Full Length Research Paper

Physico-Chemically Treated Sand for Fluoride Removal from Water: An Equilibrium Investigation

Eric Togarepi, Courtie Mahamadi* and Abigail Mangombe

Bindura University of Science Education, P. Bag 1020, Bindura, Zimbabwe.

In this study, heat and chemically treated sand was applied as an adsorbent for the removal of fluoride ions from aqueous solutions. The influence of different parameters such as calcination time, dosage, initial fluoride concentration and pH were evaluated. Results indicated that activated sand can be used for defluoridation of water. This can be achieved by coating sand with 10% Fe_2O_3, a calcination time of 3 h and pH around 6. The adsorption also increased with initial fluoride concentration and adsorbent dose. This study also showed that up to 90% of fluoride was adsorbed with 12 g of adsorbent in 50 ml of 10 mg/L fluoride solution. The sorption data were best described by the Freundlich isotherm. The maximum adsorption capacity was found to be 10.3 mg/g. According to these findings, physico-chemically modified sand has potential application as an adsorbent for fluoride ions removal.

Key words: Sand, adsorption, fluorine, defluoridation, Freundlich isotherm, Langmuir isotherm.

INTRODUCTION

Fluoride occurs mainly as fluorspar (CaF_2), sellaite (MgF_2), cryolite (Na_3AlF_6) and fluorapatite [$3Ca_3(PO_4)_2Ca(F,Cl_2)$]. General insolubility of these fluoride minerals means that they will only be present in groundwater when conditions favour their dissolution, or when they are introduced from anthropogenic sources. High fluoride levels are a cause of great concern in many geographical regions of the world. The effect of fluoride in drinking water has attracted significant research for several years (Cummins, 1985; Clifford, 1990; Mjengera et al., 1997; Rajchagool et al., 1997; Venkobachar et al., 1997). It has been shown that in optimum dose in drinking water, fluoride is advantageous to health and excess concentration beyond the prescribed limits affects health negatively, as it can cause dental and/or skeletal fluorosis and affect kidney and nerve muscle function (Emamjomeh and Sivakumar, 2009). Up to a small level (1 to 1.5 mg/L) fluoride strengthens the enamel whereas higher concentrations ranging from 1.5 to 4 mg/L cause

dental fluorosis, with the severity deteriorating to skeletal fluorosis at even higher concentrations. However, high fluoride concentrations in ground water, up to 30 mg/L occur in some parts of the world. The World Health Organization has set a guidance level of 1.5 mg L^{-1} for fluoride in drinking water (WHO, 1996).

In Zimbabwe, the urban communities rely on purified municipal water while those in rural areas mostly rely on underground water like boreholes, springs and artesian wells. Research has shown fluoride levels to be high in two of Zimbabwe's districts, Chimanimani and Gokwe. In Gokwe, water from artesian wells were found to contain between 5 and 10 mg L^{-1} fluoride concentration, and in Chimanimani levels of 6 mg L^{-1} fluoride ion concentration were recorded (Tobaiwa et al., 1991).

Dental fluorosis was reported by the same authors to be severe in school pupils in the same areas. Compared to other technologies like reverse osmosis, nanofiltration, electrodialysis and Donnan dialysis, adsorption has been considered as the most applicable technology for fluoride removal from drinking water (Crittenden et al., 2005; Hu et al., 2005; Tahaikta et al., 2007; Zhao et al., 2008).

Various types of adsorbent materials that have been investigated for the fluoride removal potential include

---
*Corresponding author. E-mail: cmahamadi@buse.ac.zw. Tel: +263-2717531/6. Fax: +263-7435.
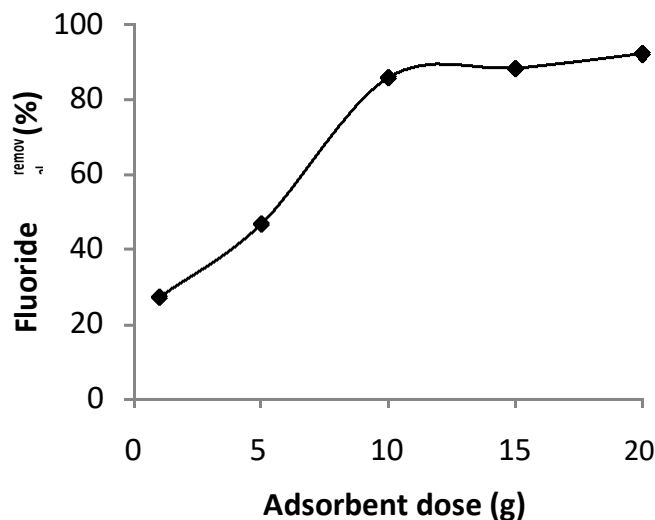
Figure 1. Effect of adsorbent dose on fluoride removal at initial fluoride concentration of 10 mg L^{-1}, pH 6, room temperature, 150 rpm agitation rate and 60 min agitation time.

activated carbon, minerals, fish bone charcoal, coconut shell carbon, rise husk carbon, and biosorbent material, with varying degrees of success (Gupta, 2007; Hu et al., 2005; Ku and Chiou, 2002; Kumar, 2009; Lv, 2007). Chidambaram et al. (2003), established that red soils adsorbed 9 mg L^{-1} of fluorides within 15 min with aqueous fluoride levels decreasing down to 0.02 mg L^{-1} in 90 to 120 min.

In the present study, naturally occurring sand from Mashonaland Central Province of Zimbabwe was activated by chemical and heat treatment and investi-gated as a possible adsorbent for fluoride ions from water. The main objective was to establish the efficacy of the treated sand in adsorbing fluoride from synthetic solutions. The influence of the following calcination time, adsorbent dose, initial metal ion concentration, agitation time and pH have also been investigated in this study.

MATERIALS AND METHODS

Instruments and chemicals

All chemicals used in this work were analytical reagent quality. NaOH, HCl, Fe_2O_3 and NaF were supplied from Sigma-Aldrich, Germany and deionized water (Conductivity 0.001 μSm^{-1}) was obtained from Trojan Nickel Mine, Bindura. The fluoride concentration was determined using a Hanna C 200 model.

Preparation of sand adsorbent

Two kilograms of sand sample was obtained from Nyaure River near Bindura, Mashonaland Central Province, Zimbabwe. The sample was sieved through 0.5 mm to remove large particles and washed with tape water until clear water was obtained. The sample was

then rinsed thoroughly with de-ionized water and soaked in 0.1 M NaOH for 24 h followed by further rinsing with de-ionized water until the pH was neutral. The sand was then set to dry in an oven at 250°C for 24 h. A portion of the sample (1 kg) was used as a control while the rest was mixed with different quantities of iron (III) oxide dissolved in excess NaOH. The sand-NaOH mixture was heated to the boiling point for 1 h and left to cool overnight. After filtration, the sample was dried in an oven at 150°C. The treatment with iron (III) oxide was done with different compositions, 5, 10 and 15% iron (III) oxide. The samples were further divided into three sets for determination of optimum calcination time at 550°C baking temperature. The baked samples were then ground, rinsed with deionized water and oven dried at 150°C.

Standard fluoride solutions were prepared by dissolving an appropriate amount of sodium fluoride in double distilled water. A stock solution 1000 mg L^{-1} F^- was first prepared and all solutions for adsorption and analysis were prepared by appropriate dilution of the freshly prepared stock solution.

Batch sorption tests were carried out to investigate the influence of various parameters on the efficiency of fluoride removal by the sand samples. The optimum adsorbent dose, agitation time, pH, and initial metal concentration were investigated in the ranges of 0.02 to 0.4 g ml^{-1}, 5 to 120 min, pH 2 to 8, 5 to 20 mg L^{-1}, respectively. Generally, the adsorbent was mixed with 50 ml of the fluoride solution and after adsorption process, the mixture was filtered through Whatman No. 42 filter paper. The filtrate was analysed for residual fluoride using the fluoride ion selective electrode. All fluoride sorption experiments were carried out at 25°C and agitation speed 150 rpm.

RESULTS AND DISCUSSION

Effect of adsorbent dose

The effect of adsorbent dose on adsorption of fluoride at pH 6.5 and fluoride concentration of 10 mg L^{-1} is shown in Figure 1. It can be seen that the removal efficiency increases from about 28 to 90% with the increase of the adsorbent dose. It is explained that the more the addition of adsorbent in the solution, the more the availability of active sites for the fluoride binding. However, generally the purpose of studying the effect adsorbent dose is to determine the optimum amount of adsorbent for the removal of the adsorbate. The results show that the amount of fluoride removed increased with an increase in adsorbent dose nearly 90% of fluoride was adsorbed with 12 g in 50 ml of solution (0.24 g/ml). Further addition adsorbent did not, however, result in an significant increases in adsorption capacity, hence a dose of 0.24 g/ml is considered to be the optimum dose and subsequently used in further studies.

Effect of contact time

Figure 2 shows that fluoride removal increased with contact time. Although kinetic experiments were not carried out in the present study, the greater the time allowed for interaction of the fluoride ions with adsorbent the great the sorption chances, with optimum sorption occurring within the first 60 min.
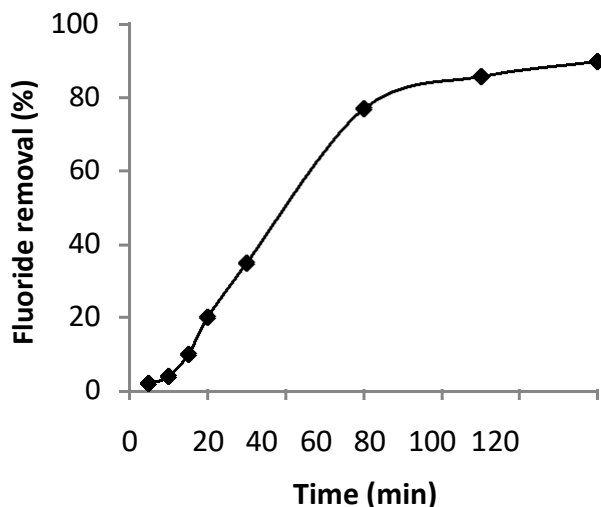
Figure 2. Effect of contact time on fluoride removal at initial fluoride concentration of 10 mgL^{-1}, adsorbent dose of 0.24 g/ml, room temperature, pH 6, and agitation rate of 150 rpm.

Effect of pH

Fluoride adsorption at an initial fluoride concentration of 10 mg L^{-1} was carried out in the pH range 2 to 8, at adsorbent dose of 0.24 g/ml and 60 min sorption time. Ph adjustements were carried out using 0.1 M NaOH and 0.1 M HCl. The results illustrated in Figure 3 show that increasing pH from 2 to 6, resulted in the fluoride removal efficiency increasing from 40 to 90%. In general, the mechanism of adsorption is likely to be coupled by the release of OH$^-$ ions, hence solution pH should have an effect on fluoride adsorption. The low adsorption of fluoride in acidic pH range can be attributed to competi-tion between adsorption behaviour and the formation of hydrofluoric acid.

According to the fluoride speciation, hydrofluoride was predominant in pH less than 3.18 (Stumm and Morgan, 1996). As the pH is increased to the alkaline range, a sharp drop in adsorption can be observed. This may be due to a descrease in surface charges of the adsorbent and competition between the fluoride ions and hydroxyl ions for adsorption onto the sand (Barnes et al., 2009).

Effect of initial fluoride concentration

Equilibrium sorption models parameters generated for the removal of fluoride by the sand adsorbent are shown in Table 1. In this study, Freundlich (1906), Langmuir (Nemr, 2009) and Temkin (Temkin and Pyzhev, 1940) isotherms were tested for their fit to the soprtion data. The results showed that the Freundlich isotherm best fitted the sorption data. A maximum value for adsoprtion capacity of 10.3 mg/g F$^-$ was obtained and is compared with other adsorbent materials in Table 2. It can be

observed that physico-chemically treated sand offered a competitive capacity for the removal of fluoride from water. The results were further analysed by determining the Langmuir separation factor, R_L, which is a dimension-less constant defined by the following equation:

$$R_L = \frac{1}{1 + bC_0}$$

The value of R_L was found to be 0.12, which, from Table 3, indicates that the isotherm was favourable.

Effect of calcination time and amount of Fe$_2$O$_3$ on removal of fluoride

A calcination temperature of 550°C was used when baking the chemically treated sand. Elsewhere, it was reported that temperature above 700°C caused a decline in F$^-$ binding above 900°C, the adsorption capacity was lost. From the results in Table 3, calcination times of 3 and 4^1/$_2$ h were quite effective in fluoride removal. On the chemical treatment, both 10 and 15% Fe$_2$O$_3$-treated sand samples showed good removal potential. On economic grounds therefore, one would recommend calcination for a period of 3 h using 10% Fe$_2$O$_3$ for chemical treatment (Table 4).

Conclusion

The removal of fluoride ions using heat and chemically treated sand was studied in a batch system with respect to adsorbent dose, pH, calcination time and amount of
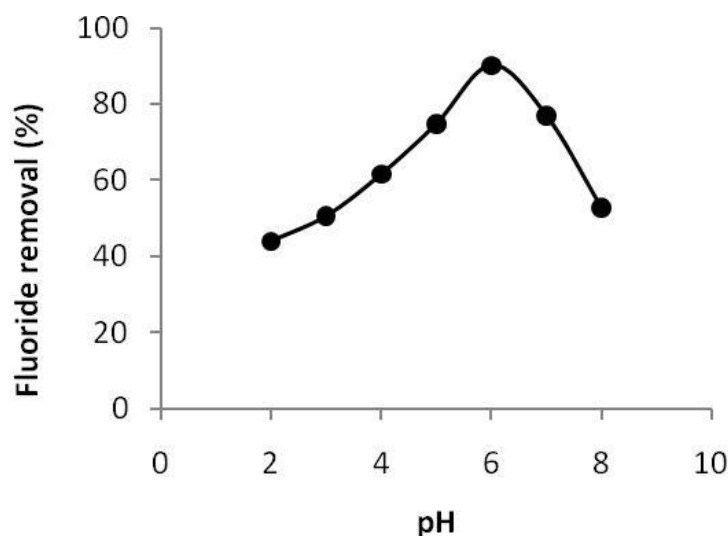
Figure 3. Effect of pH on fluoride removal at initial fluoride concentration of 10 mgL^{-1}, room temperature, 60 min contact time, 150 rpm agitation rate and adsorbent dose of 0.24 g/ml.

Table 1. The results of isotherms calculation.

Isotherm	Equation	Linear form	R^2	Constant	Value
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$	$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e$	0.98	K_f n	0.86 2.50
Langmuir	$q_e = \dfrac{Q_m K_L C_e}{1 + K_L C_e}$	$\dfrac{1}{q_e} = \dfrac{1}{Q_m} + \left(\dfrac{1}{K_L Q_m}\right)\dfrac{1}{C_e}$	0.92	K_L Q_m	2.53 10.3
Temkin	$q_e = \dfrac{RT}{b_T} Ln(A_T C_e)$	$q_e = B_T ln A_T + B_T ln C_e$	0.93	A_T	12.5

Table 2. Adsorption capacities and other parameters for the removal of fluoride by different sorbents.

Adsorbent	Adsorption capacity (mg/g)	Concentration range	Contact time	pH	Temperature (°C)	Reference
Acid treated bleaching earth	7.75	5-45 mg/dm^3	30 min	3.5	-	Mahramanlioglu et al. (2002)
Aluminium impregnated hierarchal web of carbon fibers	17.0	0.1-50 mg/L	-	-	35	Gupta et al. (2009)
Manganese-oxide-coated alumina	2.85	2.5-30 mg/L	3 h	7.0±0.2	30±2	Maliyekkal et al. (2006)
Fe(III) loaded carboxylated chitosan beads	4.23	11-19 mg/L	40 min	neutral	303 K	Viswanathan and Meenakshi (2008)
Fe(III)-treated sand	10.3	20-40 mg/L	2 h	2-8	25	Current study

Table 3. Significance of the separation factor.

R_L value	Type of isotherm
$R_L>1$	Unfavourable
$R_L=1$	Linear
$R_L=0$	Irreversible
$0<R_L<1$	Favourable

Table 4. Effect of Calcination time and amount of Fe_2O_3 on removal of fluoride.

Sample	Calcination time (h)	Fluoride removal (%)
Control	$1^1/_2$	1
Control	3	6
Control	$4^1/_2$	10
5% Fe_2O_3	$1^1/_2$	65
5% Fe_2O_3	3	72
5% Fe_2O_3	$4^1/_2$	74
10% Fe_2O_3	$1^1/_2$	80
10% Fe_2O_3	3	89
10% Fe_2O_3	$4^1/_2$	90
15% Fe_2O_3	$1^1/_2$	88
15% Fe_2O_3	3	92
15% Fe_2O_3	$4^1/_2$	97

Fe_2O_3. The Langmuir and Freundlich isotherms were used to model the equilibrium sorption data. The results showed that using an optimum dose of 0.24 g/ml, up to 90% fluoride removal could be achieved and the optimum pH was in the range 5.7 to 6.3. It was also shown that a calniation period of 3 h using 10% Fe_2O_3 for chemical treatment gave optimum results for fluoride removal.

ACKNOWLEDGEMENT

REFERENCES

Barnes A, Sapsford DJ, Dey M, Williams KP (2009). Heterogeneous Fe(II) oxidation and zeta potential, J. Geochem. Explor., 100: 192-198.

Chidambaram S, Ramanathan AL, Vasudevan S (2003). Fluoride removal studies in water using natural materials. Water SA, 29(3): 339-344.

Clifford DA (1990). 'Ion exchange and inorganic adsorption in water quality and treatment'. In: *Pontius, F.W. (ed.)*. A handbook of community water supplies. 4th ed. New York, NY, USA, McGraw Hill.

Crittenden J, Trussell R, Hand D, Howe K, Tchobanoglous G (2005). Water treatment: Principles and design, New York, John Wiley and Sons.

Cummins BT (1985). Controlling fluoride levels: a literature review. Geneva, Switzerland, World Health Organization.

Emamjomeh M, Sivakumar M (2009). Fluoride removal by a continuous flow electrocoagulation reactor. J. Environ. Manage., 90: 1204-1212.

Freundlich HMF (1906). Uber die adsorption in losungen. J. Phys. Chem., 57: 385-470.

Gupta AK, Deva D, Sharma A, Verma N (2009). Adsorptive Removal of Fluoride by Micro-nanohierarchal Web of Activated Carbon Fibers. Ind. Eng. Chem. Res.*,* 48(21): 9697-9707.

Gupta VK, Lmran A, Sain VK (2007). Defluoridation of wastewaters using waste carbon slurry. Water Res., 41: 3307-3316.

Hu CY, Lo SL, Kuan WH, Lee YD (2005). Removal of fluoride from semiconductor wastewater by electrocoagulation-flotation. Water Res., 39: 895-901.

Ku Y, Chiou HM (2002). The adsorption of fluoride ion from aqueous solution by activated alumina. Water Air Soil Pollut., 133: 349-360.

Kumar E, Bhatnagar A, Ji M, Jung W, Lee SH, Kim SJ, Lee G, Song H, Choi JY, Yang JS, Jeon BH (2009). Defluoridation from aqueous solutions by granular ferric hydroxide (GFH). Water Res., 43: 490-498.

Lv L, He J, Wei M, Evans DG, Zhoua Z (2007). Treatment of high fluoride concentration water by MgAl-CO3 layered double hydroxides: Kinetic and equilibrium studies. Water Res., 41: 1534-1542.

Mahramanlioglu M, Kizilcikli I, Bicer IO (2002). Sorption of fluoride from aqueous solution by acid treated spent bleaching earth. J. Fluorine Chem., 115: 41-47.

Maliyekkal SM, Shar AK (2006). Manganese-oxide-coated alumina: defluoridation of water. Water Res., 40(19): 3497-3506.

Mjengera HJ, Mtalo FW, Mashauri DA, Tjell CH (1997). 'Fluoride removal using heat activated animal bone media.' In: Dahi, E. and Nielsen, J.M. (eds). Proceedings of the 2nd international workshop on fluorosis and defluoridation of water, Addis Ababa, Ethiopia,

November 19-22, 1997. Dunedin, New Zealand, International Society for Fluoride Research.

Nemr AE (2009). Potential of Pomegranate Husk Carbon for Cr (VI) removal from wastewater: Kinetic and isotherm studies. J. Hazard. Mater., 161: 132-141.

Rajchagool S, Rajchagool C (1997). 'Solving the fluorosis problem in a developing country'. In: Dahi, E. and Nielsen, J.M. (eds). Proceedings of the 2nd international workshop on fluorosis and defluoridation of water, Addis Ababa, Ethiopia, Nov.19-22. Dunedin, New Zealand, International Society for Fluoride Research.

Stumm W, Morgan JJ (1996). Aquatic Chemistry. 3rd ed., John Wiley & Sons, Inc., pp. 533-549.

Tahaikta M, Habbania RE, Haddoua AA, Acharyal Amora Z, Takya M, Alamib A, Boughribab A, Hafsib M, Elmidaouia A (2007). Fluoride removal from groundwater by nanofiltration. Desalination, 212: 46-53.

Temkin M, Pyzhev JAV (1940). Kinetics of ammonia synthesis on promoted iron catalysts. Acta Physiochem., 12: 217-229.

Tobaiwa C, Musiyambiri M, Chironga L, Mazorodze O, Sapahla S, (1991). Fluoride levels and dental fluorosis in two districts in Zimbabwe. Cent. Afr. J. Med., 7(11): 353-361.

Venkobachar C, Iyengar L, Mudgal A (1997). 'Household defluoridation of drinking water using activated alumina technology'. In: Dahi, E. and Nielsen, J.M. (eds). Proceedings of the 2nd international workshop on fluorosis and defluoridation of water, Addis Ababa, Ethiopia, November 19-22, Dunedin, New Zealand, International Society for Fluoride Research.

Viswanathan N, Meenakshi S (2008). Selective sorption of fluoride using Fe(III) loaded carboxylated chitosan beads, J. Fluorine Chem. 129: 503-509.

WHO-Geneva (1996). Guidelines for drinking-water quality. Vol. 2. Health criteria and other supporting information. 2nd ed. Geneva, Switzerland, World Health Organization. http://www.who.int/water_sanitation_health/GDWQ/GWDWQindex.html

Zhao Y, Li X, Liu L, Chen F (2008). Fluoride removal by Fe(III)-loaded ligand exchange cotton cellulose adsorbent from drinking water. Carbohydr. Polym., 72: 144-150.