FLUORIDE SORPTION ISOTHERM ON FIRED CLAY

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SUMMARY: The present study assesses the fluoride-binding capacity of ordinary potters clay, calcined at 600°C and subsequently crushed. Fluoride solutions at concentrations ranging from 12.5 to 1,600 mg-F/L were added to the clay, w/v ratio 1:10. Fluoride concentration was measured after 1 h, 6 h, 24 h, 5 days and 10 days of contact. Based on the registered maximum values for fluoride adsorption in the various solutions, fluoride-binding capacities were calculated. A linear relation was found between the fluoride uptake and the fluoride concentration in solution at equilibrium, in logarithmic values. This is according to Freundlich's formula: $\ln f = \ln \alpha + 1/\beta \ln S \Rightarrow \ln f = -1.12 + 0.589 \ln S$, where f is fluoride uptake (mg-F/g) and S is the fluoride concentration in solution at equilibrium (mg-F/L). Correlation coefficient (r^2) for this relation was 0.991, p-value < 0.001. This indicates that adsorption is a major factor in the fluoride-binding process.

Key words: Defluoridation, potters clay, activated clay, fluoride, adsorption, Freundlich

INTRODUCTION

Due to high fluoride content of drinking waters, fluorosis is endemic in many developing countries[1-4], and simple low cost methods for defluoridation of water are urgently needed[5]. World Health Organization has, for more than 20 years, given this purpose high priority. A number of methods have been developed[6], but so far the ideal method for home-based fluoride removal from drinking water has not been found.

TABLE 1. Composition of potter's clay #1106 given as oxides of elements

SiO_2	58,0 %
Al_2O_3	30,0 %
K_2O	1,2 %
Fe_2O_3	1,0 %
TiO_2	0,9 %
Na_2O	0,6 %
CaO	0,3 %
MgO	0,3 %
Igneous loss	8,0 %

Calcined clay, "ceramics", is frequently used for water purification[7]. Highly sophisticated ceramic water filters are available, but simple pottery may also be used, e.g. for the removal of fluoride in water. Various researchers have tested the fluoride-binding capacity of clay and have come up with rather different results[8,9]. The general conclusion has been, however, that the physico-chemical processes involved are too slow, and that the fluoride-binding capacity of clay is too low for practical water defluoridation purposes[10].

New research has aroused new interest in clayware as a defluoridating agent. Thus Hauge et al[11], have shown that the fluoride-binding capacity of clay decrease with increasing calcination temperatures. When temperatures, however, were maintained at 600-700 °C, encouraging results were obtained. The main components of clay are oxygen, silica, and aluminum. But clay is a very heterogeneous material, and various clay-types may have strikingly different physical and chemical properties. Also the fluoride binding capacities show great variations[8,9,12].

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The aim of the present study was to assess the fluoride-binding capacity of ordinary potter's clay, calcined at 600 ^{O}C, when exposed to fluoride solutions of different concentrations.

MATERIALS AND METHODS

Fluoride solutions. A fluoride solution of 1.6 g-F/L was made by dissolving NaF in de-ionized distilled water (3.537 g NaF/L). Solutions of 800, 400, 200, 100, 50, 25, 12.5 mg-F/L were subsequently made by sequential dilution with de-ionized distilled water.

Clay. Ordinary potter's clay (1106 White St Thomas body) was used for the experiments. The composition of the clay, according to the manufacturer (Pot Clay Ltd, Stoke-on-Trent, UK), is given in Table 1.

TABLE 2. Fluoride concentration* (mg-F/L) in different solutions after exposure to fired clay

	Concentration after				
0 h	**1 h**	**6 h**	**24 h**	**5 days**	**10 days**
1600	1327	1270	1270	1140	1150
800	700	635	581	471	460
400	356	327	287	234	230
200	166	144	115	90.7	87.6
100	78.6	65.6	49.2	38.2	36.7
50	34.7	30.9	24	18.1	16.9
25	17.7	16.7	10.6	6.5	5.7
12.5	9.1	8.2	5.1	2.1	17

* mean of three samples

Dry clay was calcined in an electrical furnace, at 600 ^{O}C, for 3 hours. The calcined clay was crushed and sieved. Particles <1.0 mm and >3.0 mm were discarded. Twenty-four ten-gram samples of crushed clay were prepared. The individual samples were placed in capped plastic bottles, and 100 ml fluoride solution (w/v ratio 1:10) was added to each bottle. Three parallel samples were prepared with each fluoride concentration. The experiment were carried out at room temperature (21 ^{O}C). Test-samples of 3 ml were taken from each bottle for fluoride analyses after 1 h, 6 h, 24 h, 5 days, and 10 days. The fluoride concentration was determined with a fluoride-ion specific electrode (model 96 09 00; Orion Research, Cambridge, Mass., USA), with total ionic strength adjustment buffer (TISAB III) added to the solution as recommended by the manufacturer[13]. The lower detection limit was 10^{-6} M, ~ 0.02 mg-F/L[13].

RESULTS AND DISCUSSION

The experiment showed that the fluoride adsorption in the different solutions increased with increasing time. For all concentrations the equilibrium seemed to be established within 10 days, as shown in Table 2.

The registered maximum values for fluoride adsorption in the various solutions (most often 10-day results) were used for calculating "fluoride binding capacities", as shown in Table 3.

Adsorption is defined as a process in which molecules adhere to the surface of a solid. In ordinary physical adsorption, the molecules are held to the surface of the adsorbent by Van der Waal's forces. However, the physico-chemical reactions taking place between clay and fluoride in solution is not known in detail. According to Freundlich's adsorption isotherm[14], a linear relation exists between the fluoride uptake and fluoride concentration in a solution at equilibrium, in logarithmic values. This is in harmony with our findings, shown in Figure 1. The equation for Freundlich's adsorption isotherm is $\ln f = \ln \alpha + 1/\beta \ln S$, which when applied to potter's clay gives: $\ln f = -2.58 + 0.589 \ln S$, where f is fluoride uptake (mg-F/g) and S is the fluoride concentration in solution at equilibrium (mg-F/L). Correlation coefficient (r^2) for this relation was 0.991, p-value < 0.001. This indicates that adsorption is a major process in this reaction.

TABLE 3. Fluoride uptake in fired clay (mg-F/g)* after exposure to solutions with different fluoride concentrations

Fluoride concentration in the water at equilibrium S* (mg-F/L)	Fluoride concentration on the clay at equilibrium f* (mg-F/g-clay)
1,140	4.60
460	3.40
230	1.70
87.6	1.12
36.7	0.62
16.9	0.34
5.7	0.20
1.7	0.12

* calculated by the mean of three samples

Our study was carried out at room temperature. The rate of chemical reactions normally increases when the temperature increases. Faster reactions might therefore be expected in a hot climate, such as the African Rift Valley, were the simple home-based defluoridation techniques are most urgently needed.

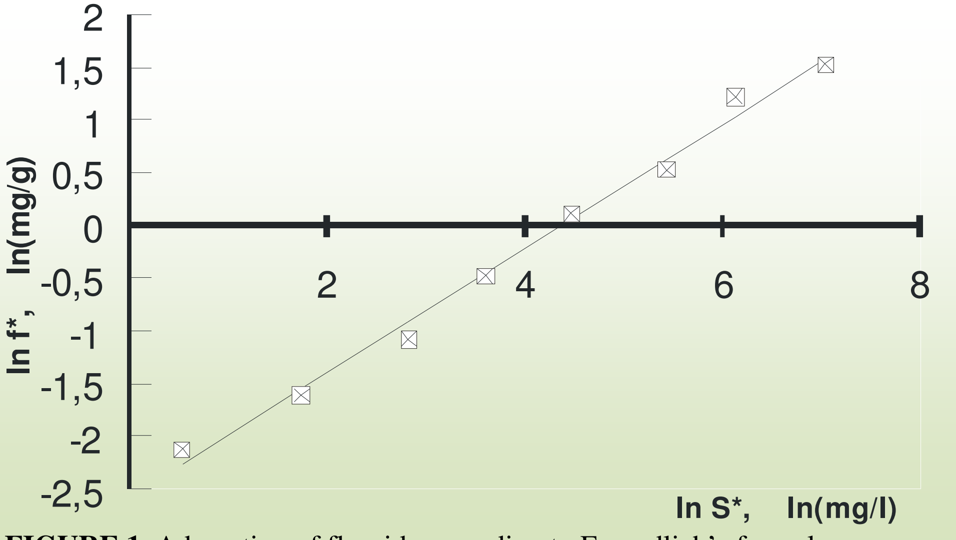

FIGURE 1. Adsorption of fluoride according to Freundlich's formula.

The fluoride binding capacity of clay depends on various factors, and can not be given as one quantity. In order to compare different types of clays, standard procedure for testing should be worked out.

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