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

**T. Nur a, P. Loganathan a, T.C. Nguyen a, S. Vigneswaran a \*, J. Kandasamy a**

a *Faculty of Engineering and Information Technology, University of Technology, Sydney, Broadway, NSW 2007, Australia.*

\*corresponding author: *S. Vigneswaran, Faculty of Engineering and Information Technology, University of Technology, Sydney, Broadway, NSW 2007, Australia.*

E-mail: [s.vigneswaran@uts.edu.au](mailto:s.vigneswaran@uts.edu.au)

Phone: +61 2 9514 2641  
Fax: +61 2 9514 2633

**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.

**Statement of significance**

The paper considered all important solution and solid-solution interface properties in determining the mechanism of F adsorption by a powerful adsorbent. The results are useful for surface chemists interested in anion adsorption. The majority of the previous studies were conducted in batch-mode experiments whereas ours’ was in both batch and column modes, the latter being more relevant to real operating systems of water treatment. The results of mathematical modeling of column data are important for designing treatment plants for the removal of F from water and wastewaters.

**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.

**Keywords**: adsorption, adsorption models, breakthrough curves, fluoride, hydrous ferric oxide, zeta potential.

**Graphical Abstract**



**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 electrodialysis, membrane and adsorption 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 H2PO42-, PO43-, SO42-, Cl-, NO3- 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. Material 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 (HFeO2), zirconium (IV) hydroxide (H4O4Zr) and α-alumina (Al2O3) 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 x 4 mm). Na2CO3 (3.2 mmol/L) and NaHCO3 (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 NaNO3 were prepared and the pH was adjusted from 2.8 to 10 utilising 0.1 M NaOH or 0.1M HNO3 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 ± 1oC). 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 ± 1oC). The aqueous samples were taken at different time intervals and the concentrations of F were measured. The amount of F adsorption at time t, qt (mg F/g), was calculated using Eq. (1).

 (1)

where C0 = initial concentration of F (mg F/L); Ct = concentration of F at time t (mg F/L);

V = volume of the solution (L) and M = mass of dry adsorbent (g). The removal percentage of F was calculated using Eq. (2)

(2)

The adsorption data were analysed by pseudo-first and pseudo-second order kinetic models. The equations for pseudo-first and pseudo-second order kinetic models and the methods of calculating the model parameters are presented in Table 1.

**TABLE 1**

*2.5.2. Equilibrium experiments*

Equilibrium adsorption experiments were conducted on all seven adsorbents in a set of glass flasks with 100 mL solutions spiked with F (10 mg F/L) and adsorbent doses of 0.1-10 g/L at room temperature (24 ± 1oC) at pH 6.5. The suspensions were agitated for 72 h in a flat shaker at a shaking speed of 120 rpm at room temperature (24 ± 1oC). At the end of this period the F concentrations in the supernatant solutions were measured. The experiments were duplicated and the average values were taken for data analysis. The difference between duplicate values was within ± 2%. In all adsorption studies the amount of F adsorption at equilibrium, qe (mg F/g), was calculated using equation (1) by replacing qt and Ct by qe and Ce, respectively. Similarly, the removal percentage was calculated by replacing Ct by Ce in equation (2).

The adsorption data were treated with both Langmuir and Freundlich isotherm models. The equations of the models and the graphical methods used to calculate the model parameters are explained in Table 1. Of the seven adsorbents, HFO had the highest F adsorption capacity (see later section). Therefore, the effect of pH of the medium and the influence of complementary ions were investigated on HFO only. For the effect of pH on the adsorption of F, samples prepared for zeta potential measurements were used.

Natural water and wastewater may contain many anions at different concentrations which can compete with F for adsorption. The extent of this competition depends on the relative concentrations of the ions and their affinity for the adsorbent. Therefore, the effect of complementary anions (Cl-, SO42-, PO43- and NO3-) on F adsorption by HFO was studied at a constant initial F concentration of 10 mg/L, adsorbent dose of 1 g/L, and pH 6.5 by varying anion concentrations from 25 to 100 mg/L using NaCl, Na2SO4, KH2PO4 and KNO3.

*2.6. Column adsorption experiments*

The fixed-bed column used for the experiments consisted of 2.5 cm inner diameter pyrex glass tubes. At the bottom of the column, a stainless steel sieve was attached followed by a layer of glass beeds in order to provide a uniform flow of the solution through the column. A known quantity (56 or 112 g) of anthracite + HFO was packed in the column to yield the desired bed heights (12 or 24 cm). The HFO content in the column was 10 and 20% of the total column weight. Anthracite was used to provide physical stability and good hydraulic conductivity to the columns and reduce the cost of the filter media. Initial trials showed that anthracite had negligible F adsorption capacity. Therefore the adsorption capacity of the column was assumed to be due to only HFO. Fluoride solutions of known concentrations (10 and 30 mg F/L) were pumped upward through the column at a desired filtration velocity (2.5 m/h) which was controlled by a peristaltic pump. The effluents at the outlet of the column were collected at regular time intervals and the F concentration was measured.

The breakthrough curves show the loading behaviour of fluoride to be removed from solution in a fixed-bed column and are usually expressed in terms of adsorbed fluoride concentration (Cad), inlet fluoride concentration (Co), outlet fluoride concentration (C) or normalized concentration defined as the ratio of outlet fluoride concentration to inlet fluoride concentration (C/Co) as a function of time. The maximum column capacity, q total (mg F), for a given feed concentration and filtration velocity is equal to the area under the plot of the adsorbed fluoride concentration, Cad (Cad = Co-C) (mg/L) versus effluent time (t, min) and was calculated manually from the breakthrough curves using Microsoft Excel spreadsheet according to equation (3).

 (3)

Equilibrium uptake qeq (mg F/g) or maximum capacity of the column is defined by equation (4) as the total amount of adsorbed fluoride concentration (qtotal) per g of adsorbent (M) at the end of the total flow time:

(4)

M

q

q

total

eq



The empirical model of Thomas [18] (Table 1) and a hybrid model based on Thomas model and artificial neural networks (ANN) were used to analyse the column breakthrough data. The ANN approach in improving the capability of Thomas model was explained by Tovar-Gómez et al. [12]. Tovar-Gómez et al. [12] showed that the hybrid model ANN-Thomas model predicted the F breakthrough in columns containing bone char better than Thomas model, especially for unsymmetrical breakthrough curves. The modelling approach of Tovar-Gómez et al. [12] was used for analysing the F adsorption data on HFO. The software, Neurosolutions, supplied by NueroDimensions Inc (USA) was used for the modeling.

*2.7. Fluoride desorption and adsorbent regeneration*

Desorption of F that had previously been adsorbed to HFO was studied in batch and column experiments. In the batch experiment, HFO was saturated with F by shaking a 50 mL F solution (10 mg/L) with HFO at a dosage of 5 g/L for 72 h, followed by filtering and drying the F-loaded HFO at room temperature. The adsorbed F was then desorbed using 0.1 M NaCl, NaOH or Na2SO4 solution. Desorption was carried out by shaking the F-saturated HFO with 50 ml of the reagents in a flat shaker at a shaking speed of 150 rpm for 30 min. The desorbed solutions were analysed for F concentrations.

Since 0.1 M NaOH was found to be the most efficient reagent in desorbing F in the batch experiment, this reagent was used in the column desorption study. Initially, F was saturated on HFO in a 24 cm length column containing 20% HFO by passing an F solution of 30 mg/L at pH 5 through the column at a velocity of 2.5 m/h until complete breakthrough of the solution occurred. Then the column was washed with distilled water followed by 0.1 M NaOH at a velocity 10 m/h for 30 min and the leachate was analysed for F to determine the amount of F desorbed. Fluoride adsorption was carried out on the regenerated HFO as previously described, after the column was washed several times with distilled water until the pH in the effluent reached 6.5. The adsorption/desorption cycle was continued three times in total.

**3. Results and discussion**

*3.1. Characteristics of HFO*

X-ray diffraction analysis showed that HFO (Fig. 1) and zirconium hydroxide (data not shown) were poorly crystalline (amorphous) whereas alpha-alumina was crystalline and having diffraction peaks conforming to its structure (data not shown). For HFO, two broad diffraction peaks at 2θ values of 34-36° and 61-64° with the corresponding d-spacing values of 0.253-0.267 Åand 0.152-0.158 Å were obtained. These peaks match with those of the poorly ordered ferrihydrite mineral [19, 20]. The SEM images showed that the surface morphology of the HFO particles was irregular and it did not change significantly after F adsorption at an F concentration of 50 mg/L and HFO dose of 10g/L (Fig. 2). The FTIR spectra of HFO before and after adsorption of F at 50 mg F/L and 10 g/L dose of HFO showed two major adsorption peaks (Fig. 3). The peaks at 3418 and 3445 cm-1 are for the stretching vibration mode of lattice water and hydroxyl groups and those at 1621 and 1636 cm-1 are for OH bending vibration mode of adsorbed water molecules [21, 22]. The spectra shows that these band intensities were significantly reduced after F adsorption indicating that the structural hydroxyl group and water molecules had an important role in F adsorption. The BET surface area of HFO was 148 m2/g. The total pore volume and pore diameter were 0.214 cm3/g and 5.4 nm, respectively.

**Fig. 1, 2, 3.**

*3.2. Batch adsorption*

*3.2.1. Batch kinetic adsorption* *modeling*

The kinetics of F adsorption at an initial F concentration of 10 mg/L and HFO dosage of 1 g/L showed that the adsorption capacity increased with contact time up to approximately 60 min and became steady afterword (Fig. 4a). Among the seven adsorbents, HFO had the highest F removal percentage (56%) followed by Dowex 21k (52%), Zirconium (IV) hydroxide (38%), Purolite A502PS (35%), Purolite FerrIX A33E (29%) and Purolite A520E (25%) within 120 min. The lowest removal percentage was found for Alumina (4%).

**Fig. 4.**

The adsorption data showed that for all adsorbents, except Alumina, the pseudo-second order kinetic model described the experimental data better than the pseudo-first order model (R2 = 0.99 for pseudo-second order model compared to R2 = 0.65-0.97 for pseudo-first order model) (Table 2). Furthermore, the values of qe calculated from pseudo-second order kinetic model were approximately equal to the experimental values of qe, while the pseudo-first order model values of qe were much lower than the experimental values of qe (Table 2) confirming the better applicability of the pseudo-second order model for describing the experimental data for all adsorbents except Alumina. The better fit of data to pseudo-second order model suggests that chemisorption process could be the rate-limiting step in the adsorption [12]. Fluoride adsorption on other adsorbents has also been reported in literature to fit better to this model than pseudo-first order model [12, 23, 24].

**TABLE 2**

*3.2.2. Batch equilibrium adsorption modeling*

Of the seven adsorbents tested, HFO produced the highest removal percentage at all dosages of adsorbents for an initial F concentration 10 mg/L from a solution volume of 100 mL (Fig. 4b). The adsorption data for all seven adsorbents satisfactorily fitted to Freundlich adsorption model (R2 = 0.66-0.98). Consistent with the removal percentage data (Fig. 4b), HFO had the highest Freundlich constant KF that is related to the adsorption capacity (Table 3). However, only the data for HFO satisfactorily fitted to the Langmuir adsorption model with positive value for the adsorption maximum (R2 = 0.91). The adsorption maxima for the other adsorbents were either negative or where positive values were obtained the R2 values were < 0.10. Negative maximum adsorption values were also reported for other adsorbents and adsorbates in literature [25]. The fit of the data to Langmuir model for HFO indicates that the adsorption sites on HFO were homogeneous with monolayer adsorption coverage. The Freundlich model fit to the other adsorbents indicates a hetrogenity of the adsorbent surfaces with different energies of adsorption.

The adsorption maximum calculated from the Langmuir model for HFO was 6.71 mg F/g. This adsorption capacity is approximately equal to the maximum adsorption capacity of 7 mg F/g at pH 6-7 obtained by Kumar et al. [13] for a ferric oxide that had similar chemical characteristics as the HFO used in this study. The Langmuir adsorption capacity obtained for HFO is among the highest adsorption capacities reported for adsorbents [7].

**TABLE 3**

*3.2.3. pH changes during adsorption*

During adsorption the pH of the suspension changed. At low pH values (equilibrium final pH, pHf  < 4.0) the pH increased from the initial value (pHi) resulting in positive values for pHf – pHi (Fig. 5). At high pH values (pHf > 4.0) the pH decreased during adsorption leading to negative values for pHf – pHi. Similar results were reported for F adsorption on HFO [14], nano-hydroxyapatite/chitosan [26] and manganese oxide–coated alumina [27] and phosphate adsorption on nano-sized magnetite [28]. The explanation for the increase in the final pH at low pH values may be the liberation of OH- from HFO during F adsorption by ligand exchange process (inner-sphere complexation) [14] as described in Eq. (5) .

HFO---OH + F-  = HFO----F + OH- (5)

At high pH values the final pH decreased from the initial pH probably due to Na+ added in NaOH for pH alteration might have exchanged with H+ electrostatically adsorbed (outer-sphere complexation) onto the increasingly negatively charged HFO [9] as described in Eq. (6).

HFO- (H+) + F- + Na+ = HFO- (Na+) + F- + H+ (6)

When the ionic strength of the solution was increased to 10-2 M by adding NaNO3 the values of pHf – pHi increased (Fig. 5) due to enhanced exchange of H+ by the additional Na+ supplied by NaNO3. At pHf = 4.0, pHf = pHi. This pH is, therefore, the point of zero charge (PZC) of HFO in the presence of F [26, 28].

**Fig. 5.**

*3.2.4. Effect of pH on F adsorption*

Fluoride adsorption continued to decrease as pHf increased from 3 to 7 (pHi 3.5 to 9.0) (Fig. 6a). The decrease in adsorption is due to an increase in the surface negative charges on HFO with increased pH (Fig. 6b) causing repulsion of the negatively charged F- ions. It is also due to the increased concentration of OH- ions at higher pH values that competed with F- for adsorption. Adsorption is favoured at low pH because of the presence of more hydroxylated sites for ligand exchange with F than at high pH. The decline in F adsorption as pH increased was also observed by other studies on HFO [14] and other adsorbents [14, 27, 29]. The actual pH where the F adsorption starts to decrease depends on the surface chemical characteristics of the adsorbent especially the PZC [7]. There was very little difference in F adsorption between the two ionic strengths (water and 10-2 M NaNO3) of the solutions. This shows that F was adsorbed by forming inner-sphere complexation on HFO [30].

Zeta potential curves at the two ionic strengths intersected close to zero zeta potential because when the net surface charge is zero the ionic strength has no effect (Fig. 6b). The pH at which the intersection occurs is the PZC [31]. Therefore, based on the zeta potential data, F is adsorbed mainly by the ligand exchange mechanism (specific adsorption or inner-sphere complexation [7]. Fig. 6b shows that zeta potential at the HFO particle surface was more negative in the presence of F at all pH values. The PZC decreased from pH 5.0 in the absence of F to pH 4.0 when F was added consistent with the PZC determined using pH change data (Fig. 6). Thus, F adsorption created negative surface charges on the HFO, thereby shifted the PZC to a lower pH, which was consistent with the inner-sphere adsorption mechanism. When the ionic strength of the solution was increased by the addition of NaNO3, the zeta potential became less negative when pH was above the PZC, whereas it behaved oppositely at pH values below the PZC. This pattern of ionic strength effects was also reported for F adsorption on alumina [32] and phosphate adsorption on variable charge soils [31].

**Fig. 6.**

*3.2.5. Effect of complementary ions*

The order of F adsorption reduction by the complementary anions was PO43− > SO42- > NO3- > Cl- (Fig. 7). This can be explained based on the adsorption mechanisms of these anions. Phosphate is known to be strongly adsorbed on high valent metal oxides and hydroxides by specific adsorption (inner-sphere complexation). It is therefore able to compete easily with F which is also specifically adsorbed [7]. Nitrate and Cl- are non-specifically adsorbed (outer-sphere complexation) to metal oxides and therefore unable to compete well with F- at equal concentrations. Sulphate, on the other hand, can be adsorbed specifically and non-specifically and therefore it competed with F- better than Cl- and NO3- but weaker than PO43- [33]. The pattern of anions competition order is similar to that reported by others [13, 14]. The ratios of the anions concentrations in natural water and wastewater are widely different and therefore such ratios need to be considered in assessing the extent of competition.

**Fig. 7**

3.3. Fixed-bed column experiments

3.3.1. Breakthrough curves

Adsorption of F by HFO is presented in the form of breakthrough curves (Fig. 8). The results show that at the lower bed height, the breakthrough occurred faster than that at the higher bed height. This pattern of breakthrough is similar to the findings of F adsorption on manganese oxide coated alumina [27]. The contact time of F with the adsorbent is shorter at lower bed height resulting in faster exhaustion of the HFO bed and less volume of treated water. The empty bed contact time available for F at the depths of 12 cm and 24 cm were 2.89 min and 5.76 min, respectively.

The F breakthrough generally occurred faster and the breakthrough curve was steeper at pH 7 than at pH 5 (Fig. 8). The time to reach the plateau of Ct/C0 (equal to 0.98) was significantly higher at a lower pH level. The plateau of Ct/C0 occurred at 5 and 12 h for the pH of 7.0 and 5.0, respectively. This is due to the higher F adsorption capacity of HFO at acidic pH than at neutral pH, as found in the batch study. Ku et al. [34] also reported faster breakthrough and steeper breakthrough curves for F adsorption on an Amberlite resin at pH 6.7 than at pH 5.5.

**Fig. 8.**

The breakthrough was also faster and the breakthrough curves were sharper with the higher influent F concentration (Fig. 8), an outcome similar to the findings of F adsorption on other adsorbents [12]. As the influent concentration increases, F loading rate increases as does the driving force for mass transfer, and there are decreases in the adsorption zone length which was also reported in other column studies on other adsorbents [12, 15]. The extended breakthrough curve (slower exhaustion of the HFO column) at the lower influent concentration indicates that a higher volume of solution can be treated.

*3.3.2. Column adsorption modeling*

The Thomas model fitted faily well to the experimental data as shown by the moderate to high R2 values (0.79-0.97) (Table 4). However, the hybrid ANN+Thomas model fit to the data was better for all scinerios (Table 4, Fig. 8 ), especially for inlet F concentration 30 mg/L, 24 cm column height, pH 5, and HFO 20% where the R2 value for Thomas model was 0.79 but for the hybrid model it was 0.98. The column adsorption capacity (qo) predictions by both the Thomas and hybrid models increased with increases in inlet F concentration and decreased with increased pH and bed height.

The values obtained for qo from the models are approximately equal to those calculated from the breakthrough curves, except for the initial F concentration of 30 mg/L at the bed height 24 cm and HFO dosage 20% at pH 7, where the breakthrough capacity was 7.06 mg F/g (similar to the Langmuir adsorption capacity of 6.71 mg F/g observed in the batch study) but q0 predicted by both modelswas 12.7 mg F/g. The above adsorption capacities were the highest estimated by the models in the experiments. Higher column adsorption capacity obtained in the models for 30 mg F/L inlet concentration than the Langmuir adsorption maximum in batch study is probably because of the lower initial F concentration of 10 mg F/L used in the batch study which would have further decreased at equilibrium due to adsorption. In the column study the solution concentration was always maintained at 30 mg/L with the passage of fresh influent solution. Higher solution F concentration is expected to produce higher F adsorption.

The increase of bed height and influent concentration decreased kTh while increased pH in turn increased kTh. Similar effects of bed height and influent F concentration were reported by Nur et al. [16] for phosphate adsorption on an iron oxide impregnated ion exchanger.

**Table 4.**

*3.4. Fluoride desorption and HFO regeneration*

Of the reagents tested in the batch study to desorb F that was already adsorbed on HFO, 0.1M NaOH was found to be the most suitable one (Fig. 9a). The high effectiveness of 0.1 M NaOH in desorbing F is due to the lowest F adsorption at very high pHs (Fig. 9a) produced by this alkaline reagent. In the study on the effect of complementary anions on F adsorption it was observed that the anions Cl- and SO42- did not significantly reduce F adsorption because of the stronger ability of F adsorption compared to these two anions. This is the likely explanation for the inability of 0.1 M Na2SO4, and 0.1 M NaCl to significantly desorb F from HFO. Dey et al. [14] also reported that among four reagents tested, the largest percentage of F desorption (80%) from an F-rich HFO was observed for NaOH and the least (15%) was for NaCl.

**Fig. 9**

The column study results showed that almost 97% of the previously adsorbed F was desorbed by 0.1 M NaOH in 30 min (21 bed volumes) and HFO was regenerated for reuse (Fig. 9b). The F removal percentage of the regenerated HFO declined to 62% (a decrease in F adsorption capacity from 5.90 mg/g for the virgin HFO to 3.63 mg/g for the regenerated HFO) (Fig. 9b). The F adsorption capacity further fell to 3.43 and 3.26 mg/g, after the second and the third cycles of adsorption/desorption, respectively, as found by others [14]. The reduction in adsorption capacity with continued reuse of adsorbents may be due to the chemisorption of previously adsorbed F, part of which was not desorbed [14] and/or the use of the highly concentrated NaOH which might have modified the adsorbent surface. Reduced adsorption capacity when HFO was reused three times was still much higher than that of many other adsorbents [7]. Therefore, HFO is proved to be a potential adsorbent for the removal of F.

**4. Conclusions**

Batch and fixed-bed column (10 or 20% HFO + 90 or 80% anthracite) experimental results showed that HFO is an efficient adsorbent for removing F from aqueous solutions. The batch adsorption was satisfactorily explained using both the Langmuir and Freundlich isotherms while the column adsorption data fitted reasonably well to Thomas model but by using an artificial neural network approach the model’s capability was improved. The Langmuir maximum adsorption capacity at pH 6.5 was 6.71 mg F/g and the highest column breakthrough adsorption capacity was 7.06 mg F/g at the inlet concentration of 30 mg F/L, 12 cm bed height, pH 5 and 2.5 m/h filtration velocity. The adsorption capacity predicted by the Thomas model was also highest (12.7 mg F/g) for these experimental conditions. The kinetic data on F adsorption on HFO was better described by pseudo-second order model than pseudo-first order model.

Solution pH had a strong effect on F adsorption which decreased continuously from pH 3 to 7. Fluoride adsorption decreased the PZC of HFO. Phosphate and SO42- reduced F adsorption whereas NO3- and Cl- had little effect on F adsorption. Consistent with this data 0.1 M NaCl and 0.1 M Na2SO4 failed to desorb F from HFO whereas 0.1 M NaOH was able to desorb nearly all adsorbed F. Data on zeta potential and PZC of HFO and complementary ions effects on F adsorption and desorption showed that F was specifically adsorbed by HFO by an inner-sphere complexation mechanism. Finally, the HFO could be regenerated by leaching the adsorbed F with 0.1 M NaOH solution and reused for at least three times but the F adsorption capacity decreased with repeated use.

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**Table 1**

The models and equations used for the description of batch and column adsorption of F by HFO.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Model | Equation | Graphical method used to calculate model constants | |
| Batch method | Langmuir Isotherm |  |  | |
| Ce = equilibrium concentration of F (mg/L), qe = amount of F adsorbed per unit mass of HFO (mg/g), qmax = maximum amount of F adsorbed per unit mass of HFO (mg/g); KL = Langmuir constant related to the energy of adsorption (L/mg) | | |
| Freundlich Isotherm |  |  | |
| Ce = equilibrium concentration of F (mg/L), qe = amount of F adsorbed per unit mass of HFO (mg/g), KF and n = Freundlich constants (mg/g) (KF is related to the F adsorption capacity of HFO). | | |
| Pseudo-first-order kinetic |  |  | |
| qe = amount of F adsorbed at equilibrium (mg/g); qt = amount of F adsorbed at time, t (min) (mg/g) and k1 = equilibrium rate constant of pseudo-first-order sorption (1/min). | | |
| Pseudo-second-order kinetic |  |  | |
| qe = amount of F adsorbed at equilibrium (mg/g); qt = amount of F adsorbed at time, t (min) (mg/g) and  k2 = equilibrium rate constant of pseudo-second-order (1/min). | | |
| Column method | Thomas model | ln(Co/Ct−1) = kThqoM/Q − kThCot | | kTh and qo were calculated from a plot of ln [(Co/Ct) −1] vs time (t) |
| kTh = Thomas rate constant (mL/min.mg), qo= equilibrium F uptake per g of HFO (mg/g), Co = inlet F concentration (mg/L), Ct = outlet F concentration at time t (mg/L), M = mass of HFO (g), Q = filtration velocity (mL/min) and t = filtration time (min). | | |

**Table 2**

Batch adsorption kinetic parameters of pseudo-first order and pseudo-second order kinetics models for the adsorption of F on seven adsorbents.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Adsorbent |  |  | Pseudo-first order model | | |  | Pseudo-second order model | | |
|  | qe  experimental  (mg F/g) |  | qe  (mg F/g) | k1  x 10-2 (min-1) | R2 |  | qe  (mg F/g) | k2  x 10-2  (g/mg. min) | R2 |
|  |  |  |  |  |  |  |  |  |  |
| Purolite A520E | 2.32 |  | 0.93 | 0.1 | 0.65 |  | 1.81 | 7.00 | 0.99 |
|  |  |  |  |  |  |  |  |  |  |
| Purolite A502PS | 2.87 |  | 1.38 | 0.4 | 0.90 |  | 2.62 | 1.90 | 0.99 |
|  |  |  |  |  |  |  |  |  |  |
| Purolite FerrIX A33E | 2.96 |  | 0.74 | 0.3 | 0.96 |  | 2.78 | 4.30 | 0.99 |
|  |  |  |  |  |  |  |  |  |  |
| HFO | 5.55 |  | 2.34 | 1.5 | 0.97 |  | 5.68 | 2.40 | 0.99 |
|  |  |  |  |  |  |  |  |  |  |
| ZH | 3.40 |  | 0.51 | 0.9 | 0.94 |  | 3.4 | 6.60 | 0.99 |
|  |  |  |  |  |  |  |  |  |  |
| Dowex21K | 4.90 |  | 1.59 | 1.4 | 0.91 |  | 5.08 | 1.80 | 0.99 |
|  |  |  |  |  |  |  |  |  |  |
| Aluminium oxide | 0.73 |  | 0.42 | 0.2 | 0.96 |  | -4.36 | 0.01 | 0.02 |

**Table 3**

Fruendlich isotherm parameters for F adsorption on seven adsorbents.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Parameters | Purolite A520E | Purolite A500PS | Purolite A33E | Dowex21K | Aluminum oxide | ZH | HFO |
| KF  (mg F/g) (L/mg F)1/n | 0.11 | 0.26 | 0.0008 | 0.56 | 0.0004 | 0.48 | 2.69 |
| n | 0.57 | 0.57 | 0.25 | 0.74 | 0.22 | 0.94 | 1.63 |
| R2 | 0.94 | 0.98 | 0.66 | 0.81 | 0.84 | 0.90 | 0.80 |

**Table 4**

HFO column adsorption model parameters and breakthrough adsorption capacities (filtration velocity 2.5 m/h)

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Models and parameters | Bed height (cm) | |  | pH | |  | Influent F concentration, C0 (mg/L) | |
|  | (C0 10 mg/L,  pH 7,  HFO 10%) | |  | (Bed height 24 cm, C0 10 mg/L, HFO 20%) | |  | (Bed height 24 cm, pH 5, HFO 20%) | |
|  |  | |  |  | |  |  | |
|  | 12 | 24 |  | 5.0 | 7.0 |  | 10 | 30 |
|  |  |  |  |  |  |  |  |  |
| Thomas Model |  |  |  |  |  |  |  |  |
| kTh (mL/min.mg) | 16.99 | 9.69 |  | 1.38 | 3.38 |  | 1.38 | 0.37 |
| qo (mg/g HFO) | 1.19 | 1.12 |  | 3.43 | 1.47 |  | 3.43 | 12.70 |
| R2 | 0.981 | 0.834 |  | 0.945 | 0.949 |  | 0.945 | 0.793 |
|  |  |  |  |  |  |  |  |  |
| ANN-Thomas Model |  |  |  |  |  |  |  |  |
| kTh (mL/min.mg) | 16.73 | 9.3 |  | 1.28 | 3.27 |  | 1.28 | 0.36 |
| qo (mg/g HFO) | 1.18 | 1.10 |  | 3.57 | 1.47 |  | 3.57 | 12.72 |
| R2 | 0.999 | 0.979 |  | 0.996 | 0.998 |  | 0.996 | 0.982 |
|  |  |  |  |  |  |  |  |  |
| Breakthrough adsorption capacity, qe (mg/g HFO) | 1.01 | 0.90 |  | 2.12 | 1.28 |  | 2.12 | 7.06 |

**Figure captions**

Fig. 1. XRD patterns of HFO.

Fig. 2.The SEM images of (a) HFO and (b) HFO+F (with magnification of 100X (Left hand side) and 5000X (right hand side).

Fig. 3. FTIR spectra of HFO (a) before and (b) after F adsorption.

Fig. 4. Effect of (a) contact time and (b) resin dose on the removal of F (initial F concentration 10 mg F/L) by seven adsorbents (adsorbent dose 1g/L).

Fig. 5. Changes in solution pH during F adsorption on HFO.

Fig. 6. Influence of final pH of HFO suspension on (a) F adsorption and (b) zeta potential at the HFO/solution interface.

Fig. 7. Effect of complementary anions on F adsorption by HFO (initial F concentration 10 mg F/L and adsorbent dose 1g/L).

Fig. 8. Breakthrough curves for different inlet F concentrations, pHs, bed heights, and HFO% (filtration velocity 2.5 m/h). Experimental values are shown by data points, and model predictions are represented by lines.

Fig. 9. (a) Desorption of F using three reagents in batch experiments and (b) breakthrough curves for F before and after desorption of F using 0.1 M NaOH in column experiments (bed height 24 cm, initial F concentration 10 mg/L, filtration velocity 2.5 m/h).

**Intensity (CPS)**

**2θ (Cu-Kα radiation)**

**Fig. 1.**

**(a)**

C:\Users\11519257\AppData\Local\Microsoft\Windows\Temporary Internet Files\Content.Word\HFO+F 02.tif

C:\Users\11519257\AppData\Local\Microsoft\Windows\Temporary Internet Files\Content.Word\HFO 02.tifC:\Users\11519257\AppData\Local\Microsoft\Windows\Temporary Internet Files\Content.Word\HFO+F 07.tif

**1 µm**

**1 µm**

**(b)**

**1 µm**

**1 µm**

**Fig. 2.**



**Fig. 3.**





**Fig. 4.**



**Fig. 5.**





**Fig. 6.**



**Fig. 7.**

 

 



**Fig. 8.**





**Fig. 9.**