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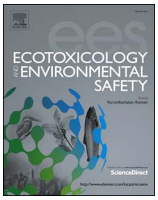

# The removal of fluoride from aqueous solution by a lateritic soil adsorption: Kinetic and equilibrium studies

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## 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

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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 $1 \times 10^{-3}$ M, $6 \times 10^{-3}$ M and $1 \times 10^{-2}$ 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 $H_2O_2$ 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.

Also, the pH was fixed to 8 excepting where the pH effect on the adsorption process was investigated. Solution pH was controlled by adding drops of $HNO_3$ or KOH solutions. The whole set of experiments were conducted in triplicate. Adsorption experiments with natural samples were studied without adjusting pH and ionic strength into the solution. Fluoride concentrations were determined with an ion selective electrode (ThermoOrion, model 0609) calibrated according to the standard methodology provided by the manufacturer. From these measurements the soil adsorption capacity for fluoride was calculated as:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where $C_0$ and Ce are both the fluoride concentration at initial and equilibrium time in the solution, respectively, expressed as $mg\,L^{-1}$, m is the soil mass (g) and V is the volume of the solution (L). In addition, the fluoride removal (%) by the soil was estimated as:

$$\text{Removal}\ (\%) = \frac{(C_0 – C_e)x100}{C_0} \tag{2}$$

## 2.5. Kinetic and adsorption isotherm models

### 2.5.1. Kinetic analysis

Kinetic models describing the reaction order of adsorption processes based in the capacity of the adsorbent including Lagergren's first-order equation (Bhattacharya and Venkobachar, 1984) and Ho´s second-order expression (Ho, 2006). In this sense, fluoride concentration values as a function of time were fitted to both pseudo-first-order (PFO) and pseudo-second-order (PSO) expressions in order to obtain the kinetic parameters from the adsorption process. The linear form of the PFO rate equation by Lagergren (Bhattacharya and Venkobachar, 1984) is given as:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{3}$$

where $k_1$ is the pseudo-first-order adsorption rate constant ($min^{-1}$), $q_e$ ($mg\,g^{-1}$) and $q_t$ ($mg\,g^{-1}$) were the quantity of fluoride adsorbed at the equilibrium and any time, respectively. Kinetic data were also tested by the PSO kinetic model described by Ho and McKay (1999) whose formula can be rewritten as (Ho, 2006):

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{4}$$

where $k_2$ is the pseudo-second-order sorption rate constant ($g\,mg^{-1}\,min^{-1}$), $q_e$ and $q_t$ were previously defined in the text. Plotting $\frac{t}{q_t}$ versus $t$ allows to determine both $q_e$ and $k_2$ from the slope and intercept respectively. Additionally, $k_2 {q_e}^2$ is the initial adsorption rate ($mg\,min^{-1}$).

### 2.5.2. Equilibrium studies

Equilibrium experiments were carried out at pH 8 by varying the fluoride concentration between 1 to 50 $mg\,L^{-1}$ with an adsorbent dose of 4 $g\,L^{-1}$ and contact time of 1 h. After that, fluoride concentration was evaluated in the supernatant and the adsorbed quantity was calculated from Eq. (1). In order determine the equilibrium adsorption parameters, obtained data were adjusted to Langmuir, Freundlich and Dubinin-Astakhov (D-A) models. The Langmuir model assumes that adsorption takes place on homogeneous sites of the solid and that only monolayer formation occurs (Langmuir, 1918). The relation between the adsorbed fluoride quantity and equilibrium concentration of the solution can be written in its linearized form as:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e} \tag{5}$$

where $Q_0$ represents the maximum coverage capacity of the monolayer ($mg\,g^{-1}$) when saturation is obtained and $K_L$ represents the constant related to the adsorption process ($L\,mg^{-1}$), more specifically it quantifies the affinity between the sorbent and the sorbate. $C_e$ and $q_e$ were previously defined in this study. Equilibrium data was also subjected to the Freundlich isotherm model which considers a heterogeneous sorption surface and active sites with different energies (Freundlich, 1906). The linear form of the exponential equation describing the isotherm is given by Eq. (6):

$$\ln q_e = \ln k_F + \frac{1}{n} C_e \tag{6}$$

where $k_F$ and $1/n$ are dimensionless isotherm constants representing the adsorption capacity and the adsorption intensity, respectively. If $1/n > 1$ the bond energy decreases with surface density, if it is $< 1$ then bond energy increases with surface density and if $1/n = 1$ then all sites at the surface are equivalent. Additionally, the D-A model, based on the concept of the potential theory of Polanyi (Inglezakis, 2007), was utilized to determine the nature (physical or chemical) of the adsorption process. D-A model equations have the advantages to including sorbent properties, temperature and the energy associated with the adsorption process. So, the amount of fluoride adsorbed in the soil under equilibrium conditions can be described as:

$$\ln q = ln q_0 - \left(\frac{1}{\sqrt{2}E}\right)^n \cdot \left[RTln\left(1 + \frac{1}{Ce}\right)\right]^n \tag{7}$$

where E (j/mol) is the adsorption energy, the heterogeneity parameter (n) and $q_0$ ($mg\,g^{-1}$) the maximum mass adsorbed species per unit mass of sorbent. Additionally, R is the universal gas constant ($8.314\ J\,mol^{-1}\,K^{-1}$), T is the temperature in Kelvin units and $C_e$ is the concentration of bulk solution at equilibrium time ($mg\,L^{-1}$). Given the adsorption capacity ($q_0$) this equation is forced to match with the experimental data changing the n value. Finally, the adsorption energy is calculated from the slope of Eq. (7) according Inglezakis et al. (2010).

## 2.6. Statistical analysis

Infostat® statistical software (Di Rienzo et al., 2011) was used to perform the analysis of variance and Pearson correlations. A normal distribution for the whole data set was confirmed by using a Shapiro-Wilks modified test and variance homogeneity was proven with the Levene test. Linear regression analysis was performed by Sigmaplot software in order to determine isotherm parameters of the cited models in this manuscript. Error bars are shown in the presentation of the results.

# 3. Results and discussion

## 3.1. Soil characterization

Physicochemical analysis from lateritic soil indicated a pH value of 5.66, organic matter 2.88%, cationic exchange capacity (CEC) of 203 $meq\,kg^{-1}$ and exchangeable acidity of 72.6 $meq\,kg^{-1}$. The interchangeable cationic content were 88.6, 39.1, 1.8, and 0.9 $meq\,kg^{-1}$, respectively, for $Ca^{2+}$, $Mg^{2+}$, $K^+$, and $Na^+$. The total nitrogen was 0.35% with a C/N ratio of 6.22. From ICP-MS analysis the oxide content was stated as; $Al_2O_3$: 22.40%, $Fe_2O_3$: 16.03%, $K_2O/Na_2O$: 1.92%, CaO: 0.46%, MgO: 0.29%, $TiO_2$: 1.49% and $SiO_2$: 55%. Textural analysis showed 55% clay, 17.50% silt and 27.50% sand. The point of zero charge was obtained from the intersection of the potentiometric titration curves as is showed in Supplementary material section (Fig. 1S). Here, $p_{zc}$ value was determined at 7.2 ± 0.3 that differs with the more acidic value of 3.98 reported previously by Sarkar et al. (2006) for laterite. The difference between these values is probably due to the differences found in the surface oxide composition. Maiti et al. (2011) reported a closer $p_{zc}$ value of 7.5 in a chemically treated laterite. Regarding superficial area measurements the studied soil presented type II nitrogen adsorption-desorption isotherm (data not shown) with a type

H3 loop associated to both low porosity materials with meso and macro-porosity and sheet agglomerations typical in clay soils. Specific surface area obtained by BET was 42.515 $m^2\ g^{-1}$ and the pore volume was 0.14 $cm^3\ g^{-1}$ (obtained by the Gurvitch method). This value could be explained by the high rate of iron compounds present in the lateritic soil. In fact, a fraction of these ferric compounds could form isolated nodules which are adsorbed on the surface of the clay particles, thus increasing the surface of exchange with the environment (Goure-Doubi et al., 2014). From EDS data, the superficial oxides were obtained: $SiO_2$: 44.13%; $Fe_2O_3$: 51.6; $TiO_2$: 2.17%; $CuO_2$: 0.98%; $K_2O$: 0.78% and CaO: 0.34%. Particularly, some differences are found regarding both iron and aluminium oxide contents, these differences can be attributed to the fact SEM is a superficial analysis while, the other implies an acid digestion of the whole sample. The SEM image from laterite revealed a random orientation and no formation of domains (group of particles that act as a unit) or cluster (see Supplementary material, Fig. 2S).

### 3.2. Effect of the adsorbent dosage

To study of the effect of soil dosage on the fluoride adsorption an experiment was conducted varying the soil mass between 0.2 and 10 g each 50 mL of solution. From fluoride concentration in the supernatant the removal (%) was calculated for each soil mass (Fig. 1).

Obtained results have shown a clear increase of the fluoride removal as a function of the soil mass until a dosage ratio of 4 g where a maximum of 60% was achieved. This observation is consistent with an increase in the number of available sites to fluoride adsorption. Similar results have been reported in literature by various researchers (Tomar et al., 2013, 2014). At the same time, the quantity of fluoride adsorbed per mass unit decreased considerably as a consequence of the adsorption sites remaining unsaturated (Bulut and Aydın, 2006). Thus, the ratio of 4 $g\ L^{-1}$ was selected for further studies in this work.

### 3.3. Conductivity and pH effects on fluoride adsorption on soil

The influence of the pH of the solution on the fluoride uptake is related to the surface functional groups of the sorbent and the ionic charge of the adsorbate in the solution. Natural groundwater that possesses higher fluoride content is characterized by low calcium content and relatively strong basic properties (Fawell et al., 2006). As a result, most materials are not appropriate for fluoride removal without a preceding acidification of the treated solution. In this work, batch experiments at pH values of 4, 6 and 8 were carried out to investigate the pH effect on the fluoride removal by using lateritic soil. Another important factor is the conductivity of the problem solutions that can affect the extension of the adsorption process. In the Fig. 2 the fluoride removal is analysed as a function of pH and ionic strength of the solutions.

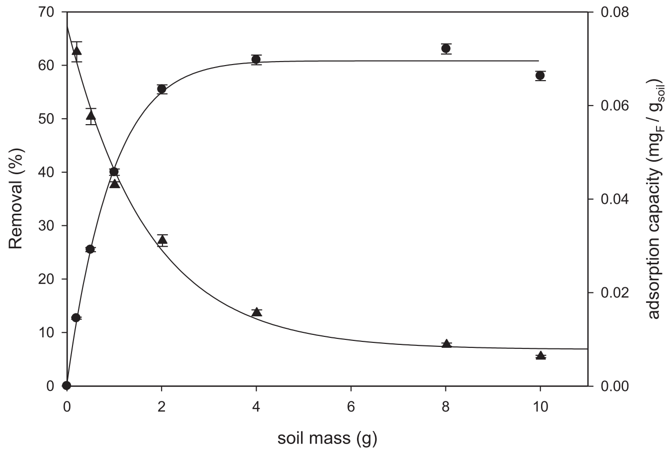

**Fig. 1.** Effect of soil dosage on the fluoride removal at 3 $mg\ L^{-1}$ $F^-$ concentration, volume 50 mL, pH 8, ionic strength 1 mM $KNO_3$ and time contact 1 h. (•) represents removal (%) and (▲) represents adsorption capacity. Error bars are SE.

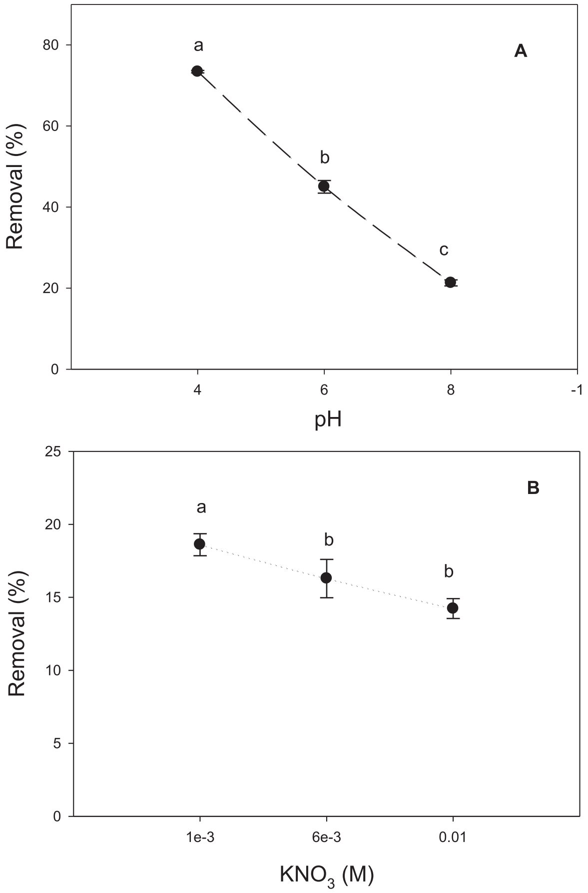

**Fig. 2.** Effect of pH (A) and conductivity (B) on the $F^-$ removal by using lateritic soil at $F^-$ concentration 2.5 $mg\ L^{-1}$, soil dosage 4 $g\ L^{-1}$ and contact time 1 h. (A) ionic strength 1 mM $KNO_3$ (B) pH: 8. Error bars represent SE and different letters represent significant differences at $p < 0.05$.

Removal (%) of fluoride from a starting solution of 2.5 $mg\ L^{-1}$ $F^-$ were 73.40%, 45.00% and 21.30% at pH values of 4, 6 and 8, respectively. These results indicate that a decrease in the pH of the treated solution from 8 to 4 improved the fluoride removal efficiency significantly. Similar tendencies were reported earlier in other studies where researchers suggested that this behavior was linked to the fact that positive charged surface attracts fluoride negative ions (Srivastav et al., 2013; Tang et al., 2009; Tomar et al., 2013; Triphaty et al., 2006). The increasing pH induced a decreasing number of positive surface charges, resulting in lower amounts of adsorbed anions (fluoride). Furthermore, the higher concentration of $OH^-$ anions in basic solutions, reduced the adsorption of fluoride even further because of the competition between the two anions for binding sites. In order to analyze the effect of dissolved ions in the solution, independent of the surface charge, batch experiments were conducted using solutions of variable ionic strength while keeping the pH at a fixed value of 8 for comparison. Hence, batch experiments were performed at low (160 $\mu S\ cm^{-1}$), medium (810 $\mu S\ cm^{-1}$) and high (1300 $\mu S\ cm^{-1}$) values of conductivity. Results are shown in Fig. 2B.

Results indicated that adsorption capacity diminishes when the conductivity increases, however, these differences lost their significance when the conductivities involved are medium and high at the $p < 0.05$ level. This result indicates that this material has the same removal efficiency at both moderate and high conductivities. Concluding, our results indicate that both surface charges and ion

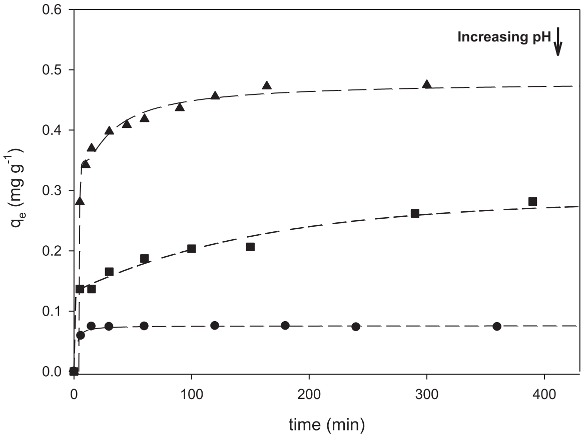

**Fig. 3.** Fluoride adsorption capacity by soil as a function of time. F⁻ concentration 2.5 mg $L^{-1}$, soil dosage 4 g $L^{-1}$, ionic strength 1 mM $KNO_3$ and pH = 4 (▲), pH = 6 (■) and pH = 8 (•).

competition are important factors to consider in fluoride adsorption through soils. However, the influence of pH on the removal efficiency is stronger than the influence of the ion concentration.

### 3.4. Kinetic studies

One of the most important factors in adsorption system designs is the necessary time at which adsorption takes place. The effect of contact time on fluoride adsorption was studied under controlled conditions of low conductivity and pH values of 4, 6 and 8 by using an initial fluoride concentration of 2.5 mg $L^{-1}$. Obtained results are shown in Fig. 3. Briefly, the adsorbed quantity of fluoride increased quickly during the first minutes of contact and after approximately 60 min an equilibrium state was attained. Additionally, the earlier described dependency on pH solution also influenced the course of the timed experiments as the more acidic solutions supported higher removal efficiency.

Experimental adsorption data as a function of time were fitted to both PFO and PSO kinetic expressions previously reported in the materials section. PSO adjustment showed a poor agreement with the experimental data for the whole time period (results not shown). Moreover, capacity theoretical values ($q_e$) at equilibrium for each experience are not according to the experimental ones. Regarding to PSO model, an excellent agreement was found as it is observed in Fig. 3S (Supplementary material) where it is shown that the pseudo-second-order equation predicts the behavior over the whole range of time studied. Kinetic parameters for both PFO and PSO are given in Table 1.

Firstly, experimental kinetic data were fitting to the PFO model and the constant rate and equilibrium adsorption capacity (theoretical) were estimated and compared with the experimental adsorption capacity (see Table 1). As result, it was observed that the equilibrium adsorption capacities were underestimated in the whole range of pH studied. Because of that, it was found that PFO model is not suitable to describe the adsorption process of fluoride onto lateritic soils. For that, it was concluding that the film diffusion is not a rate controlling. Conversely, a better adjustment was achieved with the PSO model. Particularly, the estimated adsorbed quantities of fluoride calculated from the Eq. (4) (PSO) approached to the experimental values very well and suggesting that the adsorption process follows a pseudo-second-order law at the studied pH interval. Additionally, the correlation coefficients are close to unity. Concluding, PSO model is more suitable to predict kinetic adsorption behavior at the studied pH than the PFO. Indeed, it can be stated that the rate controlling step is chemical sorption (Ho and McKay, 1999). This result is in accordance with Azizian (2004) that demonstrated that when the initial concentration of solute is not too high the sorption process obeys the PSO model.

**Table 1**
Kinetic parameters from removal fluoride by using lateritic soil. F⁻ concentration 2.5 mg $L^{-1}$, soil dosage 4 g $L^{-1}$, ionic strength 1 mM $KNO_3$.

| | pH = 4 | pH = 6 | pH = 8 |
|---|---|---|---|
| Pseudo-first order | $k_1$ = 1.97 × $10^{-2}$ $min^{-1}$<br>$q_e$ = 0.157 mg $g^{-1}$<br>$R^2$ = 0.958 | $k_1$ = 3.45 × $10^{-3}$ $min^{-1}$<br>$q_e$ = 0.192 mg $g^{-1}$<br>$R^2$ = 0.985 | $k_1$ = 1.58 × $10^{-3}$ $min^{-1}$<br>$q_e$ = 0.0028 mg $g^{-1}$<br>$R^2$ = 0.794 |
| Pseudo-second order | $k_2$ = 2.68 g $mg^{-1}$ $min^{-1}$<br>$q_e$ = 0.480 mg $g^{-1}$<br>$R^2$ = 1.000 | $k_2$ = 7.06 g $mg^{-1}$ $min^{-1}$<br>$q_e$ = 0.285 mg $g^{-1}$<br>$R^2$ = 0.998 | $k_2$ = 6.76 g $mg^{-1}$ $min^{-1}$<br>$q_e$ = 0.075 mg $g^{-1}$<br>$R^2$ = 1.000 |

Experimental values: $q_e$ (mg $g^{-1}$): 0.476 (pH = 4); 0.330 (pH = 6) and 0.075 (pH = 8).

Regarding pH conditions, sorption initial rates calculated as $k_2.qe^2$ resulted in 0.62 mg $g^{-1}$ $min^{-1}$; 0.57 mg $g^{-1}$ $min^{-1}$ and 0.038 mg $g^{-1}$ $min^{-1}$ for solution pH of 4, 6 and 8, respectively, suggesting that the sorption processes are strongly influenced by pH solution. These results should be explained taking into consideration that both, rate constants and adsorption capacity, are function of the available adsorption sites that, at the same time, are strongly pH dependent as was stated in Section 3.3 (Azizian, 2004).

Diffusional mass transport models have not been applied in this work, however, they are extremely important in adsorption processes, particularly, where ionic bonding is not as prevalent as in chemisorptions processes (Ho and McKay, 1998).

### 3.5. Adsorption isotherm

Analyses of adsorption isotherms are an important criteria to optimizing the use of adsorbent materials due to the equilibrium data are useful for the design and operation of adsorption systems. In order to obtain the relation between the concentration of F⁻ adsorbed in the soil and the equilibrium F⁻ concentration into the solution; batch adsorption experiments were conducted for different initial fluoride concentration under controlled conditions of pH and ionic strength. In Fig. 4 is showed that the adsorption capacity increased steadily with increasing Ce, up to an equilibrium concentration of around 20 mg $L^{-1}$ where $q_e$ is already constant (0.48 mg $g^{-1}$). This tendency can be explained taking into account that the greater the quantity of fluoride into the solution the higher the driving force for mass transfer to the surface became. In fact, a higher initial concentration has an enhancement effect in the fluoride adsorbed concentration (Wang et al., 2017).

There are several expressions that describe adsorption isotherms where Langmuir and Freundlich are the most commonly used models in

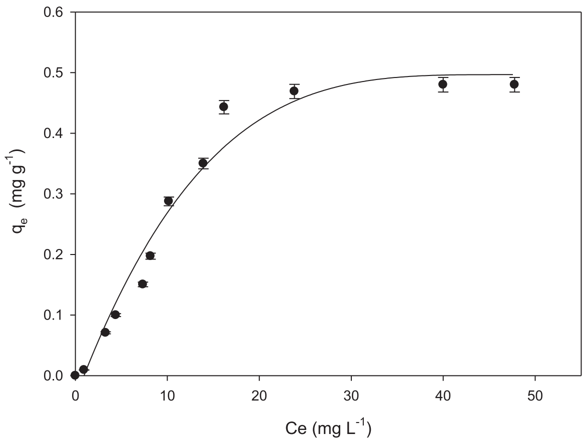

**Fig. 4.** Isotherm for removal fluoride by using lateritic soil at soil dosage 4 g $L^{-1}$; ionic strength 1 × $10^{-3}$ M $KNO_3$, pH 8 and contact time 1 h.

**Table 2**
Langmuir, Freundlich and D-A isotherm parameters for the adsorption of fluoride by lateritic soil. Soil dosage 4 g $L^{-1}$; ionic strength 1 × $10^{-3}$ M $KNO_3$, pH 8 and contact time 1 h.

| Isotherm Model | Parameters | | $R^2$ |
|---|---|---|---|
| **Langmuir** | $Q_0$ (mg $g^{-1}$) = 0.544 ± 0.015 | $K_L$ (L mg $^{-1}$) = 16.1 ± 0.3 | 0.957 |
| **Freundlich** | 1/n = 1.23 ± 0.04 | $K_F$ = 13 ± 2 | 0.972 |
| **Dubinin-Astakhov** | $Q_0$ (mg $g^{-1}$) =0.472 | n = 1 E = 0.321 Kj $mol^{-1}$ | 0.987 |

**Table 3**
Physicochemical properties of both raw and treated groundwater with lateritic soil. Soil dosage 4 g $L^{-1}$ and contact time 1 h.

| Parameter | Raw water | Treated water |
|---|---|---|
| pH | 7.8 | 8.1 |
| Conductivity μS $cm^{-1}$ | 894 | 905 |
| Total alkalinity $CaCO_3$ / mg $L^{-1}$ | 495 | 387 |
| Total hardness $CaCO_3$ / mg $L^{-1}$ | 107 | 105 |
| $Cl^-$ / mg $L^{-1}$ | 18.1 | 18.0 |
| $NO_3^-$/ mg $L^{-1}$ | 2.1 | 2.2 |
| $NO_2^-$/ mg $L^{-1}$ | < 0.01 | < 0.01 |
| $SO_4^{-2}$/ mg $L^{-1}$ | 33.4 | 33.3 |
| As / mg $L^{-1}$ | 23 | 10 |
| $F^-$ / mg $L^{-1}$ | 2.05 | 1.41 |
| Fe / mg $L^{-1}$ | < 0.05 | 0.195 |

literature (Bulut and Aydın, 2006; Vinhal et al., 2017). However, involved parameters in these models give only a limited insight on the mechanism and nature of the adsorption processes (Inglezakis, 2007). As an alternative, Dubinin-Astakhov isotherm gives information about the nature of the process and the adsorption site heterogeneity. So, experimental equilibrium data of fluoride adsorption were fitted to the previously described models (data not shown) and the corresponding parameters are listed in Table 2.

As is observed in Table 2, the best approximation to the experimental values was obtained with the D-A equations. Particularly, the correlation coefficient indicated a very good mathematical fit when the experimental maxima adsorption capacity was set. From that adjustment an important grade of heterogeneity in the adsorbent material is observed (n = 1) that could be explained with the presence of inhomogeneous distribution of active sites onto the soil surface. At the same time, data have adjusted very well to Freunlich model such as was observed before by several authors (Miretzky et al., 2008; Srivastav et al., 2013; Tomar et al., 2013; Vithanage et al., 2012). In these articles, it was attributed to the presence of both Al and Fe oxides in lateritic soil surface, contributing to different kinds of sites for fluoride adsorption. However, in this work, EDS analyses did not show aluminium oxides on the material surface. On the contrary, the weak assessment to Langmuir model based in poor estimation of the adsorption capacity compared with the experimental one and in the low correlation coefficient indicated that its conditions were not satisfied. Equilibrium data could also be used to determine the nature of the adsorption processes. Particularly, E value may estimate which is the governing process. In fact, an E value < 8 kJ $mol^{-1}$ indicates a physical adsorption, while for chemisorptions process E value lies between 8 and 16 kj $mol^{-1}$ (Sarkar et al., 2006). The estimated mean sorption energy of 0.321 kJ $mol^{-1}$ suggests that adsorption process of fluoride by lateritic soil is probably of a physical nature (Onyango et al., 2004; Sari et al., 2011). In addition, the soil performance to remove fluoride is compared with others geological materials (see Supplementary material, Table 1S). The use of adsorbents of geological origin to removal of fluoride from drinking water has as advantage to be eco-friendly, easy implementation and cost-effective technique. However, in comparison with the most used materials (such as alumina for instance) they have, in general, lower adsorption capacities and for that they are not commonly used in wastewater plants. Spite of that, their wide distribution and easy access make it possible for them to be used in a household level. In this sense, it is very important to have performed studies that permit to describe the adsorption process with the available adsorbent in a state as raw as possible and in the conditions of pH and conductivity near to the natural waters to be treated. Thus, the method propose here is fast, cost effective, does not change significantly the solution properties and permits to decrease the fluoride level until guideline value suggested by the WHO (2004).

### 3.6. *Fluoride removal from a natural groundwater*

Groundwater samples were treated with lateritic soil in order to determine the soil removal capacity in real water. For that, an exhaustive physicochemical analysis was performed before and after the adsorption process to determine if there is any change in the groundwater properties and also, to evaluate the influence in the co-occurring anions in the fluoride removal.

The concentration of cationic species $Mn^{+2}$; $Mg^{2+}$, $Ca^{2+}$, $K^+$, $Na^+$ in groundwater also were determined but data are not shown in Table 3. They have not presented any change owing to soil treatment. From Table 3 can be deduced that lateritic soil treatment is able to reduce the fluoride content. Particularly, a removal of 25% was obtained after a short time (1 h) of contact and a result, final fluoride concentration is according with the guideline proposed by the WHO (2004) of 1.5 mg $L^{-1}$ for drinking water. Another important result is the lower concentration of As in the treated water, that should be considered as an extra benefit due to they are commonly found together (Esposito et al., 2011). Additionally, the concentrations of anionic species such as $Cl^-$, $SO_4^{-2}$ and $NO_3^-$ remain constant after the treatment while the total alkalinity diminishes. So, it could be stated that these ions do not compete with fluoride adsorption process in lateritic soil. A similar result was previously reported by Sarkar (2006) who suggested that anion removal characteristic of laterite is fluoride specific. Spite of that, in clay materials sulphate and carbonate were showed as interfering ions (Vinati et al., 2015). At the same time, a change is noted in pH value that increases as the result of fluoride adsorption. This behavior could be explained taking in account that fluoride adsorption occurs in a little extension (due to physical nature) with $OH^-$ release at the solution. Similar results were observed by Wang and Reardon (2001) using a soil as adsorbent and in Chaudhary and Prasad (2015) who have used dolomite as adsorbent. In the last case, the pH changes were correlated with both removal (%) and $CO_3^{2-}$ released into the solution. Comparing these results with the obtained for synthetic samples (15%) in similar conditions a higher removal capacity was observed that could be attributed to the differences of groundwater matrix.

## 4. Conclusions

In this study, equilibrium aspects and kinetics of fluoride adsorption on lateritic soils, in aqueous solutions were studied in batch experiments under controlled conditions of both pH and ionic strength. It was observed that the necessary time to obtain an equilibrium state was approximately thirty minutes. Also, the adsorption process followed a PSO kinetic. Regarding pH of the solution, a significant diminution of the fluoride removal (between 75% and 20%) was observed with the increment of the pH from the 4–8. At the same time, initial adsorption rates were higher as the pH increases. Equilibrium adsorption studies were performed at pH 8 which is similar to the natural waters. Dubinin Ataskhov model was able to predict the nature of the process, maxima capacity adsorption and the heterogeneity degree. Particularly, it was establishing that the fluoride adsorption processes on lateritic soil have physical nature and a maxima capacity adsorption of 0.5 mg $g^{-1}$ was achieved. Finally, a natural groundwater sample was tested with laterite obtaining a reduction close to 25% from initial concentration 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 where drinking, even in the presence of another ions such as $Cl^{-}$; $SO_4^{2-}$, $NO_3^{-}$.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2017.11.016.

## References

APHA, AWWA, WEF, 1995. Standard methods for the examination of water and wastewater, 19th ed. American Public Health Association, Washington.
Ayoob, S., Gupta, A.K., 2006. Fluoride in drinking water: a review on the status and stress effects. Crit. Rev. Environ. Sci. Technol. 36, 433–487.
Azizian, S., 2004. Kinetic models of sorption: a theoretical analysis. J. Colloid Interf. Sci. 276, 47–52.
Bhatnagar, A., Kumar, E., Sillanpää, M., 2011. Fluoride removal from water by adsorption - A review. Chem. Eng. J. 171, 811–840.
Bhattacharya, A.K., Venkobachar, C., 1984. Removal of cadmium (II) by low cost adsorbents. J. Environ. Eng. 110, 110–122.
Black, C.A., Evans, D.D., Dinauer, R.C., 1965. Methods of Soil Analysis 9. American Society of Agronomy, Madison, WI, pp. 653–708.
Borgnino, L., Garcia, M.G., Bia, G., Stupar, Y.V., Le Coustumer, P., Depetris, P.J., 2013. Mechanisms of fluoride release in sediments of Argentina's central region. Sci. Total Environ. 443, 245–255.
Bourikas, K., Vakros, J., Kordulis, C., Lycourghiotis, A., 2003. Potentiometric mass titrations: experimental and theoretical establishment of a new technique for determining the point of zero charge (PZC) of metal (hydr) oxides. J. Phys. Chem. B 107, 9441–9451.
Bremner, J.M., Mulvaney, C.S., 1982. Nitrogen—total. methods of soil analysis. Part 2. Chem. Microbiol. Prop., Agron. Monogr. 595–624.
Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60, 309–319.
Bulut, Y., Aydın, H., 2006. A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. Desalination 194, 259–267.
Bundschuh, J., Bhattacharya, P., Sracek, O., Mellano, M.F., Ramírez, A.E., Storniolo, A.D.R., Martín, R.A., Cortés, J., Litter, M.I., Jean, J.S., 2011. Arsenic removal from groundwater of the Chaco-Pampean Plain (Argentina) using natural geological materials as adsorbents. J. Environ. Sci. Health A 46, 1297–1310.
Bundschuh, J., Litter, M., Ciminelli, V.S., Morgada, M.E., Cornejo, L., Hoyos, S.G., Hoinkis, J., Alarcón-Herrera, M.T., Armienta, M.A., Bhattacharya, P., 2010. Emerging mitigation needs and sustainable options for solving the arsenic problems of rural and isolated urban areas in Latin America - A critical analysis. Water Res. 44, 5828–5845.
Chaudhary, V., Prasad, S., 2015. Rapid removal of fluoride from aqueous media using activated dolomite. Anal. Methods 7, 8304–8314.
Dhillon, A., Prasad, S., Kumar, D., 2017. Recent advances and spectroscopic perspectives in fluoride removal. Appl. Spectrosc. Rev. 52, 175–230.
Di Rienzo, J.A., Casanoves, F., Balzarini, M.G., Gonzalez, L., Tablada, M., Robledo, Y.C., 2011. InfoStat versión 2011. Grupo InfoStat, FCA, Universidad Nacional de Córdoba, Argentina. URL ⟨http://www.infostat.com.ar⟩, 8, 195-199.
Espósito, M.E., Paoloni, J.D., Sequeira, M.E., Amiotti, N.M., Blanco, M.D.C., 2011. Natural contaminants in drinking waters (arsenic, boron, fluorine and vanadium) in the Southern Pampean Plain, Argentina. J. Environ. Prot. 2, 97–108.
Fawell, J., Bailey, K., Chilton, J., Dahi, E., Fewtrell, L., Magara, Y., 2006. Fluoride in Drinking Water, WHO drinking water quality series. IWA Publishing.
Freundlich, H.M.F., 1906. Über die adsorption in lösungen. Z. für Phys. Chem. (Liepzig) 57A, 385–470.
Gomoro, K., Zewge, F., Hundhammer, B., Megersa, N., 2012. Fluoride removal by adsorption on thermally treated lateritic soils. Bull. Chem. Soc. Ethiop. 26, 361–372.
Goure-Doubi, H., Martias, C., Lecomte-Nana, G.L., Nait-Ali, B., Smith, A., Thune, E., Villandier, N., Gloaguen, V., Soubrand, M., Koffi Konan, L., 2014. Interfacial reactions between humic-like substances and lateritic clay: application to the preparation of "geomimetic" materials. J. Colloid Interf. Sci. 434, 208–217.
Harrison, P.T., 2005. Fluoride in water: a UK perspective. J. Fluor. Chem. 126, 1448–1456.
Ho, Y.S., 2006. Review of second-order models for adsorption systems. J. Hazard. Mater. B 136, 681–689.
Ho, Y.S., McKay, G., 1998. A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. Process Saf. Environ. Prot. 76, 332–340.
Ho, Y.S., McKay, G., 1999. Pseudo-second order model for sorption processes. Process Biochem. 34, 451–465.
Hudson-Edwards, K.A., Archer, J., 2012. Geochemistry of As, F-and B-bearing waters in and around San Antonio de los Cobres, Argentina, and implications for drinking and irrigation water quality. J. Geochem. Explor. 112, 276–284.
Inglezakis, V.J., 2007. Solubility-normalized Dubinin–Astakhov adsorption isotherm for ion-exchange systems. Micro. Mesopor. Mat. 103, 72–81.
Inglezakis, V.J., Stylianou, M., Loizidou, M., 2010. Ion exchange and adsorption equilibrium studies on clinoptilolite, bentonite and vermiculite. J. Phys. Chem. Solids 71, 279–284.
Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. 40, 1361–1403.
Maiti, A., Basu, J.K., De, S., 2011. Chemical treated laterite as promising fluoride adsorbent for aqueous system and kinetic modeling. Desalination 265, 28–36.
Miretzky, P., Muñoz, C., Carrillo-Chávez, A., 2008. Fluoride removal from aqueous solution by Ca-pretreated macrophyte biomass. Environ. Chem. 5, 68–72.
Nelson, D.W., Sommers, I., 1982. Methods of soils analysis: Part 2. Chapter total carbon, organic carbon and organic matter. Agronomy 9, 539–579 (Amer. Soc. OfAgronomy, USA).
Onyango, M.S., Kojima, Y., Aoyi, O., Bernardo, E.C., Matsuda, H., 2004. Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9. J. Colloid Interf. Sci. 279, 341–350.
Sari, A., Uluozlü, Ö.D., Tüzen, M., 2011. Equilibrium, thermodynamic and kinetic investigations on biosorption of arsenic from aqueous solution by algae (*Maugeotia genuflexa*) biomass. Chem. Eng. J. 167, 155–161.
Sarkar, M., Banerjee, A., Pramanick, P.P., Sarkar, A.R., 2006. Use of laterite for the removal of fluoride from contaminated drinking water. J. Colloid Interf. Sci. 302, 432–441.
Sheldrick, B.H., Wang, C., 1993. Particle Size Distribution. In: Carter, M.R. (Ed.), Soil Sampling and Methods of Analysis. Canadian Society of Soil Science. Lewis Publishers, Ann Arbor, pp. 499–511.
Srivastav, A.L., Singh, P.K., Srivastava, V., Sharma, Y.C., 2013. Application of a new adsorbent for fluoride removal from aqueous solutions. J. Hazard. Mater. 263, 342–352.
Tang, Y., Guan, X., Wang, J., Gao, N., McPhail, M.R., Chusuei, C.C., 2009. Fluoride adsorption onto granular ferric hydroxide: effects of ionic strength, pH, surface loading, and major co-existing anions. J. Hazard. Mater. 171, 774–779.
Tomar, V., Prasad, S., Kumar, D., 2013. Adsorptive removal of fluoride from water samples using Zr–Mn composite material. Microchem. J. 111, 116–124.
Tomar, V., Prasad, S., Kumar, D., 2014. Adsorptive removal of fluoride from aqueous media using Citrus limonum (lemon) leaf. Microchem. J. 112, 97–103.
Tor, A., 2006. Removal of fluoride from an aqueous solution by using montmorillonite. Desalination 201, 267–276.
Triphaty, S.S., Bersillon, J.L., Gopal, K., 2006. Removal of fluoride from drinking water by adsorption onto alum-impregnated activated alumina. Sep. Purif. Techonol. 50, 310–317.
Vinati, A., Mahanty, B., Behera, S.K., 2015. Clay and clay minerals for fluoride removal from water: a state-of-the-art review. Appl. Clay Sci. 114, 340–348.
Vinhal, J.O., Nege, K.K., Lage, M.R., Carneiro, J.W.D.M., Lima, C.F., Cassella, R.J., 2017. Adsorption of the herbicides diquat and difenzoquat on polyurethane foam: kinetic, equilibrium and computational studies. Ecotoxicol. Environ. Saf. 145, 597–604.
Vithanage, M., Jayarathna, L., Rajapaksha, A.U., Dissanayake, C.B., Bootharaju, M.S., Pradeep, T., 2012. Modeling sorption of fluoride on to iron rich laterite. Colloid Surf. A 398, 69–75.
W.H.O, 2004. Guidelines for Drinking Water Quality, Geneva.
Wang, W., Li, R., Tan, J.A., Luo, K., Yang, L., Li, H., Li, Y., 2002. Adsorption and leaching of fluoride in soils of China. Fluoride 35, 122–129.
Wang, A., Zhou, K., Liu, X., Liu, F., Zhang, C., Chen, Q., 2017. Granular tri-metal oxide adsorbent for fluoride uptake: adsorption kinetic and equilibrium studies. J. Colloid Interf. Sci. 505, 947–955.
Water Treatment Technology Feasibility Support Document for Chemical Contaminants, 2003. In Support of EPA Six-Year Review of National Primary Drinking Water Regulations, EPA 815-R-03-004.