The removal of fluoride from aqueous solution by a lateritic soil adsorption: Kinetic and equilibrium studies

Analia Iriel[a],[*], Stijn P. Bruneel[b], Nahuel Schenone[a], Alicia Fernández Cirelli[a]

[a] Instituto de Investigaciones en Producción Animal / INPA(UBA-CONICET) / Centro de Estudios Transdisciplinarios del Agua (CETA), Facultad de Ciencias Veterinarias, Universidad de Buenos Aires, Av. Chorroarín 280, C1427CWO Buenos Aires, Argentina
[b] Laboratory of Environmental Toxicology and Aquatic Ecology, Department of Applied Ecology and Environmental Biology, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, Ghent, Belgium

ARTICLE INFO

ABSTRACT

The use of natural sorbents to remove fluoride from drinking water is a promising alternative because of its low-cost and easy implementation. In this article, fluoride adsorption on a latosol soil from Misiones province (Argentina) was studied regarding kinetic and equilibrium aspects. Experiments were conducted in batch at room temperature under controlled conditions of pH 4–8) and ionic strength (1–10 mM KNO_3). Experimental data indicated that adsorption processes followed a PSO kinetic where initial rates have showed to be influenced by pH solution. The necessary time to reach an equilibrium state had resulted approximately 30 min. Equilibrium adsorption studies were performed at pH 8 which is similar to the natural groundwater. For that, fluoride adsorption data were successfully adjusted to Dubinin-Ataskhov model determining that the fluoride adsorption onto soil particles mainly followed a physical mechanism with a removal capacity of 0.48 mg g^{-1}. Finally, a natural groundwater was tested with laterite obtaining a reduction close to 30% from initial concentration and without changing significantly the physicochemical properties of the natural water. Therefore, it was concluded that the use of lateritic soils for fluoride removal is very promising on a domestic scale.

1. Introduction

The presence of toxic elements in soils and waterways constitutes an important environmental issue for the biodiversity of species and the modern human life. Fluoride is present in environmental matrixes such as water, soil and air due to both natural and anthropogenic activities (Ayoob and Gupta, 2006). Under natural conditions the fluoride presence in groundwater has its origin from the dissolution of surrounding geological materials (Borgnino et al., 2013; Hudson-Edwards and Archer, 2012). Also, anthropogenic activities such as the production of semiconductors and fertilizers, glass-manufacturing and metal-processing might however result in higher concentrations in industrial wastewater.

Fluoride uptake by humans and animals, mainly through drinking water, might have both positive and negative effects depending on the uptake doses. These are mostly associated with a lower occurrence of dental caries but also with osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, Alzheimer syndrome and thyroid disorder (Ayoob and Gupta, 2006; Harrison, 2005). Therefore the recommended maximum permissible amount of F$^-$ in drinking water is 1.5 mg L^{-1} (WHO, 2004). Consequently, several technologies are being continuously improved to defluoridation of drinking water. Recently Dhillon et al. (2017) published the latest advances in fluoride removal mentioning the advantages and disadvantages of the most popular techniques. Basically, membrane techniques as nanofiltration, reverse osmosis and electrodialysis are innovative but costly and skilled operators are required. On the contrary, ionic interchange, adsorption and precipitation methods are easy handling. Particularly, adsorption processes are an attractive technology due to its environmental friendly nature and its economic viability (Dhillon et al., 2017). In this sense, adsorption in activated alumina as shown as the most appropriate technologies to remove fluoride from drinking water (USEPA, 2003) due to its efficiency and low cost. However, some difficulties need to be overcome such as its reduced performance in the presence of coexisting ions and its dependency with the solution pH (Dhillon et al., 2017; Bhatnagar et al., 2011). Additionally, residual aluminium concentrations have been reported in treated water representing a risk to consumers (Chaudhary and Prasad, 2015). On a house scale, besides scientific and economic issues, also social and cultural facets of these new methods need to be addressed (Bundschuh et al., 2010). In this sense, natural materials have been shown to have more acceptation than sophisticated ones. Among low-cost materials, land and geological

---

material represent an interesting alternative as adsorbent to several kinds of pollutants. Particularly, laterite containing metal-oxides and hydroxides could have anionic adsorption features (Bundschuh et al., 2011). Previously, several researches have studied the use of lateritic soils with and without further treatments (basically thermal and acid-basic treatments) in order to improve both their structural and adsorptive properties (Gomoro et al., 2012; Maiti et al., 2011; Vithanage et al., 2012; Wang et al., 2002; Sarkar et al., 2006, Tor, 2006). Despite of the already present background of laterite adsorption studies in literature, most of them were carried out without the adjustment of both pH and ionic strength conditions. In addition, those experiments were the pH was considered were performed at pH values lower than the natural groundwater ones. However, adsorption processes are strongly affected by pH of solution due to electrostatic nature of the processes. In the same order, ionic strength solution has an effect on the ion activity as well as in the potential of adsorption plane. So, from our knowledge from the literature survey, there is no any study where the real capacity of laterite for fluoride removal has been determined in natural groundwater conditions. In this context, the aim of this work is to study the adsorption features of an inexpensive material naturally rich in iron to remove fluoride from groundwater under those solution conditions which are present in natural groundwater. Thus, our work attempt to investigate i) how the solution pH affects the fluoride uptake kinetics, ii) the changes in fluoride removal extension resultant from varying the ionic strength of solution, iii) the nature of the fluoride adsorption process onto soil particles and iv) the feasibility to use laterite for fluoride removal in natural groundwater.

2. Materials and methods

2.1. Reagents

All the reagents used here were of analytical grade and used without further purification. A stock solution of 1000 mg L^{-1} of fluoride was prepared by dissolving a quantity of 2.210 g NaF salt (Merck) in milliQ water (Millipore GmbH). From this, synthetic working solutions were prepared ranging from 1 to 50 mg L^{-1}. In order to set pH conditions, drops of both HNO$_3$ 1 M (Merck) and KOH 1 M (Cicarelli) were added, also ionic strength was set with a KNO$_3$ 1 M (Merck) solution. Particularly, concentrations of 1×10^{-3} M, 6×10^{-3} M and 1×10^{-2} M KNO$_3$ which correspond to conductivity values of 160, 810 and 1300 µS cm^{-1} respectively (Hanna, HI 255) were employed. The total ionic strength adjustment buffer (TISAB) solution was from TermOrion.

2.2. Groundwater

Groundwater samples were obtained from Buenos Aires province (Argentina) at S 34° 3′ 42″ O 60° 05′ 22″. Physicochemical characterization including pH, conductivity (mS cm^{-1}), alkalinity, Cl$^-$ (mg L^{-1}), NO$_3$$^-$ (mg L^{-1}), NO$_2$$^-$ (mg L^{-1}), SO$_4$$^{2-}$ (mg L^{-1}), F$^-$ (mg L^{-1}), total hardness as calcium carbonate (mg L^{-1}), NH$_4$$^+$ (mg L^{-1}), As (mg L^{-1}), Ca (mg L^{-1}), Fe (mg L^{-1}), Mn (mg L^{-1}), Mg (mg L^{-1}), K (mg L^{-1}) and Na (mg L^{-1}) was carried out according to APHA et al. (1995). Briefly, conductivity and pH were measured using a combined meter Hanna HI 255, alkalinity and total hardness were determined by titration as usual. Anionic compounds were analysed by ion Chromatography using a Dionex DX 100 chromatograph and minority and trace elements were evaluated by using an ICP-OES (Perkin Elmer, model 2000).

2.3. Soil

2.3.1. Physicochemical properties and chemical composition

Soil samples were collected in Misiones province, Argentina. Samples were taken within an interval of 5–20 cm of soil depth to avoid leaves and other organic matter contaminating the samples. These red soil samples, mainly oxisols, are characteristic of the Misiones region.

Moist samples were dried under forced air at room temperature for 24 h, followed by crushing and sieving through a 2 mm stainless steel sieve. For chemical characterization standardized methodologies were used. More specifically organic matter was determined by Walkley-Black technique (Nelson and Sommers, 1982); total nitrogen by Kjeldahl method (Bremner and Mulvaney, 1982); exchangeable ions by using Schollenberger and Dreibelbis method (Black et al., 1965); exchangeable acidity (calcium acetate method) and pH (in water 1:2.5 v/v). Texture was determined using the method described by Sheldrick and Wang (1993). The oxides of K, Na, Ca, Mg, Si, Fe and Al were estimated by inductively coupled plasma-mass spectrometry, ICP-MS (Agilent, 7500 series) measurements. For that, around 1 g of soil was digested with H$_2$O$_2$ and filtered (nylon, 0.45 µm). Calibration standards were prepared with a multi-element standard solution XXI (Merck) in a nitric acid media 2%v/v.

2.3.2. Point of zero charge

Point of zero charge (p$_{zc}$) is the pH where the surface charge is equal to zero. This parameter has a very important role in adsorption experiments (in connection with the solution pH) and it is characteristic from the adsorbent material. In this work p$_{zc}$ was estimated from potentiometric mass titration according to Bourikas et al. (2003). Briefly, it can be reached as the interception of the potentiometric curve of an electrolyte solution (blank) and the corresponding curves of different amounts of soil suspended in KNO$_3$. Initially, a small amount of base KOH was added to deprotonate surface sites (turning the surface negative) and then, the suspensions were titrated by adding small volumes of HNO$_3$ solution.

2.3.3. Structural soil analysis

Specific surface area and pore volume of soil samples were determined by using a single point Brunauer–Emmett–Teller (BET) method trough Micromeritics ASAP 2020 instrument (Brunauer et al., 1938). For that, around 3 g of soil were degassed at room temperature during 24 h prior to measurement, nitrogen bath temperature was 77.54 K and the equilibrium interval used was 30 s. The morphology and surface chemical analysis of lateritic soil were determined by scanning electron microscopy (SEM) with a FEG-SEM Zeiss Supra 55vp coupled with an energy dispersive X-ray analyzer (EDS) that provides a qualitative and semiquantitative composition of the sample surface.

2.4. Adsorption batch experiments

The soil was washed using milliQ water until a conductivity of < 20 µS cm^{-1} was reached. The purpose of this washing procedure was to reduce the amount of interfering ions and to raise the adsorption capacity. Batch experiments were conducted for determining the effect of contact time, adsorbent dosage, pH solution, ionic strength and initial concentration on the adsorption process. Firstly, the effect of contact time on fluoride adsorption was studied to determinate the necessary time to reach equilibrium conditions. For that, 400 mL of solution of 2.5 mg L^{-1} of fluoride was suspended with 1.6 g soil and maintained upon magnetic stirred during 24 h where suspensions samples were obtained at several times. Suspensions were maintained in agitation with a mechanical stirrer (300 rpm) at room temperature (23 ± 1 °C). Additionally, the effect of adsorbent doses was analysed taking different soil masses 1–10 g) with 50 mL of fluoride solution. In order to study the initial concentration effect, solutions ranging from 1 to 50 mg L^{-1} of fluoride were in contact with a soil mass in a ratio of 4 g per litre of solution. At the end, samples were taken and the soil particles were removed by using a centrifuge and a cellulose nitrate filter (0.45 µm) coupled to a syringe. For fluoride measurements a volume of the supernatant was diluted with the same volume of TISAB II buffer solution to adjust the ionic strength in all the samples. All experiments were carried out at constant ionic strength of 1 mM maintained with KNO$_3$ except where the effect of ionic strength was studied.