WATER DEFLUORIDATION BY LIGNITE

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ABSTRACT

Lignite (raw or alum-treated) was found to possess about one-half the fluoride sorption capacity of commercial grade activated alumina. No significant difference in performance of raw and alum-treated lignite in five cycles of defluoridation column test at pH 5.0 ± 0.2, using hydrochloric acid as regenerant, was observed. Infrared spectra indicated interaction of fluoride with carbonyl and aromatic ring functional groups in lignite. The results call for long-duration column tests, employing fluoride-bearing groundwater of varied characteristics and at natural pH, to confirm suitability of lignite as a low-cost medium for home water defluoridation in rural areas of developing countries.

INTRODUCTION

Fluoride in concentration much higher than the World Health Organization (WHO) drinking-water guideline value of 1.5 mg/L (WHO 1993) have been reported in many rural areas of the developing world. Typical examples of fluoride belt are those extending from Turkey through Syria, Jordan, Egypt, Libya and Algeria to Morocco, from Egypt through Sudan and Kenya to Tanzania, and from Turkey through Iraq, Iran, Afghanistan, India and northern Thailand to China (Phantumvanit et al. 1988). According to a review by Commins (1985), defluoridation methods based on the combined use of lime and alum (Nalgonda technique), treated bone, bauxite, alumina, and sulphonated coal (Defluoron-2) have been used more often in developing countries; however, all these methods have their shortcomings. A charcoal-bone char point-of-use defluoridator (ICOH-defluoridator) was originally developed by Roche (1968) and improved and field-tested in Thailand by Phantumvanit at al. (1988); however, the method of regeneration is complicated (Christoffersen et al. 1991) and local taboo may restrict its acceptance in many countries. The present study was initiated to assess the potential of lignite (raw or alum-treated) as a low-cost medium for use in home water defluoridator.

MATERIALS AND METHODS

Fluoride-Bearing Water

The fluoride-bearing water used in the study was a deep tube-well water (pH 7.8-8.2, conductivity 78-84 mS/m, hardness 190-200 mg $CaCO_3$/L, calcium 65-75 mg $CaCO_3$/L, magnesium 115-125 mg $CaCO_3$/L, alkalinity 250-260 mg $CaCO_3$/L, and fluoride 0.80-0.85 mg/L) spiked with sodium fluoride to a final fluoride concentration of 5.0 0.1 mg/L.

Media

The media used were lignite (supplied by Neyveli Lignite Corporation, Neyveli, Tamilnadu, India), raw or alum-treated, and a commercial grade activated alumina (designated as AA-IPCL; supplied by the Indian Petrochemicals Ltd., Thane, Maharashtra, India) as a reference. The lignite was crushed and both lignite and AA-IPCL were sieved to a size range of 0.355-0.425 mm. Thereafter, the lignite

was washed with triple distilled water, whereas AA-IPCL was soaked in 0.1 N hydrochloric acid for two hours followed by washing with triple distilled water. Both lignite and AA-IPCL were dried overnight at 42°C.

For alum treatment of lignite, the method standardised by Osman & Chaudhuri (1990) was used. Ten grammes of raw lignite in 200 mL of 0.075 M alum [$Al_2(SO_4)_3.16H_2O$] solution (pH ca. 3) were agitated in an end-over-end shaker at 20 rpm for two hours. The treated medium (designated as alum-lignite) was then separated by filtration through Whatman No.42 filter paper, washed with triple distilled water and dried overnight at 42°C. The alum-lignite surface was presumably high in positively charged aluminium hydroxo complexes. Alum treatment of lignite was also carried out at pH 9 (by adjusting pH of the alum solution with sodium hydroxide) to produce a medium (designated as alum-lignite A) with a surface high in positively charged hydrated aluminium oxide species.

Batch Fluoride Sorption Tests

In fluoride sorption kinetic test, 500 mg of a medium in 50 mL of the fluoride-bearing water was agitated for varying contact times (5, 10, 20, 60 and 120 minutes) in an end-over-end shaker at 20 rpm. Thereafter, the medium was separated by filtration through Whatman No. 42 filter paper and the filtrate analysed for residual (unsorbed) fluoride by the SPADNS method (APHA 1995). The kinetic test was carried out at pH 5.00.2 (pH adjusted with hydrochloric acid) and 8.00.2 (unadjusted pH of the fluoride-bearing water). In fluoride sorption equilibrium test, varying amounts of a medium (100-1500 mg) in 50 mL of the fluoride-bearing water were agitated for a contact time observed necessary for equilibrium fluoride sorption in the kinetic test. Thereafter, the medium was separated by filtration through Whatman No. 42 filter paper and the filtrate analysed for residual (unsorbed) fluoride.

Batch Loading Desorption Test

One gramme of a medium in 100 mL of the fluoride-bearing water was agitated for the equilibrium contact time, separated by filtration, washed with triple distilled water and dried overnight at 42°C. The filtrate was analysed for residual (unsorbed) fluoride. The fluoride-loaded medium was then agitated in 100 mL of a regenerant for one hour, separated by filtration, washed with triple distilled water and dried overnight at 42°C. The filtrate was analysed for desorbed fluoride. This constituted one loading-desorption cycle.

Defluoridation Column Test

Downflow defluoridation column test was carried out in an 11 mm ID glass column with a 330 mm deep medium bed (30 mL or 15 grammes). The fluoride-bearing water was passed through the bed at 0.32 $m^3/m^2/h$, giving a bed flowthrough time of one hour. The time was selected keeping in view the range of flowthrough time of home water treatment devices. Effluent samples were analysed for fluoride until effluent fluoride concentration rose above 1.5 mg/L when the run was terminated. The bed was then regenerated *in situ* by hydrochloric acid and four bed volumes of distilled water were passed through the bed. This constituted one cycle of defluoridation column test.

RESULTS AND DISCUSSION

The results of the batch fluoride sorption kinetic test, conducted to study temporal as well as equilibrium fluoride sorption, may be summarised as: (a) for all media, fluoride sorption was faster and

equilibrium fluoride sorption was higher at pH 5.0±0.2 than those at pH 8.0±0.2, and (b) maximum fluoride sorption observed were 83% and 67% for AA-IPCL, 43% and 28% for alum-lignite, 37% and 20% for alum-lignite A, and 37% and 23% for lignite at pH 5.0±0.2 and 8.0±0.2, respectively in one hour contact time, and there was no further appreciable increase in sorption. The results would call for lowering raw water pH to about 5 to realise maximum fluoride sorption capacity as suggested by Rubel & Woosley (1979) for activated alumina. However, there is a possibility of dissolution of aluminium from activated alumina and formation of toxic soluble alumino-fluoro complexes at such pH (Hao & Huang 1986), whereas no such problem is envisaged with raw lignite.

Lignite, alum-lignite and AA-IPCL were then subjected to batch fluoride sorption equilibrium test at pH 5.0±0.2 with one-hour contact time. Equilibrium sorption data corresponded well with both Langmuir [$1/q_e = 1/Q^o + (1/bQ^o)(1/C)$ where, q_e = equilibrium fluoride sorption per unit weight of medium (mg F$^-$/g), Q^o = moles of fluoride sorbed per unit weight of medium to form a monolayer on the surface, b = a constant related to the energy of sorption and C = equilibrium fluoride concentration (mgF$^-$/L); and Freundlich [$\log q_e = \log K_F + (1/n)\log C$ where, q_e = equilibrium fluoride sorption per unit weight of medium (mg F$^-$/g), K_F, n = constants (the intercept, $\log K_F$, for C = 1 is roughly an indicator of sorption capacity and the slope, 1/n, of sorption intensity) and C = equilibrium fluoride concentration (mg F$^-$/L)] linearisation (Table 1). A comparison of the values Q^o and K_F indicates that equilibrium fluoride sorption capacity of lignite and alum-lignite were 40-45% and 50-55%, respectively of that of AA-IPCL.

Table 1: Langmuir and Freundlich constants.

Medium	Langmuir			Freundlich		
	Q^o	b	r*	K_F	1/n	r*
Lignite	0.406	0.380	0.982	0.117	0.55	0.981
Alum-lignite	0.515	0.373	0.977	0.144	0.57	0.977
AA-IPCL	0.917	0.488	0.988	0.288	0.68	0.992

*Correlation coefficient.

Table 2: Fluoride uptake in batch loading-desorption test.

Medium	Normality of hydrochloric acid	Fluoride uptake in loading cycle (μg/g)		
		1	2	3
	0.10	200	180	230
	0.25	200	200	240
Lignite	0.50	200	200	270
	1.00	200	260	280
	0.10	210	202	230
	0.25	210	202	260
Alum-lignite	0.50	210	230	260
	1.00	210	270	300

Performance of lignite and alum-lignite in three successive cycles of batch loading-desorption test, using 0.1 N, 0.25 N, 0.5 N and 1.0 N hydrochloric acid as regenerant, is presented in Table 2. It is interesting to note that increase in fluoride uptake (sorption) occurred after the first cycle for 1.0 N hydrochloric acid as regenerant and after the second cycle for 0.1 N, 0.25 N and 0.5 N hydrochloric acid as regenerant. Presumably, it was due to activation of fluoride sorption sites or due to adsorption of hydrogen ions resulting in increase of the cationic sites on the medium surface.

No significant difference in the performance of lignite and alum-lignite in five cycles of defluoridation column test, using 1.0 N hydrochloric acid as regenerant, were observed except that effluent fluoride concentration in the first cycle was slightly lower for alum-lignite (Fig. 1). For both media, throughput before effluent fluoride concentration reached the WHO drinking-water guideline value of 1.5 mg/L, increased from 400 mL in the first cycle to 450 mL in the second and third cycles, and 700-800 mL in the fourth and fifth cycles.

The above results and lower cost of lignite (activated alumina is 25-30 times costlier) call for long-duration column tests, employing fluoride-bearing groundwater of varied characteristics and at natural pH, to confirm suitability of lignite as a low-cost medium for home defluoridation in rural areas of developing countries. Reduced fluoride sorption capacity of lignite at natural groundwater pH may be offset by the cost of acidification to lower pH of raw water to 5 and subsequent pH adjustment following defluoridation.

An attempt was made to probe into the nature of lignite-fluoride interaction with a view to provide an understanding to the behaviour of lignite and alum-lignite in fluoride sorption. Important oxygen-containing functional groups in lignite are carboxyl, methoxyl, hydroxyl and carbonyl (van Krevelen 1961). Infrared (IR) spectra of the lignite used in the present study corroborated this. IR spectra, using identical quantities of medium in the KBr matrix, of lignite and alum-lignite with and without sorbed fluoride showed a decrease in band intensities in the region 1720-1520 cm^{-1} following fluoride sorption, which indicated possible interaction of fluoride with carbonyl and aromatic ring functional groups in lignite. In addition, there was slight increase in band intensities in this region for alum-lignite compared to lignite, suggesting an increase in relative abundance of the fluoride sorption sites following alum treatment and thus accounting for increased fluoride sorption by alum-lignite.

Analysis of the IR spectra may also be cautiously extended to provide an understanding to observed increase in fluoride uptake by lignite and alum-lignite in the loading-desorption test (Table 2) as well as increase in their fluoride removal capacity in the defluoridation column test following acid regeneration (Fig. 1). Increase in relative abundance of the fluoride sorption sites in alum-lignite (pH of alum treatment ca. 3) was plausibly due to the acid environment since alum-lignite A (alum treatment at pH 9) did not show any increase in fluoride sorption compared to lignite in batch fluoride sorption test. A similar phenomenon may account for increased fluoride uptake/removal following acid regeneration.

CONCLUSION

Lignite is potentially useful as a low-cost medium for home water defluoridation in rural areas of developing countries. Its fluoride removal capacity is about one-half that of commercial grade activated alumina. Long-duration column tests, employing fluoride-bearing groundwater of varied characteristics and at natural pH, are called for to confirm suitability of lignite for home water defluoridation.
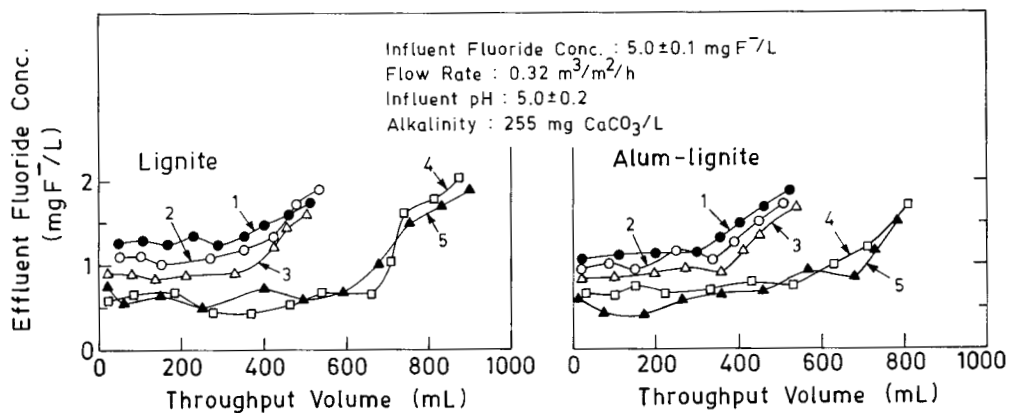
Effluent Fluoride Conc. (mg F⁻/L)

Influent Fluoride Conc. : 5.0±0.1 mg F^-/L
Flow Rate : 0.32 m^3/m^2/h
Influent pH : 5.0±0.2
Alkalinity : 255 mg $CaCO_3$/L

Lignite

Alum-lignite

Throughput Volume (mL)

Fig.1: Performance of lignite and alum-lignite in five cycles of defluoridation column test.

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