Full Length Research Paper

Effect of particle size on loading capacity and water quality in water defluoridation with 200°C calcined bauxite, gypsum, magnesite and their composite filter

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Defluoridation was carried out with bauxite, gypsum, magnesite and their composite calcined at 200°C to determine relationship between particle size, capacity and water quality, in an attempt to formulate a composite filter in the ratio of loading capacities. Particles of 0.5 to 1.0, 1.0 to 1.4, 1.4 to 2.0 and 2.0 to 3.0 mm diameter were employed in batch defluoridation. Color, hardness, pH, $F^-, Cl^-, Al^{3+}, Fe^{2+}$ were determined hourly until fluoride equilibrium was obtained. Results showed that capacities were inversely correlated to particle size obtaining polynomial, linear and logarithmic relations of capacity (mg/g) to particle size (mm); $C_s = -\phi(P_z)^2 - \delta P_z$ (composite, gypsum), $C_s = -\phi P_z - \delta$ (bauxite) and $C_s = -\phi \ln P_z + \delta$ (magnesite). Bauxite, gypsum and composite decreased but magnesite increased pH. Particle size and pH changes were positively correlated, highly for bauxite ($r^2 = 0.915$), fairly for composite and magnesite ($r^2 = 0.855$ and 0.853, respectively) and lowly correlated for gypsum ($r^2 = 0.562$). Smaller particles obtained higher apparent colour, hardness, alkalinity and sulphate. There was no relationship between particle size and Cl^-, Al^{3+}, Fe^{2+}. Sorption capacities of these materials increase with decrease in particle size, however decrease in particle size enhances colour, hardness and sulphate levels. In optimizing the materials for defluoridation particle size can be decreased while monitoring colour, hardness, alkalinity and sulphate levels. Particles of diameter 2 mm were optimum in the present experiments.

Key words: Bauxite, composite, defluoridation, gypsum, magnesite.

INTRODUCTION

Water defluoridation research has been going on world over in an attempt to mitigate dental and skeletal fluorosis. The effects of high fluoride ingestion on teeth and bone are well documented (Varol et al., 2010; Smittakorn et al., 2010; Castillo et al., 2007). Fluoride is known to cause browning and mottling of teeth and weakening of the bones leading to crippling conditions (Vasudevan et al., 2009; Feenstra et al., 2007). A number

of technologies have been researched on among which are use of bone char (Smittakorn et al., 2010), precipitation with alum and lime (Yadav et al., 2010; Nath and Dutta, 2010), employment of clay materials (Sujana et al., 2009), use of synthetic adsorbents (Maliyekkal et al., 2010), and, other advanced techniques such as electrolysis, electrodialyis (Amer et al., 2001), reverse osmosis (Fawell et al., 2006), nanofiltration (Feenstra et al., 2007), Crystalactor (Giesen, 1998), solar dew collector system (Solar, 2007), Memstil technology (Hanemaaijer et al., 2007), and The water pyramid (Aqua-Aero, 2007). Bauxite, gypsum and magnesite have been employed in experimental water defluoridation

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(Thole, 2005; Sajidu et al., 2008; Singano, 2000).

The results were promising with fairly good sorption capacities obtained for bauxite (12.31 mg/g) and gypsum (9.28 mg/g) (Sajidu et al., 2008; Peter, 2009). Low sorption capacities were recorded for magnesite (3.45 mg/g) (Singano, 2000). Despite the fluoride sorption potential of the three materials the quality of treated water appeared to change. Singano (2000) reported an increase in water pH during defluoridation with magnesite and in defluoridation with bauxite and gypsum apparent colour, turbidity and hardness were reported to increase (Thole, 2005; Sajidu et al., 2008). It is common to optimize adsorbent media through calcination at various temperatures and at times decreasing grain size among other optimisation techniques (Feenstra et al., 2007). The present research investigated similar optimisation techniques such as calcination, particle size reduction, hybridization of materials and changes in design flow rate. However among these only particle size experiment-tation is reported here, the other results are reported elsewhere (Thole et al., 2011; Thole, 2011). Research has shown the effect of grain size in defluoridation with activated alumina (Shoeman and Macleod, 1987), synthetic hydroxyapatite, bauxite and gypsum (Thole, 2005) and Magnesite (Singano, 2000).

The reported results show that decreasing grain size has a positive impact on loading capacities. The same reports indicate negative quality changes in water treated with these materials. Activated alumina, for instance, is known to contribute towards residual concentrations of aluminium whereas gypsum increases sulphate concentrations in the water. However the relationship between grain size and residual concentrations of contaminants; such as aluminium, iron, sulphate, chlorides and calcium, in defluoridation with bauxite, gypsum and magnesite has not been widely reported in literature. The current research aimed at determining effects of particle size on loading capacities and quality of the treated water with respect to pH, alkalinity, residual colour, hardness and concentrations of $Cl^-, Al^{3+}, Fe^{2+}, SO_4^{2-}$ in water defluori-dation with bauxite, gypsum, magnesite and their composite. This work contributes to research on optimizing the three materials for water defluoridation through calcination, particle size reduction and hybrid filter design.

MATERIALS AND METHODS

Bauxite, gypsum and magnesite were locally sourced within Tanzania, crushed and sieved to grain sizes of ranges 0.5 – <1.0, >1.0 – <1.4, >1.4 – <2.0 and >2.0 – <3.0 mm diameter. These are referred throughout the text as 1.0, 1.4, 2.0 and 3.0 mm, respectively. The segregated materials were then heat treated at 200°C in an open air muffle furnace for 2 h. Preliminary results had shown optimum defluoridation conditions with the materials when calcined at 200°C for all tested calcine temperatures between 150 and 500°C (Thole et al., 2011). Naturally occurring ground water

was obtained and tested for colour, hardness, pH, alkalinity and concentrations of $Cl^-, Al^{3+}, Fe^{2+}, SO_4^{2-}$ prior to use in defluoridation experiments. One gram of each grain-size of bauxite, gypsum and magnesite was placed in one litre of the ground water. The media was agitated at 125 revolutions per minute (rpm). Colour, hardness, pH, alkalinity and concentrations of $F^-, Cl^-, Al^{3+}, Fe^{2+}, SO_4^{2-}$ were determined hourly until equilibrium fluoride concentrations were obtained. A mass balance Equation 1 was employed to calculate loading capacities on the adsorbent materials.

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

In Equation 1 q_e is the amount of adsorbed fluoride at equilibrium (mg g^{-1}); V is the volume of the solution (L); C_o and C_e are the initial fluoride concentration and fluoride concentration at equilibrium (mg l^{-1}) respectively, and, m is mass of adsorbent (g). A composite of bauxite, gypsum and magnesite was prepared in the ratio of their mean loading capacities for each grain size. Batch defluoridation experiments were carried out with the composite, as described for the materials, employing Equation 1 for calculating loading capacities. In analyzing for possible relationships particle size was regressed separately with; loading capacities, apparent colour, pH, alkalinity, hardness and concentrations of $Cl^-, Al^{3+}, Fe^{2+}, SO_4^{2-}$. Standard analytical methods were employed in all determinations (HACH, 1997; APHA, 1989). Fluoride was analyzed by the ion selective electrode (ISE) technique. In this method fluoride ions were selectively absorbed by the ISE membrane establishing a potential (voltage) whose magnitude was proportional to fluoride concentration of sample.

This potential was compared to the constant potential of a reference electrode. Aluminon method was employed for determining aluminium and the calmagate spectrophotometric method was used for calcium and magnesium. Sulphates concentrations were determined through SulfaVer 4 turbidimetry and Argentometric method was employed for chloride. To determine alkalinity samples were titrated with acid to a colorimetric end point corresponding to a specific pH. Phenol alkalinity was determined by titration to a pH 8.3 end point, as evidenced by phenolphthalein colour change, and indicates the total hydroxide and one half the carbonate present. Methyl orange or total alkalinity was determined by titration to a pH between 3.7 and 5.1 and includes all carbonates, bicarbonates and hydroxides. HACH one combination pH electrode method was employed to determine pH. The APHA (1989) Platinum-Cobalt standard method was employed to test for colour. Total iron was analyzed through use of FerroVer. FerroVer reagent reacts with all soluble and most insoluble forms of iron in sample to produce soluble ferrous iron. This reacts with the 1, 10-phenanthroline indicators in the reagent to form an orange colour that is proportional to the concentration of iron.

RESULTS AND DISCUSSION

Loading capacities

The loading capacities for bauxite, gypsum, magnesite and their composite increased with decrease in particle size. Plots of loading capacity versus particle size depict the capacity-particle size relationships for bauxite, gypsum, magnesite and the composite, Figures 1 to 4.
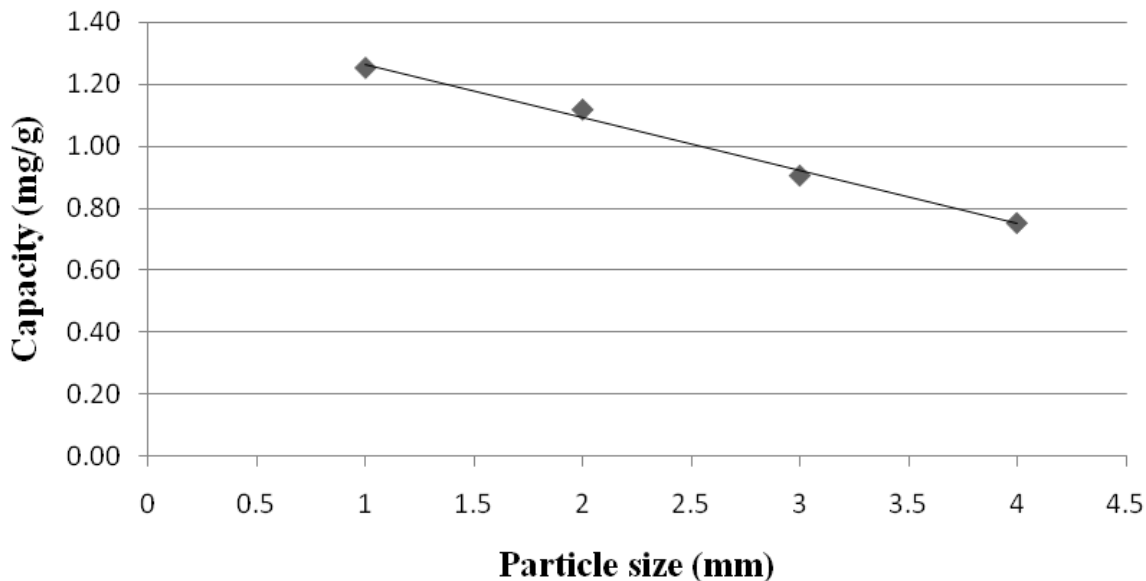
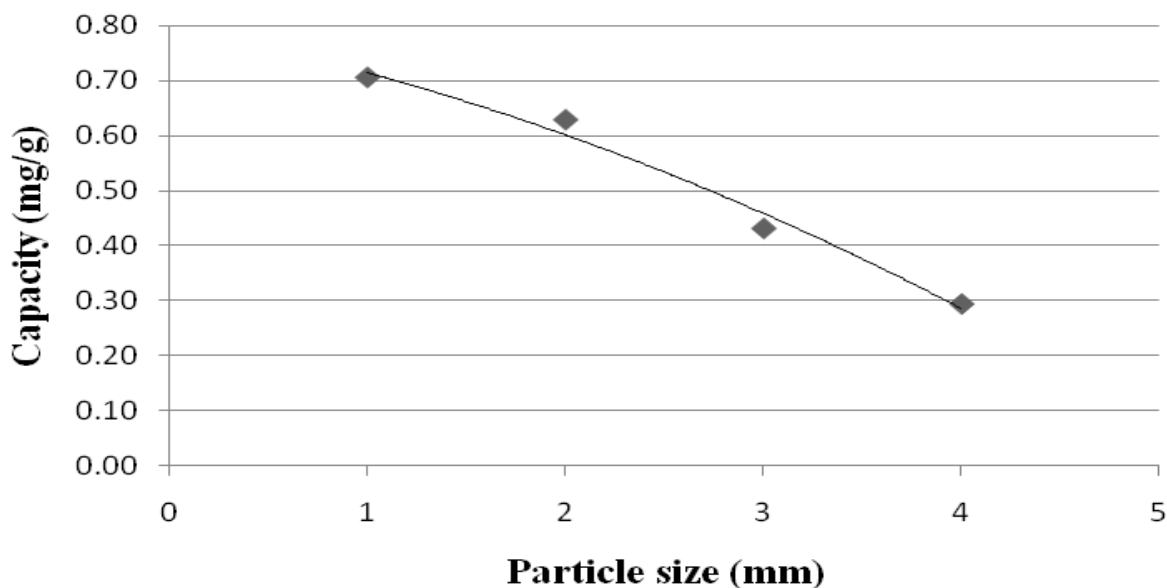**Figure 1.** Loading capacity against particle size in defluoridation with bauxite $(r^2 = 0.993)$.

Figure 2. Loading capacity against particle size in defluoridation with gypsum $(r^2 = 0.985)$.

The relation between loading capacity, (C_s, mg/g), to particle size (P_z, mm) was best represented by a linear equation for bauxite (Equation 2), polynomial equations for gypsum and the composite (Equations 3 and 5, respectively), and, natural logarithm for magnesite (Equation 4). The relation equations were;

$$C_s = -0.1718P_z + 1.4367 \qquad (r^2 = 0.993) \qquad (2)$$

$$C_s = -0.015P_z^2 - 0.0677P_z + 0.7967 \quad (r^2 = 0.985) \quad (3)$$

$$C_s = -0.189\ln P_z + 0.4082 \quad (r^2 = 0.959) \qquad (4)$$

$$C_s = -0.0513P_z^2 + 0.0688P_z + 1.0396 \quad (r^2 = 0.9969) \quad (5)$$

Respective best fit regression types were selected for each trend line based on correlation coefficient values. Exponential, linear, logarithmic, polynomial and power trend lines were tried for fitness in each plot and one with highest r^2 value was selected as best representing the relationship between C_s and P_z. In general loading
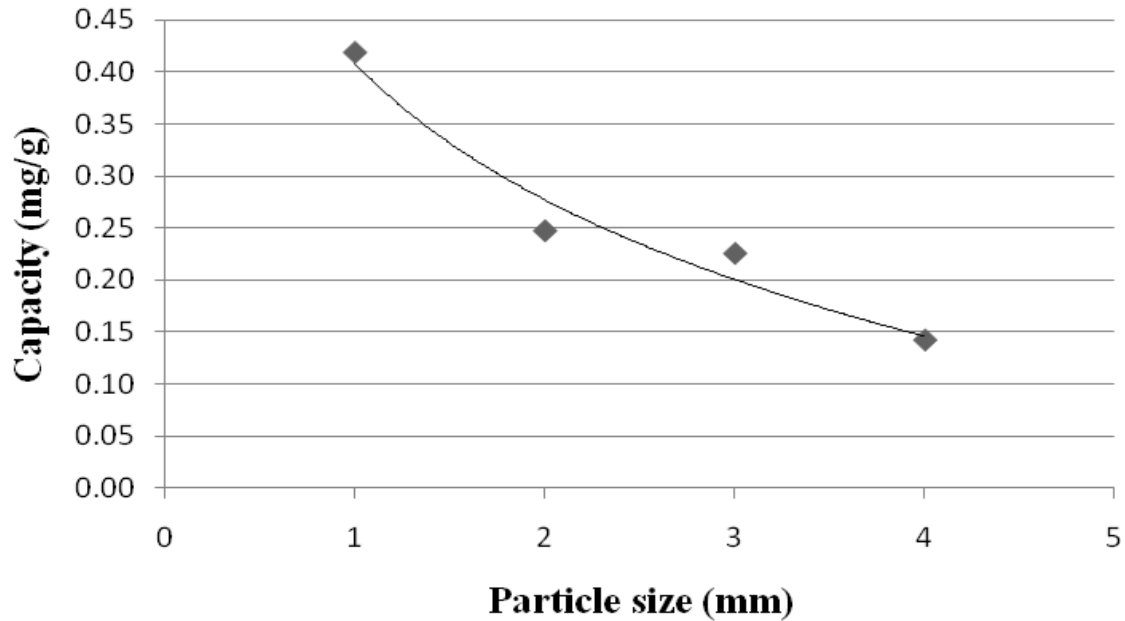
Figure 3. Loading capacity against particle size in defluoridation with magnesite *(r² = 0.959)*.
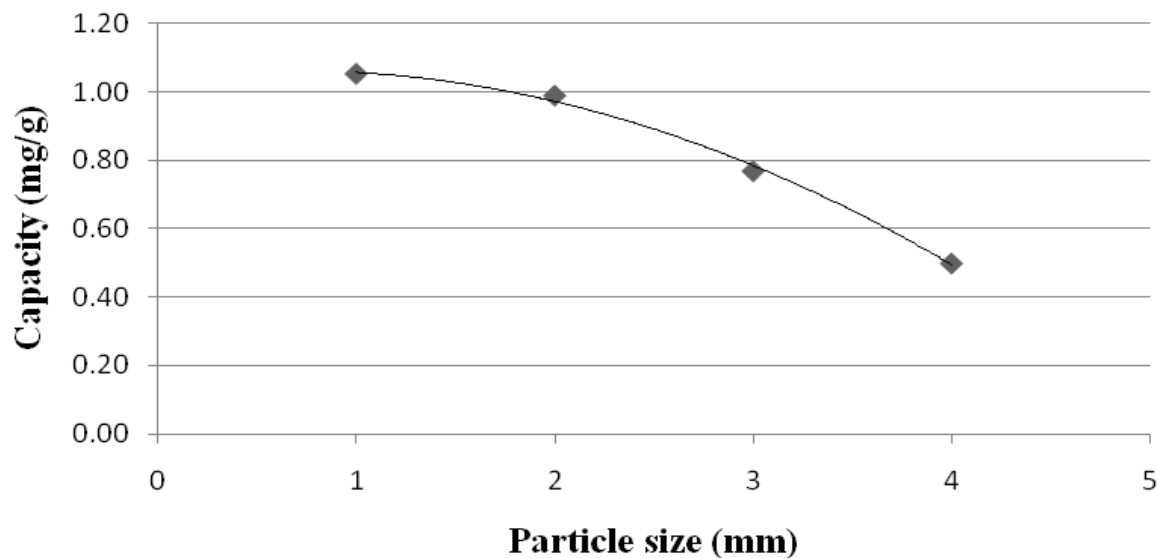
Figure 4. Loading capacity against particle size in defluoridation with composite *(r² = 0.997)*.

capacity increased with decrease in particle size.

This result could be attributed to increase in surface area available for fluoride sorption with decrease in particle size. Similar results were obtained elsewhere albeit with bone char (Ko et al., 1999), activated alumina (Shoeman and Macleod, 1987) and other adsorbents (Biswas et al., 2007; Turner et al., 2005). The results appear to suggest that for these three materials and their composite particle size may be decreased to enhance fluoride sorption. However, it must be noted that lower

particle sizes obtained greater changes in apparent colour, pH, alkalinity, residual sulphate and hardness presented in water quality. The mean capacities obtained were not comparable to those obtained in earlier experiments. The mean sorption capacities were 1.05, 0.57, 0.28 and 0.82 mg/g for bauxite, gypsum, magnesite and the composite filter, respectively. Higher sorption capacities are reported in earlier experiments for bauxite (12.31 mg/g), gypsum (9.28 mg/g) (Sajidu et al., 2008; Peter, 2009) and magnesite (3.45 mg/g) (Singano, 2000).

Table 1. Raw groundwater quality prior to defluoridation.

Concentrations in raw water (mg/l)					Alkalinity (mg/l)				pH	Colour (TCU)
Hardness as $CaCO_3$	Al^{3+}	Fe^{2+}	SO_4^{2-}	Cl^-	Phenol	OH^-	CO_3^{2-}	HCO_3^{2-}	8.72	0.0
14.5	0.00	0.02	20	20	10	0	20	70		
WHO recommended upper limits / ranges										
Hardness as $CaCO_3$	Al^{3+}	Fe^{2+}	SO_4^{2-}	Cl^-	pH			Colour (TCU)		
500	0.2	0.3	400	250	6.5 – 8.5			5 – 50		
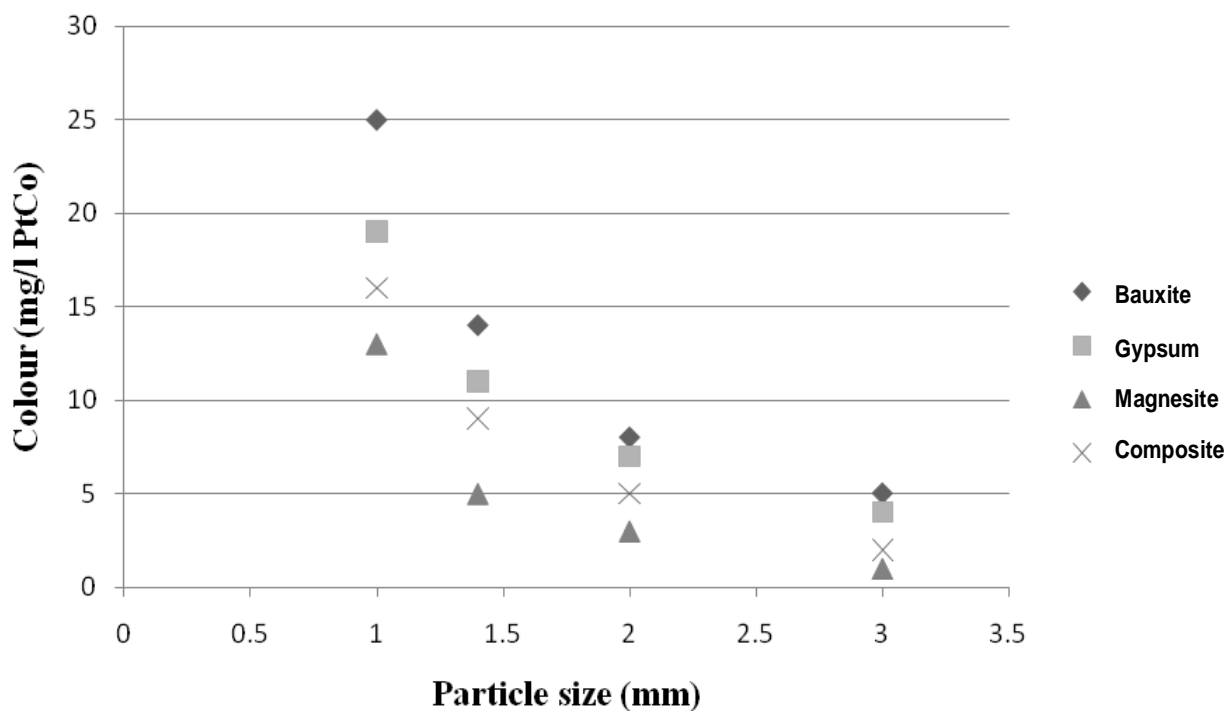
Figure 5. Plot of apparent colour against particle size at equilibrium.

The low sorption capacities obtained in the present experiments could be attributed to low initial fluoride concentrations, 2.5 mg/l, in the solutions employed that resulted in low fluoride ion availability per unit surface area of media material.

Water quality

Table 1 presents quality of the raw water before defluoridation experiments. The raw water quality was within world health organization (WHO) recommended limits in hardness, pH, colour and concentrations of aluminium, iron, sulphate, and chloride. Figure 5 depicts apparent colour at equilibrium with respect to particle size. Apparent colour was undetectable in the raw water as depicted in Table 1 as such the apparent colour obtained at equilibrium indicated colour introduced in the water by the materials. Figure 5 shows that the apparent colour was more intense in water treated with lower particle sized materials. It was also observed that, except for magnesite, all the materials with grain sizes of 1.0 mm caused colouration greater than 15 True Colour Unit (TCU) in water which is the WHO recommended upper aesthetic limit. Note that 1.0 mg/l platinum as chloroplatinate ion is equal to 1 TCU (HACH, 1997). Particles larger than 1.0 mm appeared to colour the water to intensities within this WHO limit.

This result could be attributed to the fact that larger particles settle more quickly than smaller ones as such larger sized particles, >1 mm diameter, stayed less longer in suspension enhancing early decolouration of
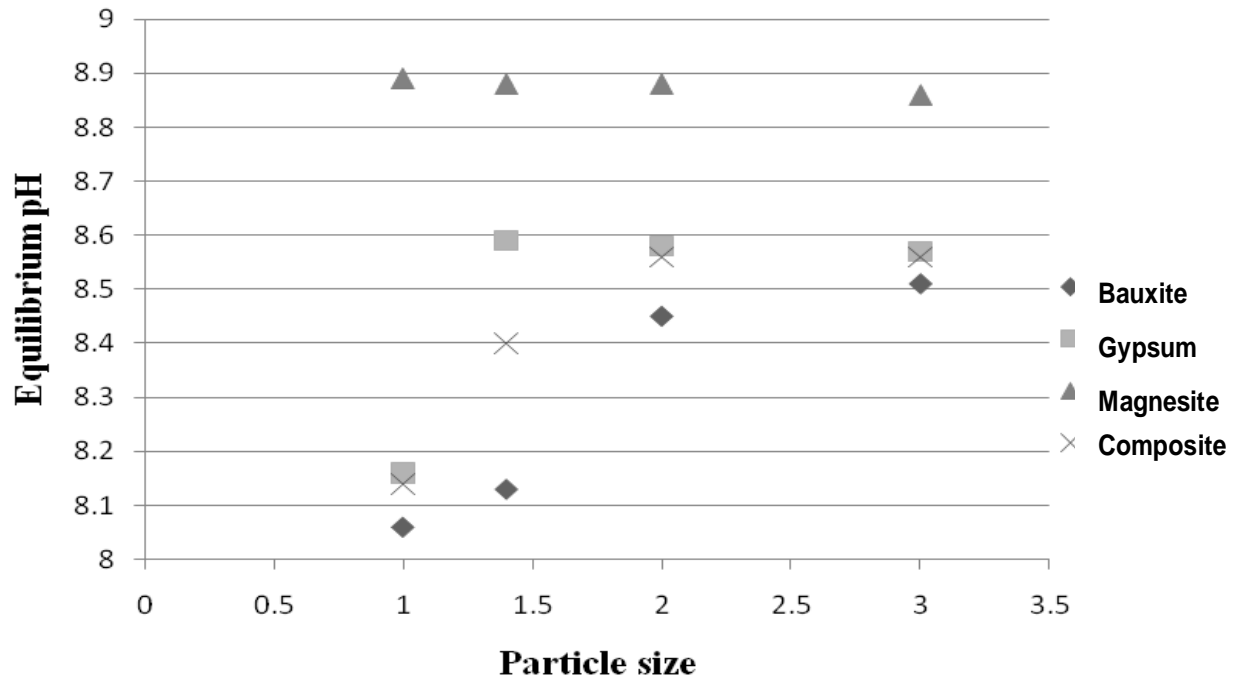
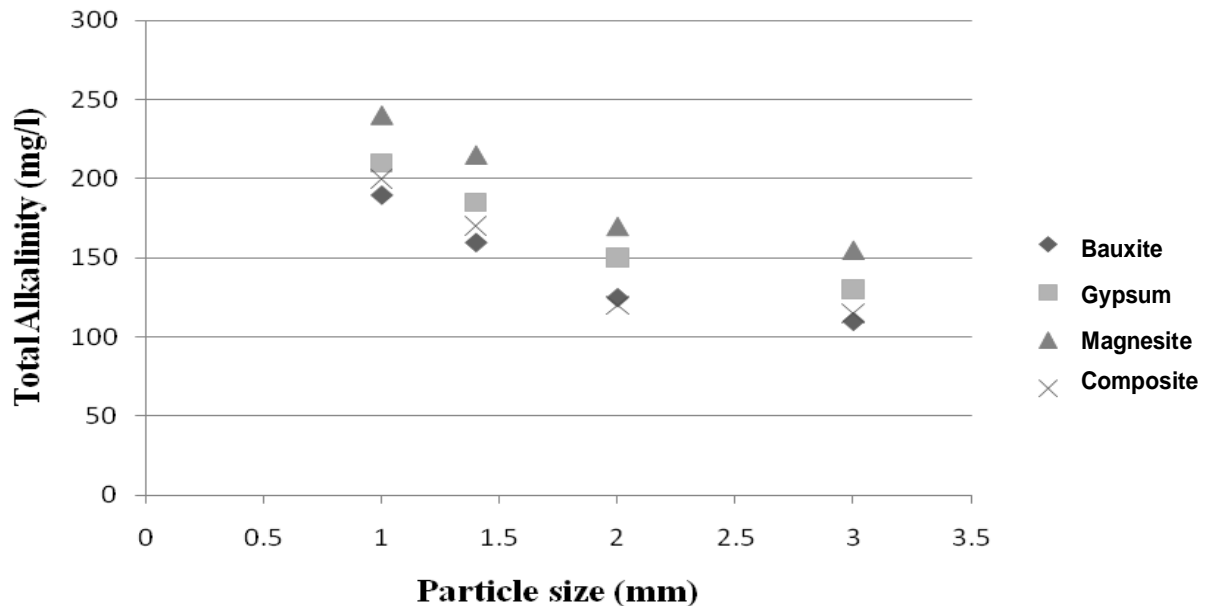**Figure 6.** Plot of equilibrium pH versus particle size (mm).

Figure 7. Alkalinity regressed with particle size.

the treated water. Similar results were obtained for pH, alkalinity, residual sulphates and hardness, Figures 6 to 9. The pH of the water before treatment was 8.72. Bauxite and the composite filters decreased pH as shown by the respective plots in Figure 6. The decrease in pH seemed to be enhanced with lower particle sizes. Particles below 1.5 mm diameter lowered the pH from the initial 8.72 to as low as 8.05, below the WHO recommended upper limit for pH of 8.50. Magnesite, on the other hand, increased the water pH to range of 8.85 to 8.91 for all particle sizes. pH changes were very minimal in defluoridation with gypsum for particles larger than 1 mm in diameter. The results showed that the combination of the three; bauxite, gypsum and
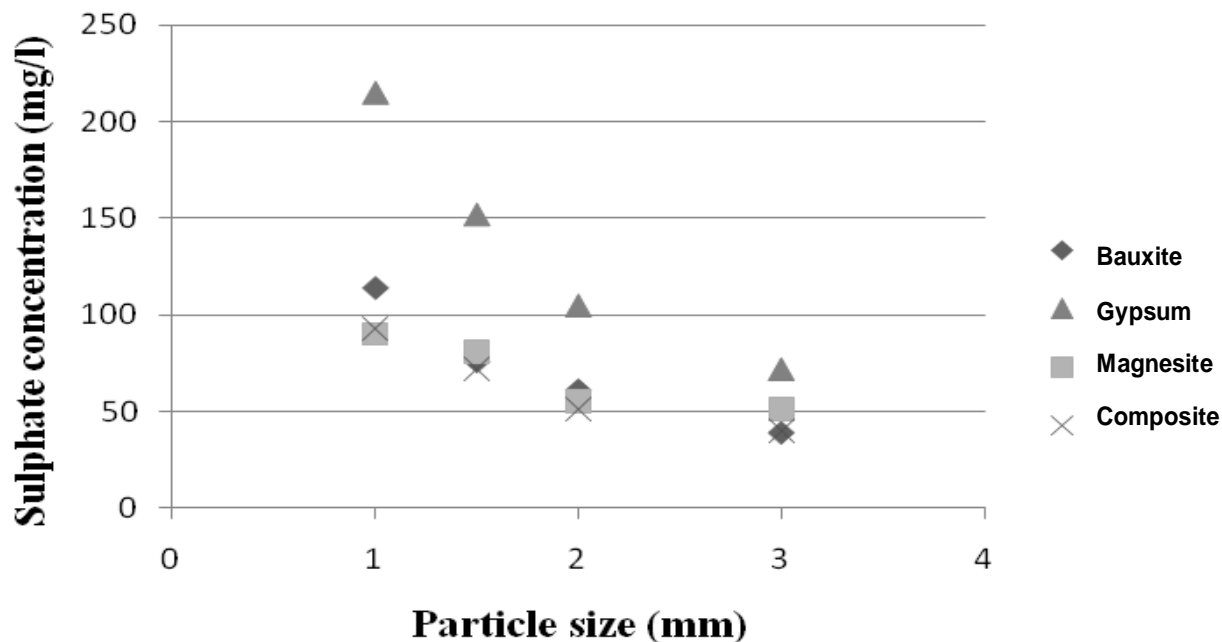
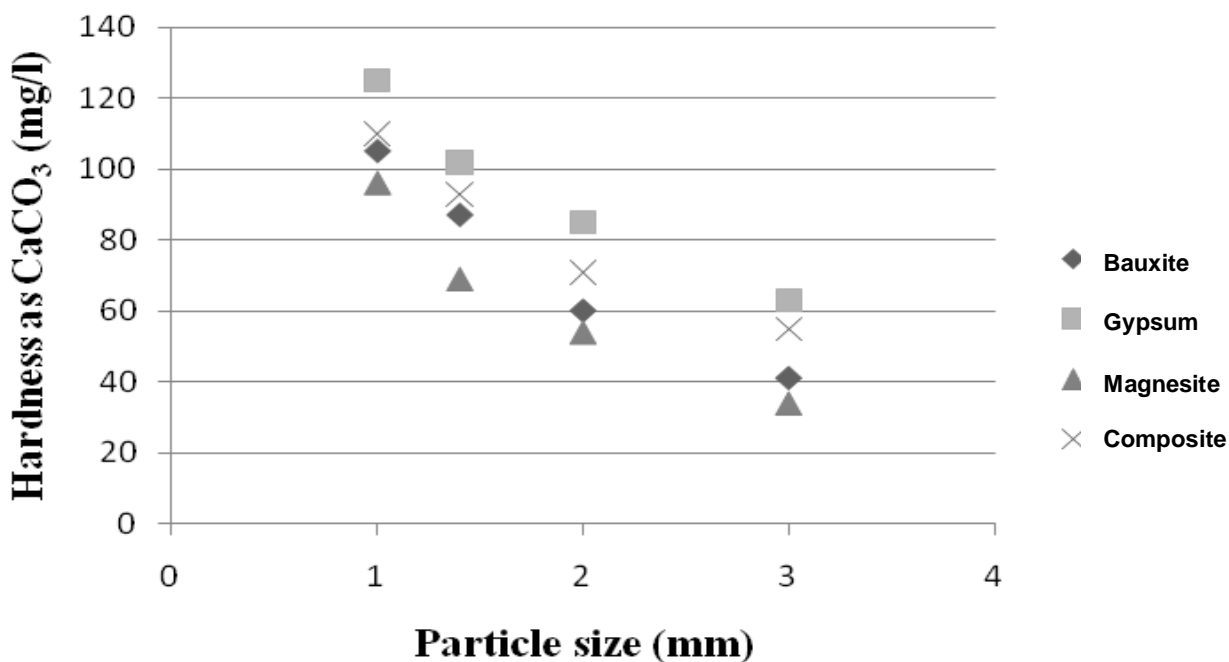**Figure 8.** Residual sulphate concentrations against particle size.

Figure 9. Hardness plotted against particle size.

magnesite, into a composite based on their loading capacities lowers pH. This may be taken advantage of where the initial water pH is higher than 8.50, a typical status in high fluoride water (Fawell et al., 2006). Total alkalinity appeared to increase with decrease in particle size with all values ranging from 100 to 250 mg/l for all the materials and their composite.

Total alkalinity being a measure that includes carbonate, bicarbonate and hydroxide alkalinities, it may be summed up that the ions $CO_3^{2-}, HCO_3^{2-}, OH^-$ are more available for dissolution when particles of these materials are smaller. The concentration of sulphates in the untreated water was 20 mg/l and the concentrations went up to

Table 2. Mean residual concentrations of Cl^-, Al^{3+}, Fe^{2+} (mg/l) in water after defluoridation with the materials of different particle sizes.

Material	Ion	1.0 mm	1.4 mm	2.0 mm	3.0 mm	*R^2
	Cl^-	71.5	57.9	68.3	73.1	0.42
Bauxite	Al^{3+}	0.5	0.3	0.4	0.4	-0.19
	Fe^{2+}	0.1	0.1	0.4	0.2	0.43
	Cl^-	69.5	72.1	54.3	64.7	-0.44
Gypsum	Al^{3+}	0.1	0.0	0.2	0.1	0.28
	Fe^{2+}	0.2	0.3	0.1	0.3	0.22
	Cl^-	145	127	151	147	0.41
Magnesite	Al^{3+}	0.2	0.4	0.3	0.3	0.19
	Fe^{2+}	0.1	0.4	0.2	0.3	0.33
	Cl^-	70.5	64.6	67.3	71.2	0.37
Composite	Al^{3+}	0.1	0.2	0.2	0.1	-0.20
	Fe^{2+}	0.2	0.3	0.1	0.3	0.22

*R^2 = correlation coefficients between ion concentration (mg/l) and particle size (mm).

about 200 mg/l with gypsum and to about 100 mg/l with bauxite, magnesite and the composite for materials of particle size range 0.5 to < 1.0 mm diameter. Gypsum introduced greatest quantities of sulphates in the water compared to the other materials. Generally, lower particle sized materials contributed more residual sulphate concentrations. The WHO upper limit for sulphate concentration is 400 mg/l. Despite that none of the concentrations went to 400 mg/l, it is still plausible that at large scale application the fine grained materials may introduce much more sulphates as to transcend beyond the upper limit. Water with sulphates beyond 400 mg/l being not safe for drinking, it may be important to identify sulphate sorption techniques to be employed alongside this defluoridation technology.

Bauxite, gypsum and magnesite changed the quality of treated water. Similar results were obtained in separate experiments. Singano (2000) reported an increase in water pH during defluoridation with magnesite and in defluoridation with bauxite and gypsum apparent colour, turbidity and hardness were reported to increase (Thole, 2005; Sajidu et al., 2008). The composite filter appeared to adjust pH downwards from 8.72 to within 8.15 to 8.43 that falls within WHO standard limits of 6.5 to 8.5. The water treated with 2 mm grains of the composite filter adhered to WHO standards in apparent colour, turbidity, hardness and residual concentrations of

$Cl^-, Al^{3+}, Fe^{2+}, SO_4^{2-}$. However this does not necessarily imply safety for human consumption because other quality parameters of naturally occurring substances such as arsenic, cadmium, lead and mercury; that have very low WHO guideline values of 0.05 mg/l and below, were not determined. Hardness determinations revealed that lower sized particles increased water hardness to a greater extent compared to large particles, Figure 9. This could be attributed again to availability of greater surface area hence greater solid-liquid surface interaction.

This effect could result into more dissolution of the cations Ca^{2+}, Mg^{2+}. The initial water hardness before defluoridation was very low, 14.5 mg/l as CaCO₃, entailing that all the materials increased hardness. Gypsum had the greatest impact on hardness seconded by the composite. Magnesite had the least effect on hardness. The major component in magnesite was MgO whereas in gypsum it was CaSO₄. It is probable that lower solubility of MgO compared to CaSO₄ resulted in less availability of total quantities of Ca^{2+}, Mg^{2+} ions from magnesite as compared to gypsum. Residual concentrations of chloride, aluminium and iron appeared not correlated to particle size.

The results are presented in Table 2 with correlation coefficients of the regressions between mean ion

concentration and particle size. The correlation coefficients between ion concentration and particle size were below 0.5 indicating absence of linearity in behaviour of ion concentration with respect to particle size. The preliminary results suggest that the dissolution of the ions; Cl^-, Al^{3+} and Fe^{2+} from these materials into aqueous medium, is independent of particle size of the solid surface.

Conclusion

Loading capacities increased with decrease in particles size in defluoridation with bauxite, gypsum, magnesite and their composite filter. Particle size reduction may thus be employed in optimizing defluoridation performance of these materials. Apparent colour, alkalinity, hardness and residual sulphate concentration appeared to increase, where as pH decreased with decrease in particle size as such these parameters limit the extent to which particle size may be decreased. It is therefore apparent that during particle size reduction for optimisation of these materials, apparent colour, pH, alkalinity, hardness and residual sulphate concentration need to be monitored. Residual concentrations of chloride, aluminium and iron seemed independent of particle size.

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