



Batch and column adsorption and desorption of fluoride using hydrous ferric oxide: Solution chemistry and modeling

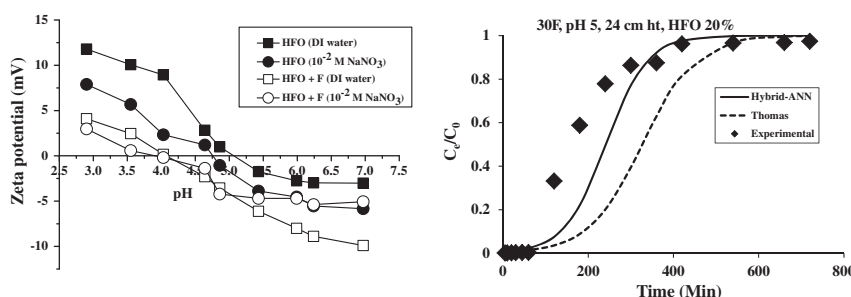
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HIGHLIGHTS

- HFO had the highest Freundlich model F adsorption capacity among seven adsorbents.
- Zeta potential data on HFO indicated a specific F adsorption mechanism.
- Column adsorption data fitted fairly well to Thomas model.
- Thomas model data fit improved by using an artificial neural network approach.
- NaOH can desorb F, not NaCl and Na₂SO₄, supporting pH and co-ions' effects on adsorption.

GRAPHICAL ABSTRACT



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ABSTRACT

Elevated intake of fluoride (F), mainly through drinking water, is a major threat to human health worldwide. A study was conducted to remove F from aqueous solution by adsorption onto hydrous ferric oxide (HFO) in batch and fixed-bed column experiments. Of the seven adsorbents (four anion exchange resins, three multivalent metal oxides) tested, HFO had the highest adsorption capacity. Fluoride adsorption on HFO fitted well to Langmuir and Freundlich models with a Langmuir adsorption maximum of 6.71 mg F/g at pH 6.5. Fluoride adsorption continuously decreased from pH 3 to 7. Point of zero charge of HFO was pH 5 which fell to pH 4 in the presence of 10 mg F/L and 1 g HFO/L, indicating that F was specifically adsorbed on HFO. Fluoride was not desorbed by 0.1 M NaCl and 0.1 M Na₂SO₄ but effectively desorbed by 0.1 M NaOH. The F adsorption capacity in column experiments (10% or 20% HFO + 90% or 80% anthracite) was progressively reduced with increasing number of adsorption/NaOH desorption cycles up to three cycles reaching a final value of 3.26 mg F/g HFO. The breakthrough data from column studies at different bed heights, inlet concentrations, and pHs were fairly well described by Thomas model, but using an artificial neural network approach improved the model capability.

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1. Introduction

Fluoride (F) contamination of drinking water is one of the world's most serious health problems [1,2]. A low concentration of F in drinking water (0.4–1.0 mg/L) has beneficial effects on teeth especially for young children as it promotes calcification of dental

enamel and protects teeth against tooth decay. On the other hand, excessive intake of F leads to various diseases such as osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, Alzheimer syndrome and thyroid disorder [3–5]. Owing to these adverse effects, the World Health Organization (WHO) has recommended a maximum allowable F concentration of 1.5 mg/L in drinking water [2].

In view of the toxic effects of F on human health, many treatment methods such as electro dialysis, membrane and adsorption

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processes and chemical precipitation have been developed for the removal of excess F from drinking water [6,7]. Of these methods, adsorption is generally considered to be the most effective and suitable one due to its simplicity, effectiveness and relatively low cost [6,7]. A wide variety of natural and synthetic adsorbents has been tested and applied for the removal of F ions from aqueous solution [6,7]. Of these adsorbents, multivalent metal (Al, Fe, La, Zr) oxides and hydroxides [7] and metals incorporated activated carbon [8,9], and calcium phosphate compounds such as bone char [10–12] were reported to have high F removal capacities.

Most studies on F removal by adsorbents have been performed in batch experiments and only a few have been reported in fixed-bed column systems which are more relevant to real operating systems on natural waters [6,7]. Moreover, many previous studies on adsorptive removal of F have not considered desorption of F after the adsorbent is saturated with F. Easy desorption of F is important for multiple reuse of the adsorbent as this reduces operational costs. The species of F in solution and the surface charge on the adsorbent are controlled by solution pH and therefore pH has been reported to influence F adsorption [13,14]. Natural water contains anions such as H_2PO_4^- , PO_4^{3-} , SO_4^{2-} , Cl^- , NO_3^- which can compete with F for adsorption [7,13,14], therefore in any F removal studies the effect of these co-ions also need to be considered.

The objectives of this study were to: (i) compare the F removal percentages of seven adsorbents expected to have high adsorption capacities and justify the selection of hydrous ferric oxide (HFO) for a detailed study; (ii) model equilibrium and kinetic batch isotherm data of F adsorption; (iii) determine the effect of pH and complementary anions on F adsorption and evaluate the mechanisms of adsorption using zeta potential data; (iv) model the breakthrough curves of F adsorption in column experiments; and (v) develop a suitable method to regenerate the adsorbent for reuse. The novelty of the study is modeling of F adsorption in fixed-bed column under different experimental conditions by applying an artificial neural network approach and determining the mechanism of F adsorption using solution and solid/solution interface chemistry.

2. Materials and methods

2.1. Adsorbents

Four ion exchange resins, Purolite A520E, Purolite A502PS, Purolite FerrIX A33E and Dowex 21K and three multivalent metal oxide adsorbents, HFO (HFeO_2), zirconium (IV) hydroxide ($\text{H}_4\text{O}_4\text{Zr}$) and α -alumina (Al_2O_3) were used to compare their efficiency in removing F from water. The basis for selecting these adsorbents is that a recent review on F adsorption reported that multivalent metal oxides and some ion exchange resins have high F adsorption capacities [7]. Purolite A520E and Purolite A502PS are macroporous strong base anion exchange resins with Type 1 quaternary ammonium functional groups and consist of polystyrene cross-linked divinylbenzene and styrene–divinylbenzene, respectively [15]. Purolite FerrIX A33E resin unites a unique blend of hydrous iron oxide nanoparticles with a spherical polymer substrate [16]. Dowex 21K XLT is a Type I strong base anion exchange resin composed of Styrene–DVB with quaternary amine functional groups [17]. These ion exchange resins were reported to have very high adsorption capacities for arsenic or phosphate [15,16] and therefore they are expected to also have high F adsorption capacities. This is because F – like arsenate/arsenite and phosphate – is specifically adsorbed on many adsorbents [7].

The Purolite and Dowex resins were obtained from Purolite Company (USA) and Dow chemical company (USA), respectively. The metal oxide/hydroxide adsorbents were obtained from Sigma Aldrich (USA).

2.2. Characterisation of adsorbents

X-ray diffraction (XRD) was conducted using a XRD Shimadzu S6000 (Japan) diffractometer on powder samples of the inorganic adsorbents, HFO, zirconium hydroxide and alpha-alumina. The X-ray diffraction unit (Theta/2Theta) was equipped with a Cu target operated at 40 kV and 30 mA with a setting of 5–45° 2-theta, step time 2° min⁻¹, 25 °C. As HFO was used for the detailed adsorption study, scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, surface area, and porosity measurements were conducted only for this adsorbent. For the SEM analysis, the samples were imaged, uncoated, in a Zeiss Evo LS15 SEM using its variable pressure mode and an accelerating voltage of 15 kV. FTIR pattern was recorded using a Nicolet 6700 FT-IR Spectrometer equipped with a room temperature DLATGS detector and a Nicolet FT-IR Smart System with Smart Accessories using a Diamond crystal HATR. Surface area and porosity were determined by nitrogen-sorption measurements carried out at 77 K with a Micromeritics 3Flex surface characterization analyzer. The BET method was used to calculate the specific surface area. The pore size distribution was derived from the adsorption branch of the isotherm by using the Barrett–Joyner–Halenda (BJH) method.

2.3. Fluoride analysis

The F analysis was carried out using a Metrohm ion chromatograph (model 790 Personal IC) equipped with an auto sampler and conductivity cell detector. The separation of anions was achieved using an A SUPP column 3 (150 mm × 4 mm). Na_2CO_3 (3.2 mmol/L) and NaHCO_3 (1.0 mmol/L) were used as mobile phase with a flow rate of 0.9 mL/min.

2.4. Zeta potential measurement

Zeta potential is the electrical potential close to a particle surface where adsorption of ions from solution phase occurs and it is positively related to the surface charge. The higher the positive zeta potential the higher the anion exchange capacity, resulting in larger amounts of anions such as F adsorption. Suspensions of 1 mg/L HFO in deionised water or 10^{-2} M NaNO_3 were prepared and the pH was adjusted from 2.8 to 10 utilising 0.1 M NaOH or 0.1 M HNO_3 solutions using a HQ40d portable pH Meter. The suspensions were agitated in a flat shaker at a shaking speed of 120 rpm at room temperature (24 ± 1 °C). Zeta potential was measured using a Zetasizer nano instrument (Nano ZS Zen3600, Malvern, UK) after measuring the final pH.

2.5. Batch adsorption experiments

2.5.1. Kinetic experiments

Batch adsorption kinetic experiments were conducted at an F concentration of 10 mg F/L in a set of glass flasks containing 100 mL of NaF solution and adsorbent dosage 1.0 g/L. The suspensions were agitated in a flat shaker at a shaking speed of 120 rpm for 6 h at room temperature (24 ± 1 °C). The aqueous samples were taken at different time intervals and the concentrations of F were measured. The amount of F adsorption at time t, q_t (mg F/g), was calculated using Eq. (1).

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (1)$$

where C_0 is the initial concentration of F (mg F/L); C_t is concentration of F at time t (mg F/L); V is volume of the solution (L) and M is mass of dry adsorbent (g). The removal percentage of F was calculated using Eq. (2)

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