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Defluoridation of Water Using Amended Clay

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Abstract - In this paper a new and simple defluoridation method is presented using silty clay (C) as a fluoride (F) sorbent. Besides, the ability of chemically amended C to adsorb F was determined experimentally. The results were extended to possible application of clay vessels in water defluoridation. Based on results it was concluded that chemically amended clay vessels appears to be an economical and efficient method for defluoridation of drinking water.

I. Introduction

Remediation and rehabilitation of polluted drinking water are key issues in environmental sciences. Elevated concentrations of F in drinking water has posed serious health problems and has reached alarming levels in several parts of the world including India, where drinking water contains naturally occurring soluble fluoride (F) much above the permissible limit of 1.5 mg/l [1]. Several methods proposed and tested worldwide are mostly based on the principles of precipitation, adsorption and ion exchange. These methods involve the use of alum, lime, aluminium sulphate, gypsum-fluorite filters, magnesite, dolomite, polyaluminium chloride, granulated bone media, bone charcoal, activated alumina, activated carbon, superphosphate and tri-calcium phosphate [2]. The management and maintenance of available defluoridation technologies requires expensive chemicals and/or high level of technological skill and can be applied only in centralized water distribution systems [3]. In developing countries these conditions may not be present.

The novel feature of this study is to explore the possibility of using clay vessels for water defluoridation. In addition the present article also reports the results on F (NaF) sorption by the soils of Agra (India) and its two fractions. Silty clay fraction (C) exhibiting maximum F sorption was further amended chemically to enhance its potential for water defluoridation --- a method when extrapolated to fabrication of vessels would have enhanced potential of utilising vast naturally occurring sorbent (i.e. C) for defluoridation of water.

II. Materials and methods

Soil samples (N = 20) was collected from uncultivated agricultural fields of Agra (27° 10' N & 78° 05'E), India at 0-15 cm depth. After removing stones and rubbles, the soil samples were gently crushed and mixed in equal proportions to generate the composite soil (CS). A part of CS was fractionated by wet sieving into coarser fraction composed largely of sand (S, particle size 0.05 – 2 mm) and

TABLE I
Experimental layout for sorption studies

Experiment conditions	Set 1	Set 2	Set 3	Set 4	Set 5	Set 6
Sample type ^a	CS, S, C	C, Al ₁ , Al ₂ , Al ₃ , Ca ₁ , Ca ₂ , Ca ₃ , Fe ₁ , Fe ₂ , Fe ₃	C, Al ₁ , Ca ₁ , Fe ₁	C, Al ₁ , Ca ₁ , Fe ₁	C, C ₁ , C ₂ , C ₃	C, C ₁
[F] _{initial} (mg/L)	5, 10	10	10	2.5, 5, 10, 15, 25	10	10
Sample/solution (g/L)	100	100	100	100	5, 10, 25, 50, 100	100
pH	≈ 4, 7, 9	initial pH ^b	≈ 4, 5, 6, 7, 10	≈ 6	initial pH ^b	initial pH ^b
Shaking time (min)	60, 180, 360	60	60	60	60	5, 10, 20, 60, 120, 180

^aSample type - C: Silty clay; S: Sand; CS: composite soil; Al₁, Al₂, Al₃: 50, 100 & 200 mg Al/g C, respectively; Fe₁, Fe₂, Fe₃: 50, 100 & 200 mg Fe/g C, respectively; Ca₁, Ca₂, Ca₃: 50, 100 & 200 mg Ca/g C, respectively; C₁: 50 mg each of Al, Fe and Ca/g C; C₂: 50 mg each of Al, Fe and Ca/g C + 2 mg NaOH/g C; C₃: 50 mg each of Al, Fe and Ca/g C + 4 mg NaOH/g C. (Al, Ca, Fe, and NaOH were added as activated Al₂O₃, CaCO₃, FeCl₃, and 1 M solution, respectively).

^binitial pH: C (8.2); Al₁ (7.63); Al₂ (7.6); Al₃ (7.43); Ca₁ (8.13); Ca₂ (8.19); Ca₃ (8.32); Fe₁(3.08); Fe₂ (2.91); Fe₃ (2.66); C₁ (6.72); C₂ (7.17); C₃ (7.35)

C fraction (particle size < 0.05 mm). XRD analysis of C revealed the dominance of illite along with small amount of kaolinite, vermiculite, feldspars and quartz.

Details of 12 separate chemical treatments given to C are enumerated in Table I. Chemical treatment of samples employed mixing of CS, S and C with HCl (70-75 mequiv/kg) or NaOH (50-60 mequiv/kg) solutions followed by incubation for a week at field moist levels to maintain their pH at ≈ 4, 7 and 9. Besides, C taken in closed plastic containers (200 g in each) was treated with aqueous solutions (170 ml of desired concentration) of activated alumina (Al₂O₃), ferric chloride (FeCl₃) and/or calcium carbonate (CaCO₃), in small aliquots with thorough mixing. Following incubation at 24 ± 2 °C at field moist level for a week, all the

samples were washed free of soluble salts with de-ionised distilled water, and were then air-dried.

Batch equilibration F sorption studies (six sets) were conducted by shaking 20 ml F solution mixed with samples (Table I) on a horizontal rotary shaker, under the conditions described in Table I. The contents were centrifuged at 11,000 rpm for 5 minutes and the centrifugates analysed for F and pH. Further, CS and C (1:4 w/w), mixed with suitable amount of water, were utilized for preparing three pots of 15 l capacity and sun dried for 5-7 days. The dried pots were baked at ≈ 300 °C for ~ 8 h, cooled at room temperature and then washed with double distilled water. Thereafter, each pot was filled with 10 l of water containing $[F] = 150$ mg/l. Subsequently, 30 ml of water was withdrawn from these pots each day for 21 days, after proper stirring and analysed for F.

Analysis of F concentrations in centrifugates and water samples was done employing Orion Ion Analyser (Model EA 940), coupled to Orion F ion selective electrode (FISE), Model 9609BN. Before F estimation 10 ml of aliquots were mixed with 10 ml of total ionic strength adjusting buffer (TISAB). Each litre of TISAB contained 58 g NaCl, 57 ml glacial acetic acid, 0.3 g tri-sodium citrate and sufficient NaOH to yield a pH of 5.3.

III. Results and Discussion

F sorption by soil and its fractions, measured as a function of pH (Table II), followed the order: pH 4 > pH 7 > pH 9 and C > CS > S thus, highlighting the potential of acidified C (at pH ≈ 4) in lowering $[F]$ from 5 to < 1.5 mg/L (i.e. below the permissible limit). In each case equilibrium F concentration ($[F]_{\text{equilibrium}}$) was doubled on increasing initial F concentration ($[F]_{\text{initial}}$) from 5 to 10 mg/L. Variations in $[F]_{\text{equilibrium}}$ as a function of shaking time were only marginal (at 5% level of significance) and largely followed the order:

At pH ≈ 4 : 1 h values \approx 6 hrs. values < 3 hrs. values

At pH ≈ 7 and 9: 6 hrs. values > 1 h values > 3 hrs. values

Table III depicts the observed effects of chemical amendments on % F removal. It is clear that amended C significantly reduced $[F]_{\text{equilibrium}}$ in the order: Fe amended > Al amended > Ca amended. However, variation in $[F]_{\text{equilibrium}}$ as a function of amendment concentration were marginal (at 5% level of significance). Furthermore, chemical treatment of C altered its pH significantly. Fe amendment caused considerable decrease in pH of C as compared to Al amendment, while a slight increase in pH was noted when C was amended with Ca. Thus, the observed variations in % F removal by C amended with Al, Fe and Ca (Table III) may also be attributed to pH_{initial}.

TABLE II
F levels with respect to pH, $[F]_{\text{initial}}$ and shaking time for soil and its fractions

Sample type	$[F]_{\text{initial}}$ (mg/L)	$[F]_{\text{equilibrium}}$ (mg/L)		
		pH ≈ 4	pH ≈ 7	pH ≈ 9
CS	5	1.70 ^a	3.79 ^a	3.30 ^a
		2.16 ^b	3.00 ^b	2.80 ^b
		1.62 ^c	3.71 ^c	3.70 ^c
	10	3.60 ^a	7.49 ^a	7.20 ^a
		4.19 ^b	6.60 ^b	6.90 ^b
		3.82 ^c	7.51 ^c	8.00 ^c
S	5	2.17 ^a	4.00 ^a	3.50 ^a
		2.52 ^b	3.67 ^b	4.32 ^b
		2.30 ^c	4.02 ^c	3.91 ^c
	10	3.97 ^a	8.40 ^a	7.90 ^a
		4.62 ^b	7.77 ^b	7.90 ^b
		4.20 ^c	8.42 ^c	8.51 ^c
C	5	0.38 ^a	3.20 ^a	3.00 ^a
		1.04 ^b	2.30 ^b	2.80 ^b
		0.91 ^c	3.50 ^c	3.70 ^c
	10	1.60 ^a	6.60 ^a	6.50 ^a
		2.04 ^b	5.80 ^b	6.50 ^b
		1.81 ^c	6.80 ^c	7.90 ^c

^a60, ^b180, ^c360 minutes

TABLE III
F levels and accompanying pH changes by unamended/amended C Clay amount, 100g/L; $[F]_{\text{initial}} = 10$ mg/L; shaking time, 60 min; temperature, 30 ± 2 °C

Sample type	pH		$[F]$	
	Initial pH	Equilibrium pH	$[F]_{\text{equilibrium}}$	% removal
C	8.20	7.84	7.1	25
Al ₁	7.63	---	2.1	78
Al ₂	7.60	7.99	1.0	90
Al ₃	7.43	7.49	0.62	94
Ca ₁	8.13	8.18	6.5	32
Ca ₂	8.19	8.23	5.2	45
Ca ₃	8.32	8.30	4.6	52
Fe ₁	3.08	3.23	0.20	98
Fe ₂	2.91	2.91	0.44	95
Fe ₃	2.66	2.72	0.57	94

Fe additions to C significantly decreased its pH which was possibly due to the formation of various hydrolysed species viz. FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, and $\text{Fe}(\text{OH})_3^0$ [4-5]. Enhanced F removal by Fe amended C was possibly due to formation of fluoro-complexes (viz. FeF^{2+} , FeF_2^+ , and FeF_3^0) at acidic pH and interaction of F with precipitated hydroxides at high pH. Ca additions to C raised its pH slightly, probably by neutralizing the residual acidity of C by replacing H^+ ions from colloidal complexes. Precipitation of fluorite (CaF_2) and fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) at pH 5.5 - 7.0 and > 4.9, respectively, are probably responsible for F

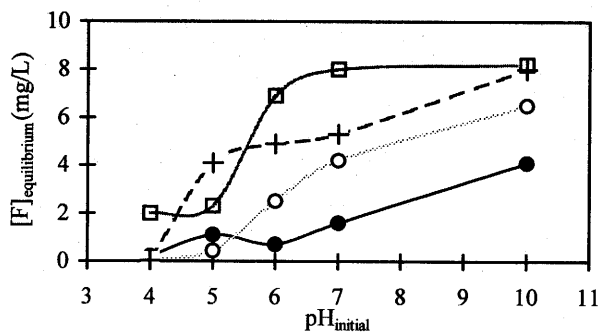


Fig. 1 Variation in $[F]_{\text{equilibrium}}$ with $\text{pH}_{\text{initial}}$ for amended C as a function of pH; C amount, 100 g/L; $[F]_{\text{initial}}$, 10 mg/L; shaking time, 60 min; temperature, $30 \pm 2^\circ\text{C}$ (Al_1 : \bullet ; Fe_1 : \circ ; Ca_1 : $+$; C: \square)

removal by Ca amended C [6]. The possibility of CaF_2 formation by reaction of F with soluble or exchangeable Ca present in soil at near neutral pH has been reported by some workers [7-8]. Significant F removal was also noted by Al amended C which may be attributed to ion exchange phenomenon [9].

Fig. 1 depicts the variations of $[F]_{\text{equilibrium}}$ with pH and suggests that F level in liquid phase remain within permissible limit on using sample type (i) Fe_1 at $\text{pH} < 6$ (ii) Al_1 at $\text{pH} < 7$, and (iii) Ca_1 at $\text{pH} < 5$. In general, $[F]_{\text{equilibrium}}$ increased with pH which may be due to the existence of an hydroxyl envelope on solid particles causing negative surface charge, which would effectively repel F from the sorption sites and simultaneously compete with them [10]. Table IV depicts F sorption data at $\text{pH} \sim 6$ employing Al_1 , Fe_1 , Ca_1 and C as a function of initial F concentration.

TABLE IV

F levels (mg/L) and accompanying pH changes as a function of $[F]_{\text{initial}}$; Sorbent amount = 100 g/L; shaking time = 60 min; temperature = $30 \pm 2^\circ\text{C}$.

	$[F]_{\text{initial}}$ (mg/L)				
	2.5	5	10	15	25
Al_1					
$\text{pH}_{\text{initial}}$	6.08	6.36	6.22	6.20	6.08
$\text{pH}_{\text{equilibrium}}$	6.99	7.51	7.50	7.08	7.29
$F_{\text{equilibrium}}$	0.58	0.78	1.50	2.10	4.90
Fe_1					
$\text{pH}_{\text{initial}}$	6.23	6.04	6.23	6.07	6.32
$\text{pH}_{\text{equilibrium}}$	5.70	7.64	7.75	7.12	7.60
$F_{\text{equilibrium}}$	1.20	0.73	1.20	2.90	3.90
Ca_1					
$\text{pH}_{\text{initial}}$	6.22	6.14	6.38	6.33	6.38
$\text{pH}_{\text{equilibrium}}$	7.51	7.52	7.42	7.56	7.58
$F_{\text{equilibrium}}$	1.70	2.70	4.90	7.40	13
C					
$\text{pH}_{\text{initial}}$	6.27	6.33	6.33	6.32	6.40
$\text{pH}_{\text{equilibrium}}$	7.11	7.06	7.25	7.37	6.70
$F_{\text{equilibrium}}$	1.80	3.10	6.40	9.60	18

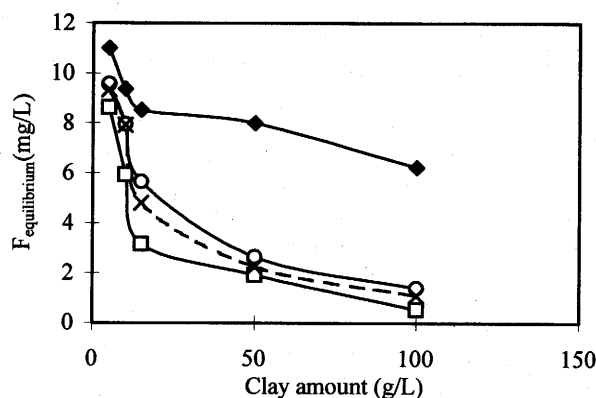


Fig. 2 Variation in $[F]_{\text{equilibrium}}$ with clay amount for amended/unamended C (refer Table 1 for sample type); $[F]_{\text{initial}}$, 10 mg/L; shaking time, 60 min; temperature, $30 \pm 2^\circ\text{C}$ (C: \blacklozenge ; C_1 : \square ; C_2 : \circ ; C_3 : \times)

Studies conducted hitherto required pH adjustment of amended C before F sorption for improved water defluoridation. This may not be feasible at the end user level. Considering this, and also that pH of potable waters should lie between 6.5 - 8.5 [1] further studies were conducted on amended C, adjusted to pH 6-7 during incubation of the C sample. Fig. 2 depicts variation of $[F]_{\text{equilibrium}}$ with C amount. It is clear that the use of C_1 , C_2 and C_3 , at silty clay: solution 100 g/L, lowered $[F]_{\text{equilibrium}}$ below 1.5 mg/L. On the other hand, for C the $[F]_{\text{equilibrium}}$ was 6.2 mg/L. The observed variations in $[F]_{\text{equilibrium}}$ (mg/L) were: C (11 - 6.2) > C_2 (9.6 - 1.4) > C_3 (9.3 - 1.1) > C_1 (8.6 - 0.5). The F sorbed was positively correlated with C, C_1 , C_2 , and C_3 ($r = 0.93, 0.86, 0.92$ and 0.90 ; $p < 0.05$, respectively). The results showed C_1 to be the most potent sorbent for F. Rapid and enhanced F removal by C_1 was probably due to interaction of F with charged groups mainly, polymeric metal hydroxo species on C surfaces, and fluorite precipitation.

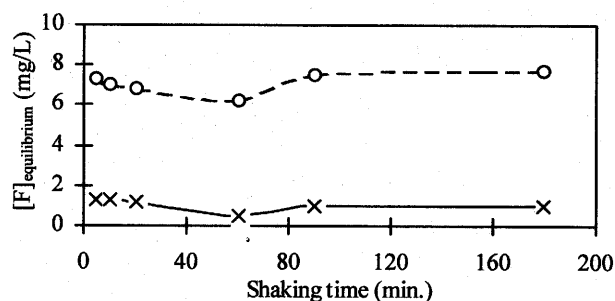


Fig. 3. Variation in $[F]_{\text{equilibrium}}$ with shaking time for amended/unamended C; C_1 (50 mg each of Al + Fe + Ca/g S); C (control); $[F]_{\text{initial}}$, 10 mg/L; C amount, 100 g/L; temperature, $30 \pm 2^\circ\text{C}$ (C_1 : \times ; C: \circ)

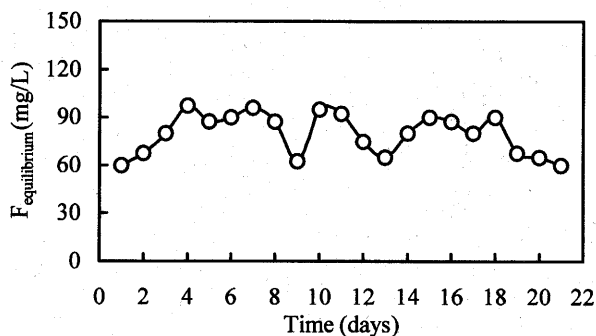


Fig. 4 Plot of $[F]_{\text{equilibrium}}$ vs. time for earthenware pot at $[F]_{\text{initial}}$, 150 mg/L

Fig. 3 illustrates the variation of $[F]_{\text{equilibrium}}$ with shaking time for C_1 and C. Rapid and significant sorption of F by C_1 was evident as compared to C. In both cases constancy in F sorption data was observed, however, a maxima in F sorption was noted at 1 h.

Fig. 4 depicts results of three weeks F sorption studies from the stored water ($[F] = 150$ mg/L) by clay vessels as a function of time. After 12 hrs. $[F]_{\text{equilibrium}}$ in water is lowered substantially from 150 mg/L to 60 mg/L. However, the values fluctuated in next 20 days but at the end of 21 days $[F]$ levels were significantly reduced to 60 mg/L. These fluctuations in $[F]_{\text{equilibrium}}$ values are probably indicative of very low attainment of equilibrium, which might be due to the competitive sorption and desorption occurring simultaneously.

IV. Conclusions

The present study clearly highlights the significant potential of clay vessels for F removal from stored water. Amending C with 50 mg/g each of Al, Fe and Ca significantly improved its F sorption capacity. Therefore, adding a calculated quantity of F free salts of activated Al_2O_3 , $FeCl_3$ and $CaCO_3$ in the clay rich soil during fabrication of vessels, might enhance the F removal capacity of conventionally used clay vessels (pots) considerably.

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