Environmental Geology (1993) 21: 251–255

K. B. P. N. Jinadasa · C. B. Dissanayake · S. V. R. Weerasooriya · A. Senaratne

Adsorption of fluoride on goethite surfaces-implications on dental epidemiology

Received: 6 July 1992 / Revision received: 18 August 1992

Abstract Fluoride ion interaction with synthetically prepared goethite has been investigated over a range of pH values (4–9) and F^- concentrations (10^{-3}–10^{-5} M). The amount of F^- retained by goethite suspensions was found to be a function of pH, media ionic strength, F^- concentration, and goethite concentration. The lowest ionic strength (0.001 M KNO_3) gave the highest adsorption medium. Uptake was minimal at $pH > 7$ and increased with decreasing pH. Thermodynamic properties for fluoride adsorption at 298 K and 323 K were investigated. The isosteric heat of adsorption (ΔH_r) was calculated and the heterogeneity and homogeneity of the surface examined for goethite. In view of the importance of fluoride in dental health, the interaction of fluoride on goethite in the physical environment has important implications on dental epidemiology.

Key words Fluoride—Goethite-Dental epidemiology

Introduction

Fluoride is considered as an essential element, although dental health problems may arise either from a deficiency or an excess of fluorides. Many water supply schemes, particularly in developing countries where dug wells and tube wells form the major water source, contain excess fluorides harmful to dental health (Dissanayake 1991). Concentrations of fluorides in drinking water generally greater than 1.5 mg/l) are detrimental to health. Due to the fact that iron oxide minerals in soil have significant numbers of adsorption sites, extensive research has been carried out aimed at understanding adsorption phenomena on these minerals (Djafer and others 1991).

The mobility of any water-soluble fluoride introduced into soils or sediment by natural or industrial process, is influenced by the adsorption capacities of the solid phases and chemical interactions. The ability of soils to adsorb F^- from dilute solutions (milligrams per liter) has been well established (Bower and Hatcher 1967; Fluhler and others 1982; Gupta and others 1982) but views differ on the soil component(s) responsible for the reaction process. Pickering (1985) observed that the mobility of F^- tends to be a function of soil type, system pH, and F^- levels, with retention being favored in acidic sediments containing clays and poorly ordered hydrous oxides of aluminum.

While the majority of F^- ions added to soils tends to become firmly fixed, it has been shown in percolation studies that migration through a soil column can release soluble Al and Fe species (Polomski and others 1982). The geochemistry of F^- ion (ionic radius 1.36 Å) is similar to that of the OH^- ion (ionic radius 1.40 Å) and there can be easy exchange between them. Detailed research has been carried out on the fluoride–hydroxyl exchange in geological materials (Gillberg 1964; Stormer and Carmichael 1974; Munoz and Ludington 1974).

The main objectives of this study were to study the trapping capacity of fluoride on prepared goethite at various ionic strengths, media pH, and fluoride concentrations, and the surface characterization using thermodynamic properties.

Materials and methods

Preparation of goethite

Goethite was prepared synthetically according to Djafer and others (1989). The x-ray diffractometry and IR spectroscopy analysis confirmed the presence of goethite (α-FeOOH) and no other iron oxide was found. The

K. B. P. N. Jinadasa · C. B. Dissanayake · S. V. R. Weerasooriya
Department of Environmental Sciences, Institute of Fundamental Studies, Hantana, Kandy, Sri Lanka

A. Senaratne
Department of Geology, University of Peradeniya, Sri Lanka

Correspondence to: C. B. Dissanayake

sample had a BET nitrogen surface area of 34 m^2/g. The pH_{iep} (isoelectric point) of goethite at 25°C as determined as 9.2 by acid—base titrations using an autotitrator (model Metrohm 645 Multi-Dosimat/Dosigraph 625).

Fluoride adsorption on goethite

Solutions of sodium fluoride and potassium nitrate as supporting electrolytes were prepared just prior to use. Distilled, deionized water was used in all experiments. The first set of adsorption runs involved a survey of the adsorption characteristics of fluoride ions (10^{-4} M) on goethite (0.95 g/l) at different ionic strength conditions (0.001 M, 0.001 M and 0.1 M KNO_3). The required solutions of goethite and fluoride ion concentration were added to the distilled, deionized water in 50-ml plastic vessels. The ionic strength was adjusted using KNO_3. The suspension pH was adjusted, adding microamounts of acid (HNO_3) or base (KOH). The system was left to be continuously shaken overnight under a N_2 atmosphere. The following day, the equilibrated pH of the system was measured and the suspensions, contained in the plastic tubes, centrifuged to measure fluoride concentration. The effect of goethite concentration (0.95–9.5 g/l) on fluoride adsorption (5×10^{-4} M) at 10^{-2} M KNO_3 ionic strength was also measured, when the initial pH of the solution was 5.0. The fluoride ion concentration of the supernatant was determined in duplicate samples by a solid-state ion-selective electrode (Orion model 92-00) and a single-junction reference electrode (Orion model 90-00) using an expandable ion analyzer (Orion model EA 920).

Fluoride adsorption with temperature on goethite

In this experiment, fluoride adsorption on goethite (2.85 g/l) were studied at temperatures of 273 K and 323 K. Ionic strength of the media used was 10^{-2} M KNO_3 and initial pH was 5. Used Fluoride concentrations used were 10^{-5}, 4×10^{-5}, 8×10^{-5}, 10^{-4}, 4×10^{-4}, 8×10^{-4} and 10^{-3} M. After 24 h, the supernatant fluoride concentration was determined.

Results and discussion

Effect of pH and ionic strength on fluoride removal

Figure 1 shows the fluoride adsorption curves on goethite (α-FeOOH). Initially, fluoride removal was investigated for 10^{-4} M fluoride concentration at three ionic strengths (0.001, 0.01, and 0.1 M KNO_3) in the pH range of 4.0–10.0. Fluoride removal is clearly affected by pH of the solution, the percent removal decreasing with increasing pH. At pH > 7, no significant retention of F^- was detected. The highest adsorption of 66.3 percent was observed for the lowest ionic strength, 0.001 M KNO_3.

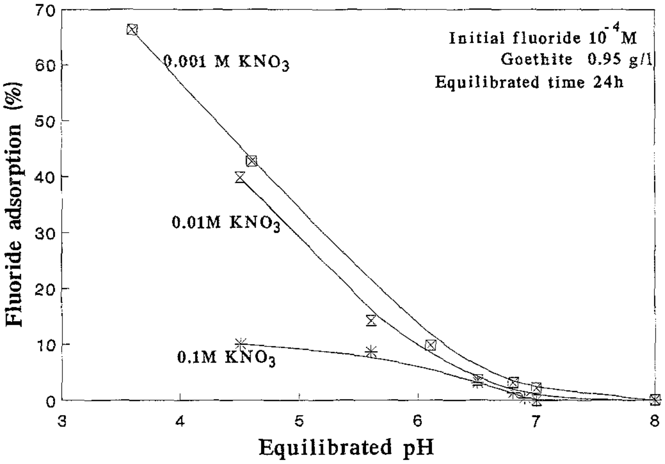

Fig. 1. Effect of pH and ionic strength on fluoride adsorption on goethite

Site-binding models are formulated around the assumption that the oxide–water interface is populated by surface hydroxyl groups, which act both as adsorption sites and as sources of surface charge development. Surface hydroxyl groups result from the hydrolysis of surface species that have unsatisfied coordination sites. These surface hydroxyl groups are amphoteric, that is they can act as either an acid or a base, by adsorbing or desorbing H^+ (Kent and others 1986). These oxide surfaces acquire electrical charges, which vary according to the pH of the solution. Important variable-charge constituents in the soil environment are the oxides of iron, aluminum, titanium, and manganese. The term "oxide" is used here to include oxy-hydroxides such as goethite (α-FeOOH). Adsorption of fluoride ions to α-FeOOH can be considered here as a surface complexation reaction between aqueous fluoride ions and hydroxyl-specific surface sites. In this study experiments were conducted above pH 4.

Amphoteric reactions at the goethite α-FeOOH surface

$$FeOH_2{}^+{}_{(s)} = FeOH_{(s)} + H^+{}_{(aq)}$$

$$FeOH_{(s)} = FeO^-{}_{(s)} + H^+{}_{(aq)}$$

where $FeOH_{(s)}$ represents a single protonated surface oxide site while $FeO^-{}_{(s)}$ and $FeOH^+{}_{(s)}$ refer to ionized surface functional groups. In addition, the surface sites can enter into complexation reactions with ions in solution:

$$Fe(OH)_{(s)} + M^{n+}/A^{n-}{}_{(aq)} + mH_2O_{(aq)}$$

$$= FeO\text{-}M(OH)_m{}^{(n-m-1)}{}_{(s)} + (m+1)H^+{}_{(aq)}$$

M or A represent cationic and anionic adsorbates, respectively and $M(OH)_m{}^{n-m-1}$ refers the hydrolytic species of the metal.

Thus the possible adsorption reactions of fluoride onto α-FeOOH are: