A RAPID METHOD FOR THE DEFLUORIDATION OF FLUORIDE-RICH DRINKING WATERS AT VILLAGE LEVEL

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Many water supply schemes. particularly in developing countries where dug wells form the major water source, contain excess fluorides normally detrimental to dental health. A simple and inexpensive method of defluoridating these fluoride-rich waters was required and it was found that kaolinitic clay forms a suitable raw material in the defluoridation process. Fluoride adsorption and desorption reactions in clay were investigated. At equal concentrations of total fluoride in solution, fluoride retention was greatest at pH = 5.6 and decreased both at low and high pH. Fluoride sorption conformed to both Langmuir and Freundlich isotherms over the entire range of fluoride concentrations (5–25 ppm). However, fluoride desorption conformed only to the Freundlich isotherm. These properties make it possible for the use of kaolinitic clay as defluoridating material to be used in potable water supplies at village levels.

KEY WORDS: Drinking water. fluoride, village, fluorosis.

INTRODUCTION

Several attempts[1-3] have been made to determine the relationship between the occurrence of dental fluorosis, the prevalence of dental caries and fluoride contents of potable waters in Sri Lanka. Fluoride at optimum concentrations (WHO recommended level 1 ppm) prevents dental caries, whereas high concentrations of fluoride in drinking water (generally greater than 1.50 ppm) is detrimental to health. During the past few years, the general public has become aware of the effects of fluoride in water on human health and the need to defluoridate fluoride-rich waters has caused much concern. It has also been noted that in addition to the fluoride levels in drinking water, climatic conditions may also influence the prevalence of dental fluorosis at the community level.[4]

However, water treatment for removal of fluorides is not generally simple and inexpensive. Several methods[5-7] have been suggested for the defluoridation of fluoride-rich waters and these may be broadly divided into two types:

A) those based on ion–exchange and chemical precipitation, and

B) those based on the addition of chemicals for precipitation or adsorption.

The availability of inexpensive and effective materials for the removal of excessive fluorides from potable waters at village levels would undoubtedly be a boon to the public health worker. Kaolinitic clay has often been considered as such a material and it has been studied previously[8,9] for its fluoride adsorption/desorption particularly in agricultural chemistry.

The objective of this investigation is to examine the capacity of kaolinitic clays to trap the excess fluoride in the water so that the water could be defluoridated to reach

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the optimum level that would be extremely beneficial to the dental health of communities. It must be noted that even though there are many methods now available for the defluoridation of water, nearly all of these are expensive and only suitable for large central water supply schemes. This investigation, therefore, is aimed at providing a simple technique that could be used at community level, particularly in developing countries as exemplified by Sri Lanka.

EXPERIMENTAL

The clay samples used for the present study were collected from the kaolinite region at Pussellawa in the Highlands of Sri Lanka. There is an abundance of this raw material in Sri Lanka and hence suits the objective of this study. The samples were air dried and the powdered material passing through the +230 mesh used for the study.

Preliminary studies were carried out in order to estimate the equilibration time that is required for the fluoride–clay adsorption process. One gram of clay was mixed with 20 ml of 10 ppm fluoride and the fluoride ion concentration was closely monitored for 12 hours, the measurements being carried out on the supernatant solution. An equilibration time of 12 h was found to be satisfactory since the adsorption process was completed during this time interval.

In order to determine the effect of pH on fluoride–clay complex, the acidity of 10 ppm fluoride solutions added to clay was adjusted to pH (3.0–8.5) with buffered solution (NaOAC/HOAC and $NaH_2PO_4Na_2HPO_4$). It was noted, that a pH of 5.6 was the optimum for the maximum fluoride–clay adsorption process. In all other studies, the fluoride solutions were buffered to a pH of 5.6 so as to obtain the optimum conditions.

The fluoride adsorption isotherms were obtained using five standard solutions of concentration range of 5–25 ppm of F.

Twenty millilitres of each solution was mixed with 1 g of the clay and shaken for 30 min at room temperature and allowed to stand for 12 hours. Adsorption curves were also obtained using fluoride made up in various NaCl solutions to determine the effect of monovalent ions.

Desorption experiments were carried out using 1% (W/v) NaOH. One gram of fluoride–clay complex was shaken with 20 ml of NaOH and kept for 24 hours.

Measurements of fluoride ions were carried out by the use of fluoride specific ion electrode (Orion model no. 94/09/00) single junction reference electrode (Orion model 90/01/00) and Orion Ionalayzer (model 470A).

RESULTS AND DISCUSSION

Figure 1 shows the plot of the fluoride adsorped with time. The time required to attain an apparent equilibrium between fluoride ions in liquid and solid phases was very rapid, 95% of F adsorption occurring within the first 30 min and 97% within 6 h. As shown in Figure 2, it was observed that the retention of fluoride was greatest at about pH 5.6, the fluoride levels decreasing both at high and at low pH values. Thus, for a given level of fluoride retention, the concentration of fluoride in the solution tended to be high at both low and at high pH. The decreased adsorption at low pH appeared to have been caused by the formation of complexes between fluoride and the cations (e.g. Al) formed in solution.[10] The changes in the fluoride species present
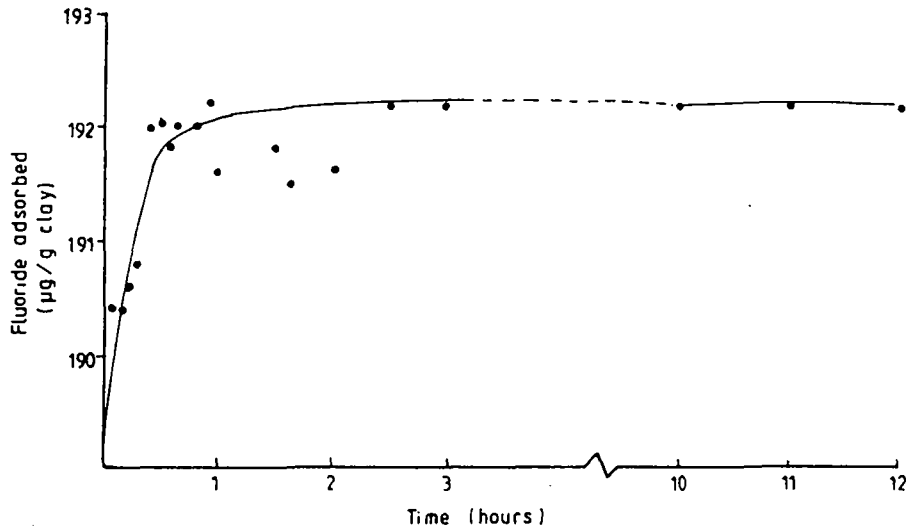
Figure 1 Effect of time on the retention of fluoride with clay.

due to the dissociation of the acid HF, have only a minor effect because dissociation is virtually completed at a pH about 5.0.[11] As a result, only a small proportion of the total fluoride in solution was present as fluoride ions. At equal concentrations of fluoride ions, fluoride retention decreased with increasing pH. This effect is caused by the increasingly unfavourable electrostatic potential. The change in electrostatic potential with pH for fluoride is shown in Figure 3 and has been compared with that of phosphate. It may be shown that the closer the plane of adsorption of the ion to the
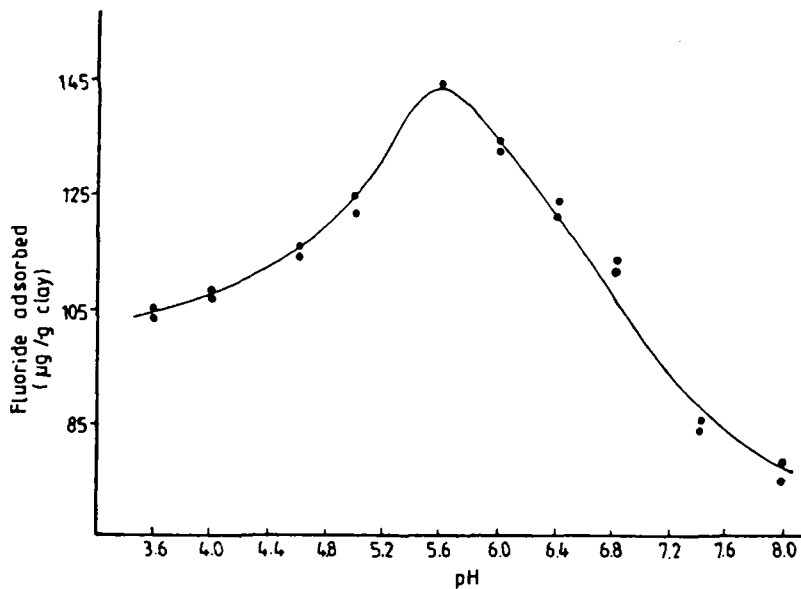

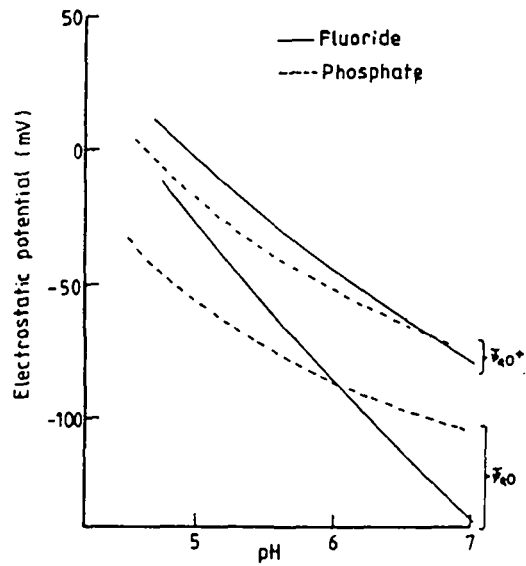**Figure 2** Adsorption of fluoride on clay in relation to pH variations.

Figure 3   The effect of pH on mean electrostatic potential ($\bar{\psi}$ao) and for the mean plus one standard deviation (σ). Analogous values obtained for phosphate are also shown. (After Barrow.[12])
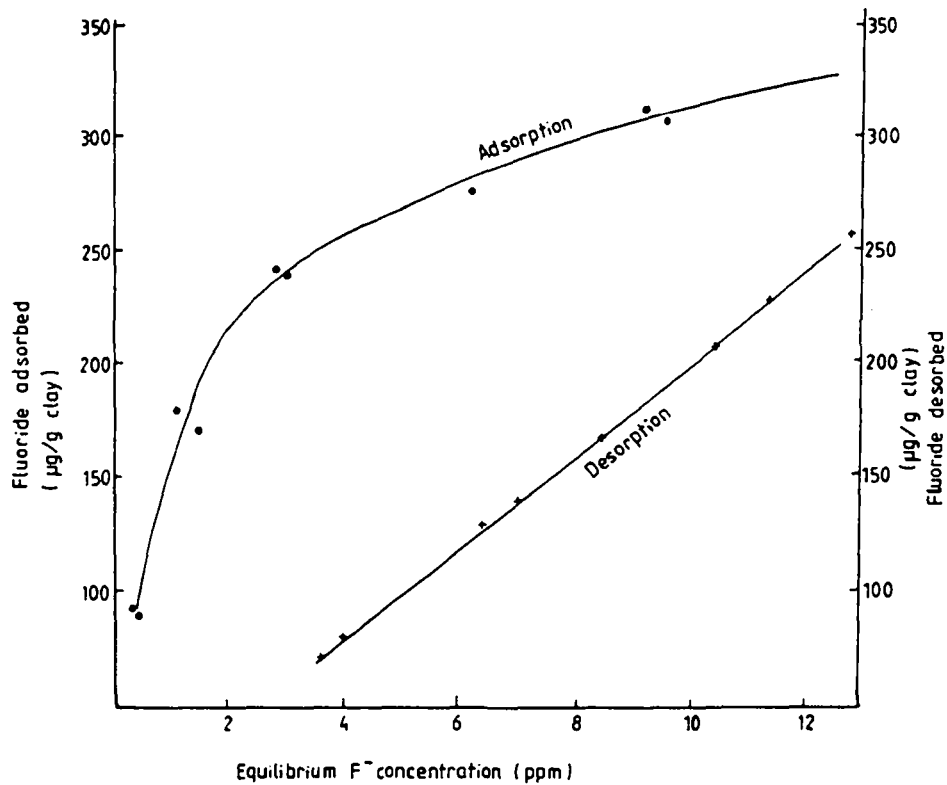

Figure 4   Fluoride adsorption/desorption in relation to the equilibrium fluoride ion concentration.

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plane of adsorption of H+ and OH− ions, the greater the change in the potential of the plane of adsorption with change in pH (Figure 3). This fact is consistent with both the size of the fluoride ion and the tendency of fluoride ions to displace OH− ions.[12]

The adsorption and desorption curves for fluoride on clay are shown in Figure 4. Stoichiometric release of OH^- from kaolinite by F^- has been reported by Dickman and Bray,[13] who concluded that F is replacing the hydroxyl ions found in the clay. Earlier studies[14-16] have shown that with the degradation of the mineral structure, Al is released into the solution from phyllosilicate clays and amorphous aluminium hydroxy oxides, with the concomitant entry of fluoride into the mineral structure. The formation of cryolite (Na_3AlF_6) after treatment of clay minerals with F^- also supported the idea that F^- did not simply replace OH^- in the lattice, but actually decomposed it.[17,18] Fluoride adsorption conformed to both Langmuir and Freundlich isotherms over the entire initial F concentration range for the clay (Figures 5 and 6). Desorption of F by 1% (w/v) NaOH conformed only to the Freundlich isotherm for the clay. It is important to note that while these isotherms are used for comparisons between soils and clays, and as predictive tools, they cannot be used to determine reaction mechanisms.

In comparing the Freundlich isotherm for adsorption and desorption, the data
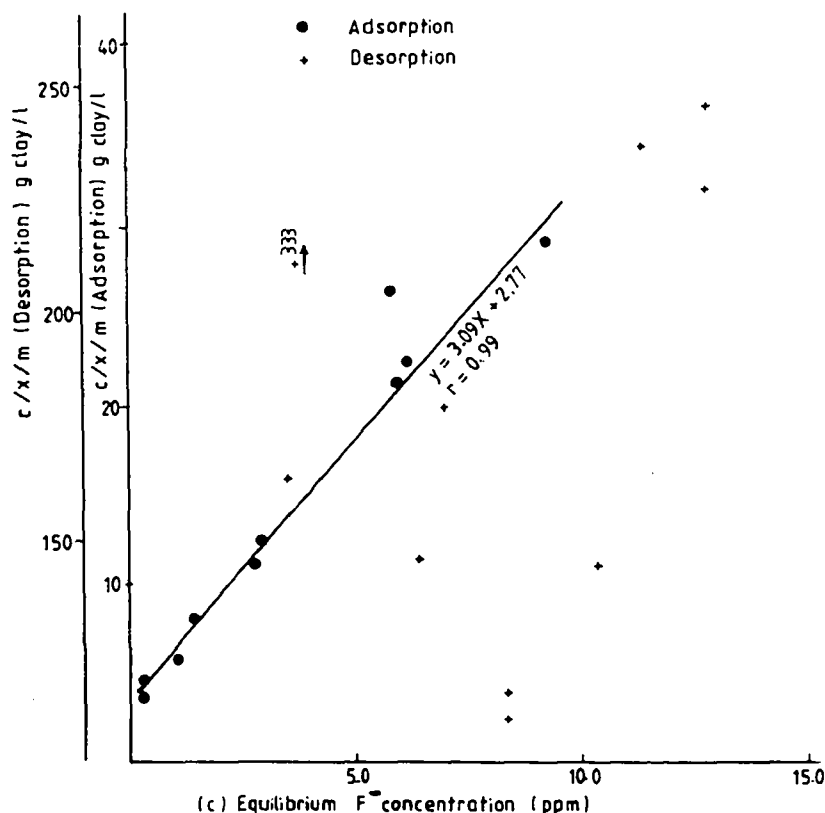

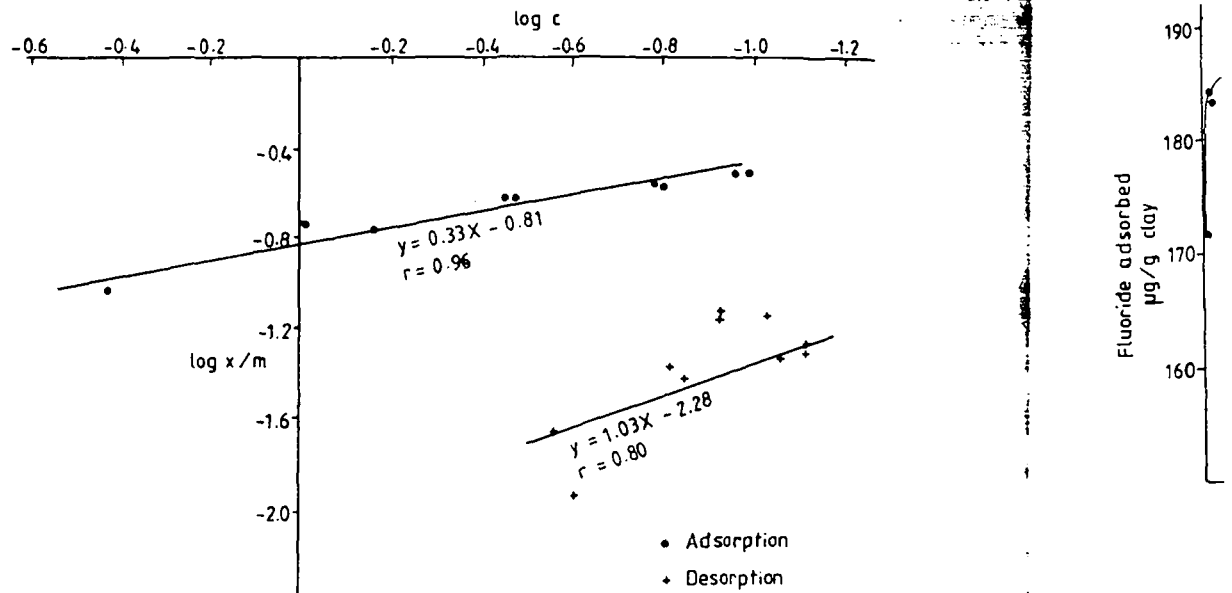Figure 5   Langmuir isotherms of fluoride for (i) adsorption, (ii) desorption.

Figure 6   Freundlich isotherms of fluoride for (i) adsorption, (ii) desorption.

points for fluoride desorption did not fall on the line plotted for fluoride adsorption, indicating possible hysteresis. Fluoride adsorption has previously been found to be reversible in acid soils and hysteretic in calcareous soil.[19] Reversibility of fluoride adsorption on geothite and gibbsite has been explained by the fact that fluoride forms only monodentate bonds with an adsorbent.[20] The hysteretic behaviour suggests that the mechanism of F sorption on clays is more complex than a simple monodentate ligand exchange reaction. Furthermore, the partial desorption of F^- from 1% (w/v) NaOH solution is explained due to $OH^- \rightleftharpoons F^-$ exchange phenomena and it further suggests the possible occurrence of F-clay complexes that cannot be desorped easily.

The concentration of the salts present in the solution affects the concentration of fluoride absorbed onto clay. Figure 7 shows the variation of fluoride adsorbed with NaCl concentration. It can be seen that the resulting graph has a very steep rise up to 0.1M NaCl concentration. However, a downward shift was observed at much higher solute levels. As the concentration of NaCl increases, the double layer contracts in the same way as the atomic number of monovalent cations increases the fraction of charge that was balanced by cations in the Stern layer would increase.[21] In both cases, repulsion of the fluoride ion from the surface would be decreased, and the surface electrostatic potential would now be more favourable for adsorption. Several studies[22,23] have shown, an increase in pH as a result of fluoride adsorption, ascribed to the replacement of OH^- by F^-. It appears that the increase of fluoride concentration associated with the increase in soil exchangeable sodium level is caused by increased displacement of adsorped F^- with OH^- ions from solution.[24] The higher concentration of soluble F^- with exchangeable sodium content in soils is also favoured by the presence of excess sodium which forms NaF, one of the most soluble fluoride compounds.
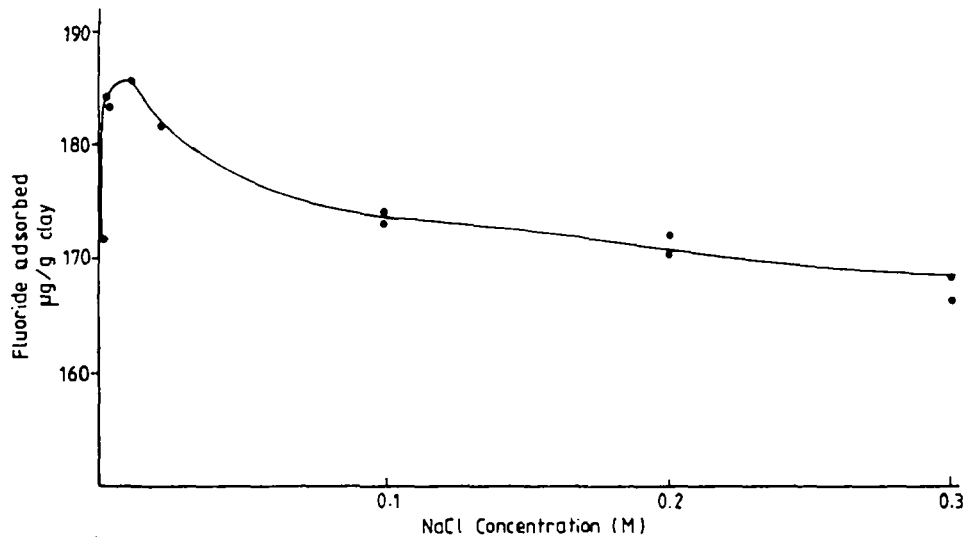
Figure 7 Fluoride adsorption on clay as a function of solute concentration.

POSSIBLE APPLICATION FOR DEFLUORIDATION OF WATER AT VILLAGE LEVEL

The results of this study, together with those reported previously[25,26] make it possible to outline preliminary guidelines regarding the defluoridation of water at village level. The excess fluoride in water can be efficiently removed by the use of natural clays in the kaolinitic region of Sri Lanka. The pH of 5–6 and the specific conductivity of 490 μS should be maintained to maximize the adsorption. A 10 ppm fluoride containing natural water sample has been brought down to values below the maximum permissible level of 1 ppm F by simply mixing with the clay. The following water quality variations were noted (Table I). It should be noted that, however, the fluoride removal capacity of clay will be reduced at higher conductivity levels (>2100 μS). The addition of calcium fluoride seeds accelerated the precipitation of calcium fluoride considerably and improves the fluoride removal efficiency.[25]

Table I

Parameter	Well water[a] (untreated)	Well water (treated with clay)		
		8 hours	24 hours	32 hours
pH (units) at 298K	6.70	6.55	5.90	6.30
Specific conductivity (s)	160	120	118	118
Total alkalinity (as $CaCO_3$ mmol/l)	0.636	0.410	0.370	0.318
F^- (ppm)	10.05	0.95	0.85	0.80
Cl^- (ppm)	15.0	17.5	16.3	16.3

[a] Location: Kandy.

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