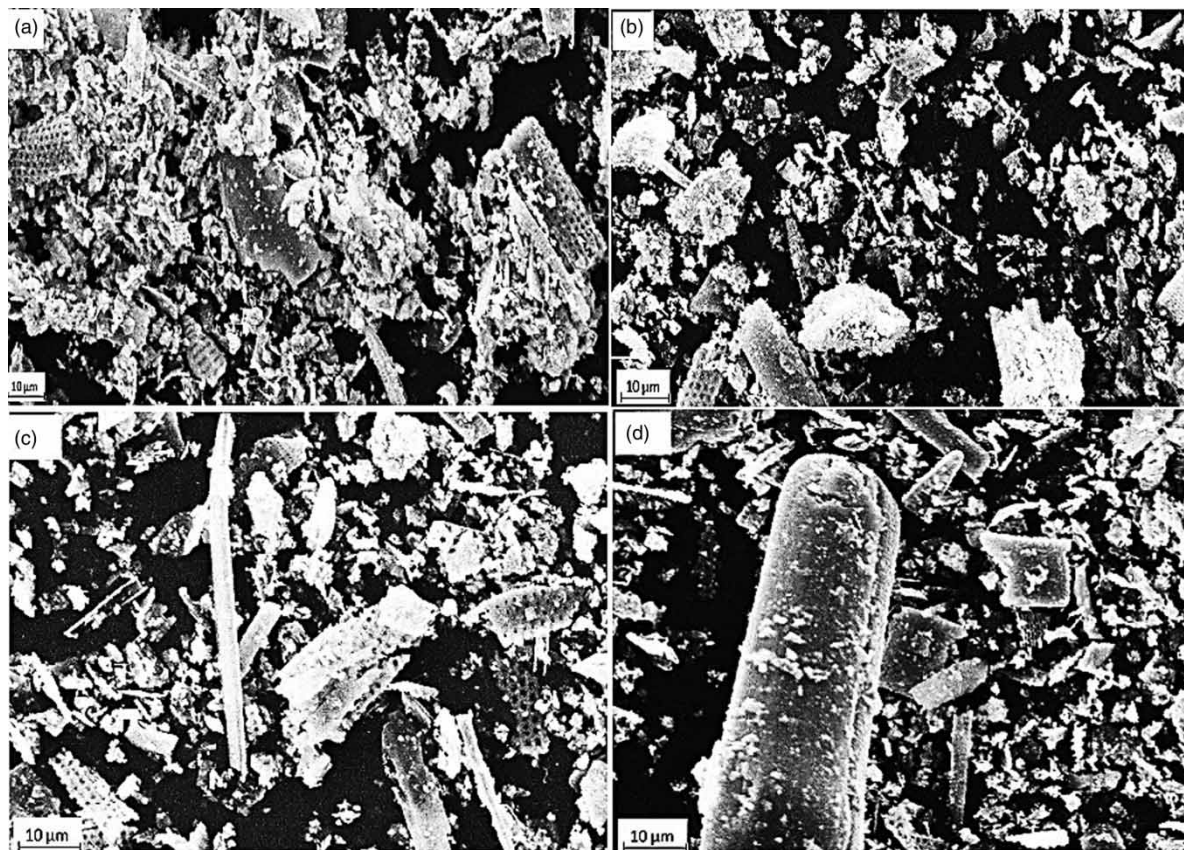


Figure 1 | SEM images of Al/Fe oxide-modified DE calcined at (a) 200 °C, (b) 400 °C, (c) 600 °C and (d) 900 °C.

Energy dispersion X-ray spectroscopy

The results of the energy dispersion X-ray spectroscopy of the raw and Al/Fe oxide-modified DE are presented in Figure 2. The EDX image of raw DE shows there was no noticeable presence of Al and Fe in the material. However, with modification of the raw DE with Al and metal oxides, it was possible to record the mean weight per cent values of 1.99% and 3.38% for Al and Fe, respectively. The mean weight per cent of oxygen increased from 45.22% in the raw DE to 49.16% in the modified sample. This clearly shows that the metal oxides were actually incorporated into the pores of DE on modification.

Metal leaching assessment of the sorbent

Table 1 gives the results of the Al and Fe analysed by ICP-MS after blank correction. The extent of metal leaching

from Al/Fe oxide-modified DE at different solution pH is related to the sorbent's stability in the solution. The least concentration of leached Al (0.17 mg/L) was recorded at pH 6.70. The more that metals were lost from the sorbent, the lower was the fluoride removal from water. Fluoride removal was observed to be maximum (92.3%) at the minimum leaching of Al, that is at pH 6.70. Considering the effect of leached Al on human health, at those levels of pH evaluated, the treated water would be least hazardous at pH 6.70 as Al concentration is within the limit of 0.1–0.17 mg/L in water treatment facilities (WHO 2011).

Except for the lowest solution concentration of Fe at pH 4.58, dissolution of Al_2O_3 and Fe_2O_3 from the sorbent was minimal within the equilibrium pH range 6.70–8.12. This pH range compares to that for the least metal leaching from the raw DE reported previously by the authors (Izuagie *et al.* 2015). The highest loss of Al^{3+} was observed at pH 11.12, closely followed by the loss at pH 2.51. The

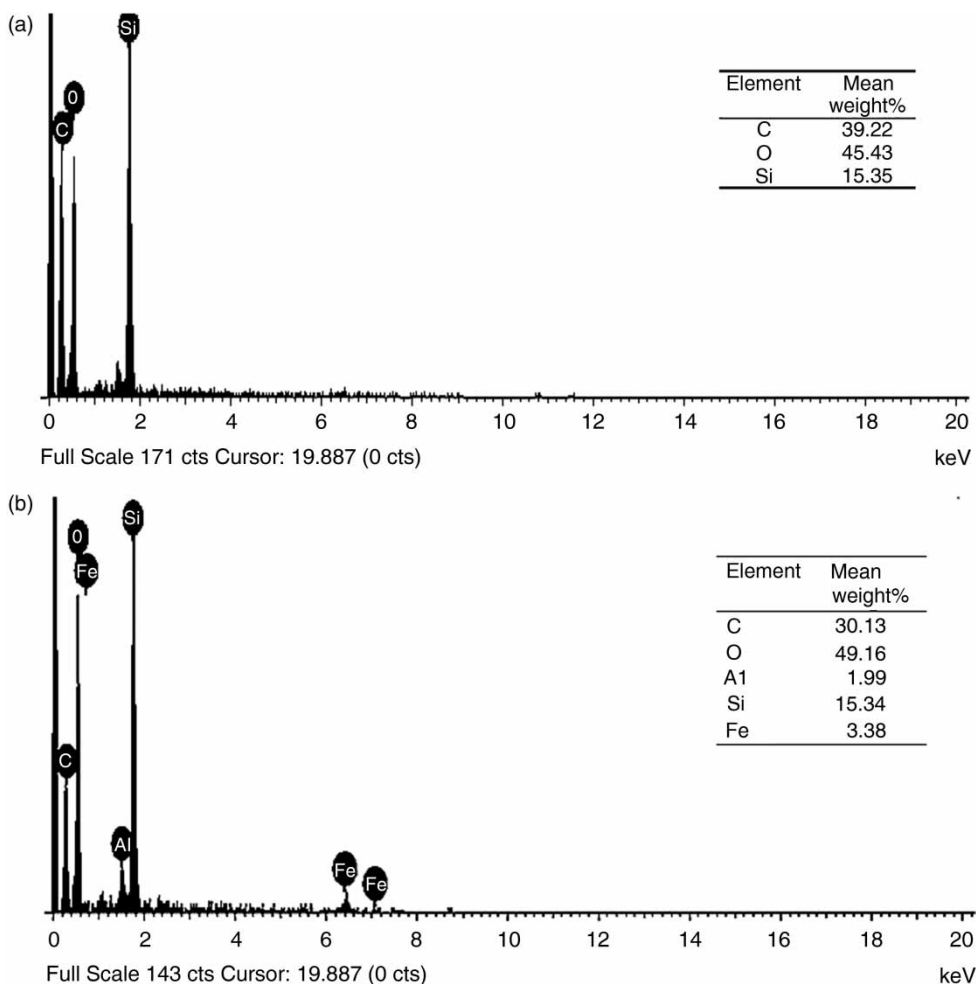


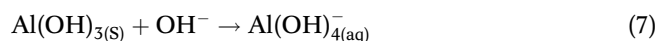
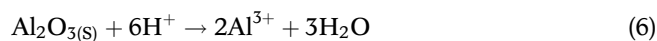
Figure 2 | Energy dispersion spectrograph of (a) raw DE and (b) Al/Fe oxide-modified DE.

Table 1 | Variation of fluoride removal with equilibrium pH and leached metals

Equilibrium pH (pH _e)	Fluoride removal (%)	Al (mg/L)	Fe (mg/L)
2.51	27.5	60.89	11.42
4.58	44.8	7.90	0.04
6.70	92.3	0.17	0.16
8.12	69.8	0.46	0.38
10.49	0.44	35.92	0.98
11.12	0.44	86.27	7.07

appreciable loss of Al₂O₃ at pH values of 4.58 and 2.51 is in accord with those reported in the literature where at pH < 5 Al₂O₃ gets dissolved leading to loss of sorbent (Bishop & Sancoucy 1978; Shrivastava & Vani 2009). Al₂O₃ or Al(OH)₃

is amphoteric, being able to react with either acid (H⁺) or base (OH⁻) to form salt. This explains why higher values of Al³⁺ were observed at the low and high pH values. The reactions of the metal oxide or hydroxide with acid or base (Matthews 1992; Lee 2007) are represented by Equations (6) and (7), respectively:



The least silica dissolution was observed around pH 2. Figure 3 shows how the concentration of Si in the supernatants varied with the equilibrium pH. Dissolution of

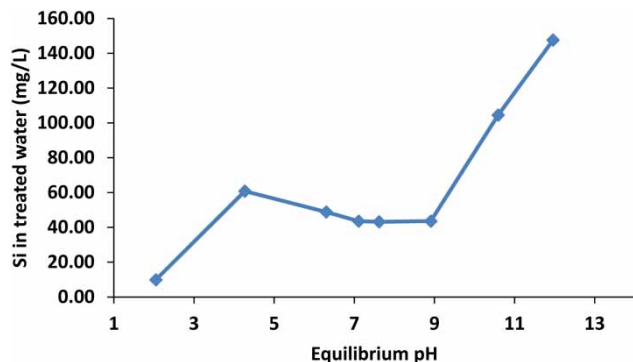
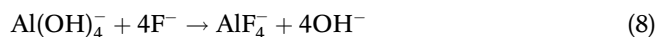


Figure 3 | Loss of silica from DE as a function of solution pH (initial fluoride concentration: 8 mg/L; dosage of raw DE: 0.4 g/50 mL; shaking speed: 200 rpm; temperature: 297 K).

silica assumed a constant value within the pH range of about 7 to 9. Above pH 9, silica dissolution increases significantly with increasing pH. At a very high pH there could be possible dissolution of the hydrous form of Fe_2O_3 to form the soluble complex $[\text{Fe}(\text{OH})_6]^{3-}$ (Lee 2007). The highest Fe dissolution occurred at the most acidic solution of pH 2.51 (Table 1). The hydrous oxide $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (also written as $\text{FeO} \cdot \text{OH}$) is soluble in acids, giving $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (Housecroft & Sharpe 2005; Lee 2007). The supernatants from the sorbent–fluoride solution equilibration were colloidal and brownish. The brown colour was as a result of Fe^{3+} in solution.

The pH at point-of-zero charge (pHpzc) of Al/Fe oxide-modified DE was determined to be 6.0 ± 0.2 (Izuagie *et al.* 2016). Fluoride removal by the sorbent at $\text{pH} > \text{pHpzc}$ would be by exchange of fluoride ions in solution with hydroxyl ions on the sorbent as represented by Equations (8) and (9). At $\text{pH} > \text{pHpzc}$, the surface of the sorbent is negatively charged.



At $\text{pH} < \text{pHpzc}$, the surface of the sorbent would be positively charged so that fluoride removal from solution would occur through the attraction of fluoride ions to the positively charged surface as illustrated by Equations (10) and (11). Equations (8)–(10) are as predicted by the speciation model PHREEQC Interactive Version 3 (Parkhurst & Appelo 2012) used to evaluate the speciation of Al and

Fe from Al/Fe oxide-modified DE at different values of $\text{pH} < \text{pHpzc}$.



Sorbent calcination

Effect of calcination on composite metals

The results of the ICP-MS analysis of the Al and Fe in the supernatants of calcined Al/Fe oxide-modified DE were corrected for blank. Figure 4 shows the trend in the metal constituents of the calcined sorbent at different temperatures. The two metals show a similar trend across the calcination temperature. The slight increase in the dissolved metal as temperature increased might be as a result of an increase in the solubility of the metal oxides' phases with calcination temperature. The very low concentrations of metals in the supernatants at temperatures above 600°C are indicative of significant loss of metals to evaporation at those temperatures. The loss increased with increase in temperature. Hence, Al/Fe oxide-modified DE is not stable above 600°C .

Defluoridation with calcined sorbent

The stability of Al/Fe oxide-modified calcined DE at different temperatures was evaluated by comparing the results of fluoride removal by the calcined samples. The plots of the per cent

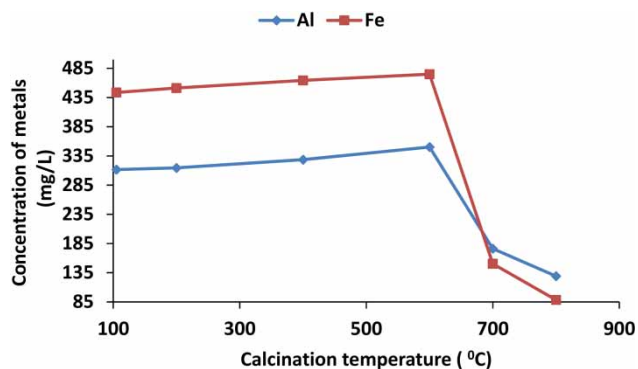


Figure 4 | Concentration of Al and Fe in Al/Fe oxide-modified DE as a function of calcination temperature (adsorbent dosage: 0.5 g/50 mL of acid solution).

fluoride removal against calcination temperature as presented in Figure 5 show that fluoride removal declined remarkably from the calcination temperature of 600 °C. The progressive reduction in percentage fluoride removal as the calcination temperature increased must be due to loss of metals from the adsorbent by evaporation. At 900 °C, the structure of DE which served as a support for the Al/Fe oxide could become completely destroyed through Si-O bond rupture (Ibrahim & Selim 2012). The netlike structure had crumbled such that it was impossible to separate the sorbent calcined at 900 °C from the mixture by centrifuging. The particles looked fragile and were floating in the intensely coloured suspension. The defluoridation experiment therefore provides evidence that loss of sorbent occurred appreciably from the calcination temperature of 600 °C.

Thermogravimetric analysis

The thermograms of Al/Fe oxide-modified DE and Al/Fe oxide show a similar trend of weight loss with increasing temperature (Figure 6). A rapid weight loss occurred as heating proceeded from 28 °C to 200 °C, where any moisture and adsorbed gases would have been lost. The thermogram of Al/Fe oxide-modified DE shows a steeper profile at 380 °C. This was most likely due to the loss of the structural water of DE. A new trend of weight loss was noticed around 600 °C for both thermograms. The results therefore agree with the evidence provided by the metal analysis and defluoridation with calcined sorbent. Hence, Al/Fe oxide-modified DE is only stable to a limit of 600 °C.

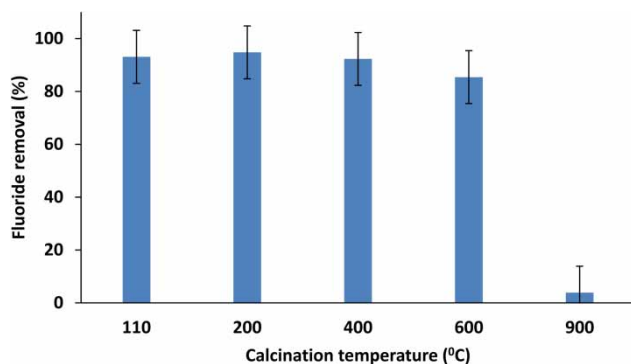


Figure 5 | Variation of percentage fluoride removal with calcination temperature (initial fluoride concentration: 10 mg/L; sorbent dosage: 0.6 g/100 mL; contact time: 50 min; shaking speed: 200 rpm).

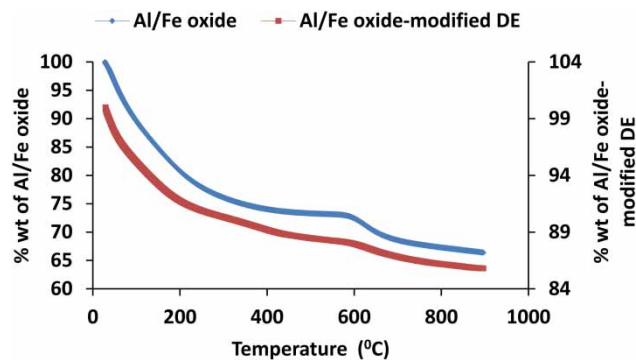


Figure 6 | The thermograms of Al/Fe oxide and Al/Fe oxide-modified DE.

Sorbent regeneration and reuse

Regeneration of spent Al/Fe oxide-modified DE using 0.1 M K_2SO_4 solution proved to be the most reliable of the evaluated regenerants. By the second defluoridation cycle, a dosage of 0.8 g/100 mL was able to reduce the concentration of 10 mg/L fluoride in water by 81.8%. With the use of 0.01 M NaOH and 0.01 M Na_2CO_3 for fluoride desorption from the fluoride-loaded (spent) sorbent, percentage fluoride removal at the second and higher defluoridation cycles were far less than that observed at the first application of the sorbent. The worst trend was observed with the use of Na_2CO_3 in particular. Both reagents gave a high desorption pH, which led to appreciable loss of silica, a condition already discussed above. The dissolution of silica implied the loss of Al/Fe oxide. This was evident from the intense brown colour of the supernatants, which showed the loss of Fe^{3+} from the adsorbent. Apart from the problem associated with the alkaline pH of regeneration with Na_2CO_3 , CO_3^{2-} was found to be strongly bound to the sorbent such that it was practically impossible for the anion to be replaced by fluoride in solution. It is widely reported that CO_3^{2-} competes highly with fluoride in batch experiments involving fluoride removal with adsorbents (Kamble *et al.* 2007, 2009; Bansiwala *et al.* 2010). Therefore, NaOH and Na_2CO_3 are not suitable reagents for regeneration of spent Al/Fe oxide-modified DE, but K_2SO_4 solution is.

The trends in percentage fluoride removal by the regenerated sorbents at different cycles is shown in Figure 7.

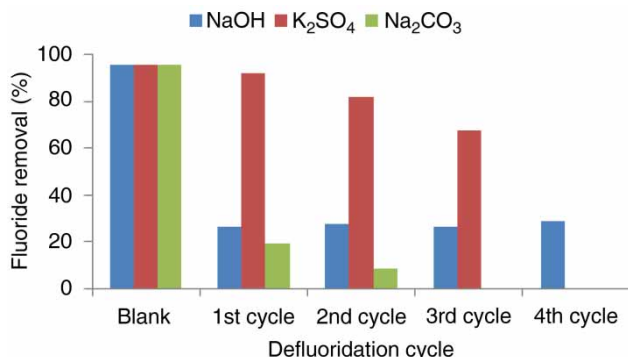


Figure 7 | Percentage fluoride removal at different defluoridation cycles using 0.01 M NaOH, 0.1 M K₂SO₄, and 0.01 M Na₂CO₃ (initial concentration of fluoride: 10 mg/L; sorbent dosage: 0.8 g/100 mL).

CONCLUSIONS

The study evaluated the stability of Al/Fe oxide-modified DE sorbent at different solution pH and calcination temperatures and appraised the reusability of spent sorbent regenerated from different solutions. Findings showed that Al and Fe were leached most from the sorbent under acidic and alkaline conditions, with Al more significantly lost than Fe. ICP-MS analyses provide evidence that Al/Fe oxide-modified DE is unstable at temperatures above 600 °C. It was found that calcination did not improve the fluoride uptake capacity of Al/Fe oxide-modified DE. The thermogravimetric analysis of Al/Fe oxide-modified DE showed that the limit of its stability was 600 °C. K₂SO₄ solution proved to be the most suitable regenerant for spent Al/Fe oxide-modified DE compared with NaOH and Na₂CO₃.

ACKNOWLEDGEMENTS

This study was funded by WRC Project No. K5/2363/3, NRF Project No. CSUR13092849176, Grant No. 90288 and THRIP Project No. TP12082610644, and the Directorate of Research & Innovation, University of Venda.

REFERENCES

Antonides, L. E. 1998 *Diatomite. US Geological Survey Mineral Commodity Summaries*. US Geological Survey, USA.

- Bansiwal, A., Pillewan, P., Biniwale, R. B. & Rayalu, S. S. 2010 Copper oxide incorporated mesoporous alumina for defluoridation of drinking water. *Microporous and Mesoporous Materials* **129**, 54–61.
- Bishop, P. L. & Sancoucy, G. 1978 Fluoride removal from drinking water by fluidized activated alumina adsorption. *Journal of American Water Works Association* **70**, 554–559.
- Housecroft, C. E. & Sharpe, A. G. 2005 *Inorganic Chemistry*, 2nd edn. Pearson Prentice Hall, USA.
- Ibrahim, S. S. & Selim, A. Q. 2012 Heat treatment of natural diatomite. *Physicochemical Problems of Mineral Processing* **48**, 413–424.
- Izuagie, A. A., Gitari, W. M. & Gumbo, J. R. 2015 Defluoridation of groundwater using diatomaceous earth: optimization of adsorption conditions, kinetics and leached metals risk assessment. *Desalination and Water Treatment* **57** (36), 16745–16757.
- Izuagie, A. A., Gitari, W. M. & Gumbo, J. R. 2016 Synthesis and performance evaluation of Al/Fe oxide coated diatomaceous earth in groundwater defluoridation: towards fluorosis mitigation. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering* **51** (10), 810–824.
- Kagne, S., Jagtap, S., Thakare, D., Devotta, S. & Rayalu, S. S. 2009 Bleaching powder: a versatile adsorbent for the removal of fluoride from aqueous solution. *Desalination* **243**, 22–31.
- Kamble, S. P., Jagtap, S., Labhsetwar, S. N., Thakare, D., Godfrey, S., Devotta, S. & Rayalu, S. S. 2007 Defluoridation of drinking water using chitin, chitosan and lanthanum-modified chitosan. *Chemical Engineering Journal* **129**, 173–180.
- Kamble, S. P., Dixit, P., Rayalu, S. S. & Labhsetwar, N. K. 2009 Defluoridation of drinking water using chemically modified bentonite clay. *Desalination* **249**, 687–693.
- Lee, J. D. 2007 *Concise Inorganic Chemistry*, 5th edn. John Wiley & Sons, Inc, India.
- Lemonas, J. F. 1997 Diatomite. *American Ceramics Society Bulletin* **76**, 92–95.
- Ma, Y., Shi, F., Zheng, X., Ma, J. & Gao, C. 2011 Removal of fluoride from aqueous solution using granular acid-treated bentonite (GHB): batch and column studies. *Journal of Hazardous Materials* **185**, 1073–1080.
- Manna, S., Saha, P., Roy, D., Sen, R. & Adhikari, B. 2015 Defluoridation potential of jute fibers grafted with fatty acyl chain. *Applied Surface Science* **356**, 30–38.
- Matthews, P. 1992 *Advanced Chemistry*. Cambridge University Press, Cambridge, UK.
- Mohamedbaker, H. 2010 Diatomite: its characterization, modifications and applications. *Asian Journal of Materials Science* **2** (3), 121–136.
- Parkhurst, D. L. & Appelo, C. A. J. 2012 *PHREEQC Version 3 – A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations*. US Geological Survey, Denver, CO, USA.
- Sadiju, S. M. I., Masamba, W. R. L., Thole, B. & Mwatseteza, J. F. 2008 Groundwater fluoride levels in villages of Southern

- Malawi and removal studies using bauxite. *International Journal of Physical Sciences* **3**, 1–11.
- Saha, G., Maliyekkal, S. M., Sabumon, P. C. & Pradeep, T. 2015 A low cost approach to synthesize sand like AlOOH nanoarchitecture (SANA) and its application in defluoridation of water. *Journal of Environmental Chemical Engineering* **3**, 1303–1311.
- Sakhare, N., Lunge, S., Rayalu, S., Bakardjiva, S., Subrt, J., Devotta, S. & Labhsetwar, N. 2012 Defluoridation of water using calcium aluminate material. *Chemical Engineering Journal* **203**, 406–414.
- Seecharran, K. R. 2010 *Bayer Process Chemistry*. Alumina Plant, Guymine, Linden, Guyana.
- Shrivastava, B. K. & Vani, A. 2009 Comparative study of defluoridation technologies in India. *Asian Journal of Experimental Sciences* **23**, 269–274.
- Tomar, V., Prasad, S. & Kumar, D. 2013 Adsorptive removal of fluoride from water samples using Zr–Mn composite material. *Microchemical Journal* **111**, 116–124.
- Volzone, C. & Garrido, L. B. 2008 Use of modified hydroxy-aluminium bentonites for chromium(III) removal from solutions. *Journal of Environmental Management* **88**, 1640–1648.
- Wang, J., Kang, D., Yu, X., Ge, M. & Chen, Y. 2015 Synthesis and characterization of Mg–Fe–La trimetal composite as an adsorbent for fluoride removal. *Chemical Engineering Journal* **264**, 506–513.
- World Health Organization (WHO) 2011 *Guidelines for Drinking-Water Quality*, 4th edn. Gutenberg, Malta.
- Xu, L., Gao, X., Li, Z. & Gao, C. 2015 Removal of fluoride by nature diatomite from high-fluorine water: an appropriate pretreatment for nanofiltration process. *Desalination* **369**, 97–104.
- Yu, Y. & Chen, J. P. 2015 Key factors for optimum performance in phosphate removal from contaminated water by a Fe–Mg–La tri-metal composite sorbent. *Journal of Colloid and Interface Science* **445**, 303–311.
- Yuan, P., Wu, D. Q., He, H. P. & Lin, Z. Y. 2004 The hydroxyl species and acid sites on diatomite surface: a combined IR and Raman study. *Applied Surface Science* **227**, 30–39.

First received 11 January 2016; accepted in revised form 15 August 2016. Available online 11 October 2016