Water defluoridation with 150–300°C calcined Bauxite-Gypsum-Magnesite (B-G-Mc) filters

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Abstract

Research on water defluoridation with composite filters of bauxite, gypsum and magnesite was carried out at Ngurdoto Research Station to determine capacity, nature of fluoride-sorbent interaction and changes in water quality. The objective was to identify an optimum composite filter that would not alter the water quality beyond World Health Organisation recommendations. The three materials were characterized through X-Ray Fluorescence. The major components were Al_2O_3 (30.33%) for bauxite, CaO (28.09%) for gypsum and MgO (34.57%) for magnesite. The materials were calcined at temperatures of 150, 200, 250 and 300°C. Six composite filters were prepared for each calcine temperature of bauxite:gypsum:magnesite in the ratios 1:2:3, 1:3:2, 2:1:3, 2:3:1, 3:1:2 and 3:2:1. The highest capacity, 11.77 mg F/g, was obtained with the 3:1:2–200°C calcine. The optimum filter was however the 1:2:3–200°C calcine with capacity of 10.19 mg F/g. This filter did not alter the water quality beyond the considered WHO limits. The fluoride-sorbent interaction could best be described by Langmuir isotherm for the 200 and 300°C, and Temkin isotherm for the 150 and 250°C composites. Most composites changed water quality beyond WHO standards in Al^{3+}, Fe^{2+}, and SO_4^{2-}, however a composite filter of these materials is plausible.
Keywords: defluoridation, bauxite, gypsum, magnesite, composite filter, calcine, Langmuir, Temkin, Freundlich.

1 Introduction

One water quality parameter impacting on human health in a number of countries within Sub-Saharan Africa, such as Malawi, Tanzania and Kenya, is

the fluoride content. Fluorides are essential to human health at low concentrations but harmful to health at higher concentrations. It is established that fluoride toxicity at concentrations greater than 1.5 mg/l is associated with dental fluorosis (Maliyekkal [1]). At levels between 3.0 to 6.0 mg/l in drinking water skeletal fluorosis may be observed and when concentrations reach beyond 10 mg/l crippling fluorosis can ensue (Nath and Dutta [2], WHO [3]). Fluoride occurs in groundwater in various concentrations in different geographic areas. In Malawi fluoride is distributed in different rock types. Calcium fluoride in carbonatite fluoride bearing rocks occurs around Lake Chilwa Island in Zomba and Kangankhunde in Balaka (Sajidu et al. [4]). Phosphatic fluoride bearing rocks are located around Tundulu in Mulanje and at Songwe in Karonga (Msonda et al. [5], Carter and Bennet [6]). High groundwater fluoride concentrations have been reported; 8.6 mg/l at Ulongwe in Machinga District (Sibale et al. [7]), 7 mg/l at Mazengera in Lilongwe, 9.6 mg/l in Nkhotakota, 8.0 mg/l in Karonga, 5.8 mg/l in Nsanje and 3.4 mg/l in Mwanza (Masamba et al. [8]). In Tanzania higher water fluoride levels than those for Malawi have been reported in Arusha (80 mg/l in Arumeru), Kilimanjaro (25 mg/l), Mwanza (18 mg/l), Shinyanga (60 mg/l) and Shingida (67 mg/l) (Mjengera [9], Singano [10]). The fluoride and fluorosis challenge in Malawi and Tanzania has a number of potential solutions from the researched and tested defluoridation technologies. The technologies include use of bone char filter (Mjengera [9], Kongpun [11]), application of magnesite filter (Singano [10]), bauxite, clay and gypsum filters (Thole [12]). Other examples are; the use of zeolites (Onyango et al. [13]), Magnesia amended SiO_2 (Zhu et al. [14]), electrocoagulation with Mg-Al-Zn alloys (Vasudevan et al. [15]), Gypsum (Sajidu et al. [4]), Gypsum + fluorite, reverse osmosis and electrodyalysis, Nalgonda (Alum + lime) (Feenstra et al. [16]), Mg/Al-CO_3 Hydrotalcite (Hongtao et al. [17]), Synthetic hydroxyapaptite Thole [12], and use of activated carbon (Melisa [18], Bablia [19]).

Despite the wide range of available defluoridation technologies and variant levels of capacity, employment of each technology poses some challenges. A number of technologies change water pH beyond standard limits, for example Alum and Poly Aluminium Chloride (PAC) lower pH (PAC reduces pH to 4.3) whereas magnesite and lime increase pH, (Magnesite increases pH to 10) (Singano [10]). W.H.O. Standard water pH is 6.5–8.5. The Nalgonda technology increases concentration of *Al* (Nawlakhe and Bulusu [20]), gypsum introduces *Ca* and SO_4^{2-} in the water, whereas bauxite and clays raise the turbidity and colour of the water (Sajidu et al. [4], Thole [12]). Search for alternative defluoridation technologies for specific areas is therefore ongoing and the present research investigates the potential of composite filters of bauxite, gypsum and magnesite locally sourced within Tanzania. The specific objectives of the reported experiment were to determine capacities of composites calcined at different temperatures within temperature range 150 to 300°C, and, to identify an optimum composite filter within this calcine–temperature range.

2   Experimental section

2.1   Materials sourcing and preparation

Raw bauxite was sourced from Kwemashai, Usambara mountains, in Lushoto district. Gypsum was obtained from Makanya in Mwanga and magnesite from Chambogo in Same district, Tanzania. The media preparation involved calcining the said materials at 150, 200, 250 and 300°C. The calcined materials were then mixed in ratios of 1:2:3, 1:3:2, 2:1:3, 2:3:1, 3:1:2 and 3:2:1 as mass ratios in the order bauxite: gypsum: magnesite.

2.2   Experimental methods

The raw materials were characterized through X-Ray Fluorescence (XRF) to determine composition. Natural groundwater was analysed for initial alkalinity, pH and concentrations of $F^-, SO_4^{2-}, Cl^-, Al^{3+}, Ca^{2+}, Mg^{2+}, Fe^{2+}$.   Batch equilibrium experiments were then carried out with the said composites in which 1 g fine powder (d $\leq$0.5 mm) of composite filter was placed in 500 ml of natural fluoritic groundwater. Similarly 75 g of mixed grain size filter (0.5 mm $\leq$ d $\leq$ 1.5mm) were placed in 500 ml of fluoritic water. Alkalinity, pH and concentrations of $F^-, SO_4^{2-}, Cl^-, Al^{3+}, Ca^{2+}, Mg^{2+}, Fe^{2+}$ were followed until equilibrium fluoride concentration was obtained. Ion selective electrode potentiometric methods were used for fluoride determinations. Sulphates were determined through sulfer var 4 turbidimetry and chlorides were analysed by the argentometric method. Calmagite methods were employed to determine calcium and magnesium whereas aluminium and iron were determined through aluminion and phenanthroline direct reading spectrometry. Alkalinity, pH and ion concentration values obtained at equilibrium were employed in comparing the water quality with WHO standards. The equilibrium fluoride concentrations were used in trying fitness of data into Langmuir, Freundlich and Temkin sorption isotherms to determine nature of filter-fluoride interaction.

3   Results and discussion

3.1   Material characteristics, capacities and water quality

The major components of the bauxite were Al_2O_3 (30.33%), SiO_2 (15.0%) and Fe_2O_3 (14.3%). The gypsum mainly contained CaO (28.09%), SO_3 (34.96%) and SiO_2 (9.01%). The magnesite was mainly composed of MgO (34.57%) and SiO_2 (19.3%). The initial fluoride concentration of the raw water was 13.18±0.02 mg/l and, among the composites, the highest capacity, 11.77 mg F/g, was obtained with the 3:1:2–200°C calcine obtaining an equilibrium fluoride concentration of 1.43 mg/l. This filter however registered high residual concentrations of Al^{3+} and SO_4^{2-}. The best filter seemed to be the 1:2:3–200°C calcine with capacity 10.19 mg/l because the water treated with this filter

adhered to all WHO water quality recommendations considered in these experiments. Another filter of interest appeared to be the 3:2:1 composite. This composite obtained comparably high capacities at three of the four calcination temperatures and when calcined at $300^{\circ}C$ gave its best defluoridation capacity of 10.63 mg F/g that reduced the fluoride concentration to 2.57 ± 0.02 mg/l. High residual SO_4^{2-} concentration was determined as the only limitation in the use of this filter. Table 1 contains the initial alkalinity, pH and concentrations of selected ions in the water before defluoridation.

Table 1: Alkalinity, pH and ion concentrations in water before defluoridation.

Concentrations of selected ions in raw water (mg/l)						Alkalinity (mg/l)				pH
Al^{3+}	Ca^{2+}	Mg^{2+}	Fe^{2+}	SO_4^{2-}	Cl^-	Phenol	OH^-	CO_3^{2-}	HCO_3^{2-}	8.60
0.00	0.11	0.01	0.02	20	20	20	0	40	160	
World Health Organisation Recommended Upper limits/ Range of some Parameters (mg/l)										
Al^{3+}		Hardness (as CaCO₃)		Fe^{2+}	SO_4^{2-}		Cl^-		pH	
0.2		500		0.3	400		250		6.5 – 8.5	

The raw water quality was within WHO recommended limits except for pH that was 0.1 unit above the upper limit. The calculated hardness of the water, 0.32 mg/l, also adhered well to WHO limits. The raw water was found to be very soft which confirmed earlier finding (Mjengera [9], Singano [10]). Table 2 presents the highest capacity filter (C_1), the optimum filter (C_2), (best possible filter with respect to WHO potable water standards) and the average capacity (C_μ) for all the six composite filters at each temperature. pH, residual hardness and residual concentrations for the ions Fe^{2+}, Cl^-, SO_4^{2-}, and Al^{3+} are included in the table.

The composite filter 3:2:1 obtained optimum capacities at three of the experimental temperatures. However there were limitations mainly of high residual concentrations of sulphate. Composite filter 1:2:3 calcined at $200^{\circ}C$ proved the best among the optimum filters in that the water filtered through it adhered to all WHO parameters experimented on. The observation that the composite filter 3:2:1 generally obtained higher capacity compared to the rest could be attributed to the greater proportion of bauxite in this composite. Previous research did identify that bauxitic material provided higher defluoridation capacities as compared to gypsum and magnesite (Thole [12], Peter [21]). This confirms earlier research findings on the affinity of Al for Fluoride (Gupta et al. [22]).

Water defluoridated with bauxite calcined at 150 and $200^{\circ}C$ registered higher residual concentrations of Al^{3+} and Fe^{2+} than standard requirements. The 250 and the $300^{\circ}C$ calcines increased the residual Fe^{2+} concentration beyond

Table 2:   Summary of highest and optimum capacities, residual ion concentrations and pH for the four calcine temperatures.

		Residual Ion Concentration and hardness (CaCO$_3$) in mg/l					pH
		Al^{3+}	Fe^{2+}	SO_4^{2-}	Cl^-	Hardness	
WHO limit		0.2	0.3	400	250	500	6.5 – 8.5
150°C	Capacity mg F/g	Al^{3+}	Fe^{2+}	SO_4^{2-}	Cl^-	Hardness	pH
Bauxite	11.95	20.0	0.73	0.0	117.0	137	7.23
Gypsum	8.38	0.0	0.79	3380	103.0	355	7.57
Magnesite	8.09	0.0	0.90	0.0	221.0	258	8.85
C$_1$ (3:2:1)	9.96	0.0	0.58	180	110.5	280	7.97
C$_2$ (3:2:1)	9.96	0.0	0.58	180	110.5	280	7.97
C$_\mu$	7.94	0.67	0.36	1680	89.6	380	8.02
200°C							
Bauxite	12.31	10.0	0.63	0.0	101.3	200	7.28
Gypsum	9.28	0.0	0.75	2730	92.3	262	7.61
Magnesite	9.54	0.0	0.89	0.0	183.5	193	8.82
C$_1$ (3:1:2)	11.77	1.0	0.191	2079	56.5	243	8.00
C$_2$ (1:2:3)	10.19	0.0	0.30	302	90.2	233	8.01
C$_\mu$	10.95	0.83	0.45	2328	75.6	236	8.02
250°C	Capacity mg F/g	Al^{3+}	Fe^{2+}	SO_4^{2-}	Cl^-	Hardness	pH
Bauxite	7.08	0.0	0.61	0	78.4	132	8.40
Gypsum	4.37	1.0	0.72	80	92.2	149	8.18
Magnesite	4.67	0.0	0.87	2076	121.3	182	8.72
C$_1$ (3:1:2)	9.60	5.0	0.40	2476	58.4	127	7.86
C$_2$ (3:2:1)	8.96	0.0	0.31	2488	54.0	138	8.01
C$_\mu$	8.97	2.5	0.32	2312	73.8	142	7.91
300°C							
Bauxite	7.12	0.0	0.57	82	76.5	150	8.59
Gypsum	3.84	0.0	0.73	124	95.4	146	8.01
Magnesite	4.02	0.0	0.82	2381	100.3	148	8.77
C$_1$ (3:1:2)	10.68	0.5	0.30	2948	49.8	126	8.09
C$_2$ (3:2:1)	10.63	0.0	0.30	1155	53.3	132	8.09
C$_\mu$	10.23	0.1	0.28	2148	70.4	142	7.99

standard limits however; they left the water residual Al^{3+} within the standard requirement. This result could be attributed to the decrease in solubility of Al^{3+} compounds with increase in calcination temperature confirming earlier research observation (Masamba et al. [8]). The residual Fe^{2+} limitation appeared not to be addressed by increase in calcination temperature within the temperature range of the current experiment. Gypsum filters calcined at the lower temperatures (150 and 200°C) left higher residual concentrations of Fe^{2+} and SO_4^{2-} compared to standard limits. When calcined at 250°C the limitation observable was high residual Al^{3+} and Fe^{2+}. The 300°C gypsum-calcine registered a high residual concentration of Fe^{2+} only. The trend seemed to show that higher temperature gypsum calcines would introduce less ionic contaminants in water albeit within the limits of this experiment. However the capacity was observed to generally decrease from 8.38, 9.28, 4.37 and 3.84 mg F/g for the

temperatures 150, 200, 250 and 300°C respectively. This contradicts earlier findings where gypsum calcined at higher temperature of 400°C had a higher capacity compared to the low-temperature calcines (Thole [12]). It is probable that the difference in the quality of the gypsum could be responsible for this variation. The 2005 research was carried out with Malawi gypsum (predominantly $CaSO_4$) where as the current work has employed Tanzania gypsum (predominantly CaO). This result is not very conclusive since the 400°C gypsum calcine is yet to be experimented on in the current research. All magnesite calcines had similar limitations of introducing higher residual Fe^{2+}concentrations and higher pH in the treated water compared to the standard limits. The pH increase was earlier observed in water defluoridation with magnesite calcines (Singano [10]); the current research identifies Fe^{2+} as an additional limitation for use of this Chambogo magnesite in water defluoridation.

   The bauxite-gypsum-magnesite composite that had no limitations, within the context of this preliminary work, was the 1:2:3 calcined at 200°C that registered a capacity of 10.19 mg F/g. Another potential composite is the 3:2:1 that obtained high residual SO_4^{2-} concentrations albeit depicting good performance at three of the four calcine temperatures. This composite, a candidate for further research, obtained capacities of 9.96, 8.96 and 10.63 mg F/g when calcined at 150, 250 and 300°C respectively with a single limitation of high residual Fe^{2+} (at 150°C) and SO_4^{2-} at 250 and 300°C. Most composites left higher residual concentrations of at least two ionic species among the ions Al^{3+}, Fe^{2+} and SO_4^{2-}. Notable was the adherence to pH standard requirements in all experiments except for magnesite as a lone filter that increased pH beyond standard limits.

3.2 Nature of sorbent-sorbate interaction and sorption isotherms

The nature of filter-fluoride interaction was investigated with the 3:2:1 bauxite-gypsum-magnesite composite at the four temperatures. Mixed sorption was observable with Langmuir (mono-layer heterogeneous sorption) more pronounced for 200 and 300°C calcines, and, Temkin (Chemisorption) generally enhanced for the 150 and 250°C calcines. Regression coefficients for the three sorption isotherms, Langmuir, Freundlich and Temkin, were however very comparable indicative of mixed sorptive interactions between sorbent and sorbate. The equations below represent these isotherm relationships;

$$\frac{c_e}{q_e} = \frac{1}{Qb} + \frac{c_e}{Q} \tag{1}$$

$$qe = K_f C_e^{\frac{1}{n}} \tag{2}$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln c_e \tag{3}$$

$$q_e = a + b \log c_e \tag{4}$$

Langmuir isotherm assumes sites are energetically the same and there is monolayer formation with no movement of particles over the surface from one site to another (Coulson and Richardson [23]). This is represented by eqn (1). In This relationship c_e is equilibrium fluoride concentration (mg/l), q_e is equilibrium amount of sorbate on sorbent (mg/g), and, Q (mg/g) and b (dm^3/mg) are Langmuir isotherm constants related to capacity and energy respectively. A plot of $\dfrac{c_e}{q_e}$ against c_e will yield a straight line with slope $\dfrac{1}{Q}$ and intercept $\dfrac{1}{Qb}$ where the sorption follows Langmuir isotherm. Freundlich Isotherm, represented by eqns (2) and (3), is associated with multi-layer formation on heterogeneous sites. Eqn (3) represents the linear form of the Freundlich isotherm. The parameters K_f (dm^3/g) and $1/n$ signify capacity and intensity respectively Coulson [23]). The intensity values <1 indicate favourable conditions exist for multi-layer formation on heterogeneous sites. A plot of lnq_e vs lnc_e should yield a straight line with slope $1/n$ and intercept lnK_f if the media-fluoride interaction is Freundlich in nature. The terms q_e and c_e denote equilibrium concentrations in the solid phase and liquid phase respectively. Temkin isotherm considers chemisorption as such where the medium-solute relationship is chemisorption it will follow the Temkin isotherm (Coulson and Richardson [23], Biswa et al. [24]). This has mathematical expression represented by eqn (4). The constants a and b obtainable from plot of q_e against Log c_e are Temkin constants and q_e, c_e have the same meaning as earlier described. Table 3 presents the isotherm parameters obtained for fluoride sorption.

Figures 1 to 3 are isotherm plots and linear equations, for the 150°C calcines, and exemplify plots from which the data in Table 4 was obtained. Plots for the rest of the calcines are not shown in this paper.

Table 3:   Isotherm parameters for fluoride sorption on 3:2:1 composite filter at 20±1°C and pH 8.6±0.2.

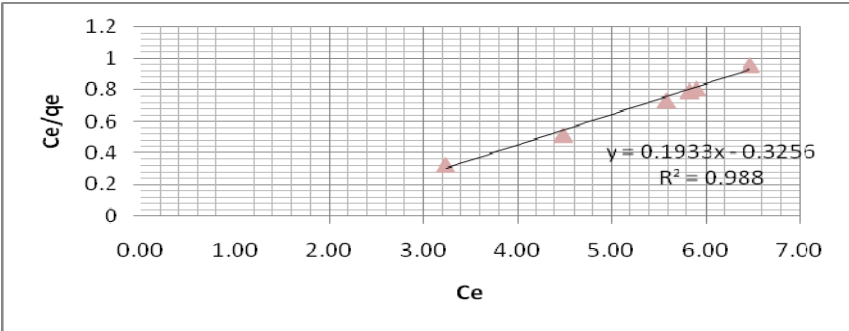| Parameter	Value			
	Langmuir			
	150°C	**200°C**	**250°C**	**300°C**
Θ (mg F/g)	5.17	9.12	4.82	7.65
b (dm^3/mg)	-0.59	-2.95	-0.51	-1.37
R^2	0.9880	0.9988	0.9852	0.9986
	Freundlich			
K_f	927.47	345.54	1170.58	452.06
n	-1.81	-5.23	-1.64	-3.26
R^2	0.9792	0.9895	0.9739	0.9936
	Temkin			
a	15.49	12.56	16.04	13.56
b	-10.64	-4.84	-11.34	-7.11
R^2	0.9917	0.9927	0.9898	0.9962

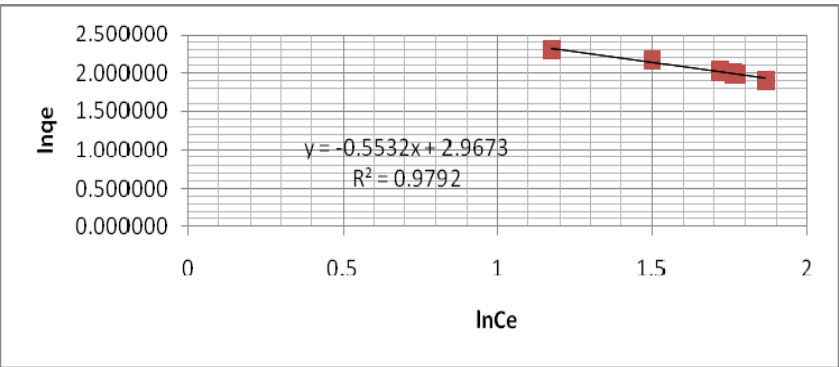Figure 1:   Langmuir isotherm for 150°C Calcine.

Figure 2:   Freundlich isotherm for 150°C Calcine.
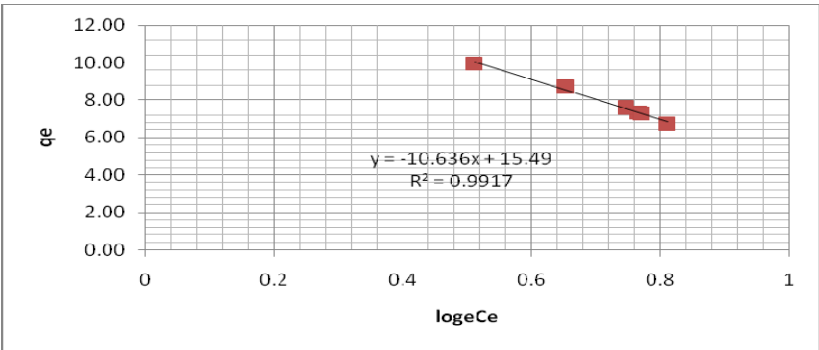

Figure 3:   Temkin isotherm for 150°C Calcine.

Results also demonstrated that the Langmuir isotherm constants related to capacity and energy, Q (mg/g) and b (dm^3/mg) respectively, are inversely proportional with highest capacity corresponding to lowest energy term, (9.12 mg/g and -2.95 dm^3/mg) obtained for the 200°C calcine, and lowest

capacity corresponding to highest energy term, (4.82 mg/g and -0.51 dm³/mg) obtained with the 250°C calcine. A plot of energy term (*b*) against capacity (*Q*) gave a correlation coefficient of 0.9061 and a linear relation governed by linear equation *b = -0.525Q + 2.1575*. The Freundlich intensity parameters, 1/n, were below unity for all four temperature calcines denoting favourable conditions for Freundlich isothermal interaction implying multilayer formation on heterogeneous sites. This is in agreement with the mixed nature of the composite filters created from the three different materials. Temkin parameters *a* and *b* seemed to be inversely correlated through linear equation *a = -0.5324b + 9.8961* and had a correlation coefficient of 0.9951.

4   Conclusions and further work

4.1 Tentative conclusions

Water defluoridated with the 1:2:3–200°C (bauxite:gypsum:magnesite) calcine adhered to WHO recommended limits for pH, hardness, and concentrations of $SO_4^{2-}, Cl^-, Al^{3+}, Fe^{2+}$ as such this composite is potentially the best among the experimented compositions within the four experimental calcine temperatures. This composite obtained a capacity of 10.19 mg F^- /g of filter, and an equilibrium residual fluoride concentration of 3.01 mg/l. This filter may obtain fluoride concentrations below 1.5 mg/l for most fluoritic waters with initial concentrations below 11.69 mg/l, in the present experiments however the initial fluoride concentration was 13.2 mg/l. Another promising composite was the 3:2:1 that obtained high capacities at three of the four calcine temperatures. This composite had one major limitation of high residual sulphate concentrations in the treated water.

Bauxite, gypsum, magnesite and the rest of the composite filters increased residual concentrations of either, Al^{3+} and Fe^{2+}, Fe^{2+} and SO_4^{2-} or Al^{3+} and SO_4^{2-} in the treated water. pH changes were within acceptable limits except for defluoridation with magnesite where pH rose higher than 8.5.

Sorption mechanisms appeared mixed with monolayer homogeneous interactions, heterogeneous and chemisorption interactions discernible, as inferred from Langmuir, Freundlich and Temkin isotherms of the 3:2:1 composite being very comparable. However Langmuir was more pronounced for the 200 and 300°C calcine whereas Temkin was enhanced for the 150 and 250°C calcine.

There exist limitations of residual Al^{3+} and Fe^{2+}, Fe^{2+} and SO_4^{2-} or Al^{3+} and SO_4^{2-} in the treated water in defluoridation with bauxite, gypsum, magnesite and their composite filters, nevertheless an optimum composite of these materials is plausible.

4.2 Further work

Experimentation with different masses of bauxite, gypsum and magnesite, varying flow rates, and initial fluoride concentrations will be carried out to determine the optimum composite ratios for different initial fluoride concentrations. This will be within the temperature range 150°C to 500°C. Investigations involving bed depth service time (BDST) design model and empty bed residence time (EBRT) optimization model, on fixed bed columns with identified optimum composite filters, will also be carried out in an attempt to determine possible composite filters and optimal design configurations in water defluoridation with these materials.

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