Modeling and experimental approaches for determining fluoride diffusion kinetics in bone char sorbent and prediction of packed-bed groundwater defluoridator performance

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ABSTRACT

Fluoride (F) in groundwater (GW) in excess of 1.5 mg/L is a globally distributed problem impacting the health of hundreds of millions of people, many of whom cannot access centralized treatment infrastructure. Animal (e.g., cow) bone char has received emerging interest as a low-cost F sorbent for use in decentralized household and community water treatment. Pilot column tests using full-sized granular bone char particles can be used to assess treatment performance of fixed-bed contactors, but are costly, time consuming, and require large amounts of test water. Rapid small-scale column tests (RSSCTs) can be used to simulate F uptake in bone char contactors if the relationship between F intraparticle diffusion kinetics and bone char particle size is known. Two common approaches to the RSSCT assume either constant (CD) or linear proportional (PD) sorbate diffusivity as a function of sorbent particle size. This study used experimentally determined pseudo-equilibrium and kinetic F sorption data in model groundwater as inputs to the homogeneous surface diffusion model (HSDM) to determine F intraparticle diffusion coefficients for different-sized bone char particles, and to fit RSSCT and pilot column breakthrough data to evaluate CD and PD approaches. Results of this study, corroborated by incorporation of additional literature data, indicate approximately linearly proportional diffusivity of F as a function of bone char particle size. Congruently, the PD-RSSCT approach provided a superior simulation of pilot column F breakthrough compared to the CD-RSSCT. PD-RSSCT breakthrough data closely matched pilot breakthrough on a scaled service time basis up to around 500 bed volumes, corresponding to a relative F breakthrough of about 40%, and provided a slightly conservative indicator of F removal thereafter. The PD-RSSCT was compared with a hybrid modeling and empirical workflow using the HSDM with experimentally determined pseudo-equilibrium and kinetic parameter inputs as time-and-cost-saving approaches to evaluating full-sized groundwater treatment system performance. This comparison and a sensitivity analysis of HSDM input parameters used in the hybrid workflow indicated that greater precision can be obtained using the PD-RSSCT.

Introduction

Naturally-occurring fluoride (F) contamination in groundwater is a globally distributed problem. It is estimated that over 200 million people in more than 30 countries worldwide are exposed to harmful levels of fluoride through groundwater (Amini et al., 2008; Ayoob et al., 2008; Fawell et al., 2006; Kimambo et al., 2019). The World Health Organization Guideline Value for fluoride in drinking water is 1.5 mg/L (WHO, 2011). Fluoride intake above this level can lead to severe dental fluorosis, evident in the staining and pitting of teeth. Above 10 mg/L, crippling skeletal fluorosis occurs where bones become deformed and brittle (Fawell et al., 2006; Irigoyen-Camacho et al., 2016). Young children are at an increased risk for these effects especially if undernourished, which is common in low-resource regions (Irigoyen-Camacho et al., 2016). The advancement of affordable, decentralized community and point-of-use defluoridation technologies is necessary to provide safe drinking water in these settings.

The use of pyrolyzed animal bones (bone char) as a low-cost sorbent for removing excessive F from water has drawn considerable interest in recent years (Abe et al., 2004; Alkurd et al., 2019; Brunson and Sabatini, 2014; J. Kearns et al., 2018; Kennedy Anthony and Arias-Paic, 2020; Leyva-Ramos et al., 2010; N. A. Medellin-Castillo et al., 2007; N. A. Medellin-Castillo et al., 2007).
A. Medellin-Castillo et al., 2014; Nahum Andres Medellin-Castillo et al., 2016; Nigri et al., 2017; Rojas-Mayorga et al., 2013). Most studies have been conducted in batch format using crushed bone char, for example bottle-point isotherm tests. Only a few studies (Brunson and Sabatini, 2014; J. Kearns et al., 2018; Kennedy Anthony and Arias-Paic, 2020; Nigri et al., 2017) have evaluated bone char sorbents in fixed-bed (column) configuration, although fixed-bed contactors are a common configuration of groundwater treatment systems. The dynamics of sorption differ between batch and column systems. For example, crushed sorbent is exposed to a declining aqueous concentration gradient of sorbate in batch contactors as equilibrium is approached, whereas sorbent located in the mass transfer zone of a column contactor is exposed to an increasing aqueous sorbate concentration gradient. Noting these differences underscores the importance of column testing for deriving design and operational specifications of fixed-bed contactors.

Pilot column tests using granular sorbent with the same particle diameter (dₚ), bed depth (L), and empty bed contact time (EBCT) as the full-scale contactor provide the most accurate simulation of water treatment systems. However, pilot testing is costly in terms of time, money, and experimental resources (e.g., the experimental duration and the volume of test water required to obtain a complete sorbate breakthrough profile). The rapid small-scale column test (RSSCT) method was developed to simulate full-scale water contaminant removal in a fraction of the time and using a fraction of the experimental resources necessary for pilot testing. It does so by employing the concept of similitude to scale the sorption process using dimensionless parameters developed from the dispersed-flow pore and surface diffusion model (PSDM) (John C. Crittenden et al., 1986; John C. Crittenden et al., 1987). The RSSCT was originally developed to simulate organic compound removal by granular activated carbon (GAC), but has been extended to other sorbates and sorbents such as arsenic and granular ferric hydroxide (GFH) (Badruzzaman et al., 2004a; Westerhoff et al., 2005). There are two common RSSCT design approximations – proportional diffusivity (PD) and constant diffusivity (CD). The CD approach assumes that sorbate intraparticle diffusion kinetics does not depend on sorbent particle size, whereas the PD approach assumes a linearly proportional dependence of sorbate intraparticle diffusion kinetics on sorbent particle size. At this time there is no clearly superior approach for all situations (Summers et al., 2014).

To our knowledge, only two studies have applied RSSCT methods for simulating F sorption by unmodified bone char. Brunson and Sabatini (2014) used the CD-RSSCT approach and found good agreement between F breakthrough curves from columns containing bone char granules of slightly different average particle sizes 0.64 mm (log mean 0.54 mm) and 0.30 mm (log mean 0.29 mm). Kennedy and Arias-Paic (2020) (Kennedy Anthony and Arias-Paic, 2020) conducted CD- and PD-RSSCT experiments for comparison with pilot column results. They found that the CD approach better approximated the shape of the pilot column breakthrough curve but substantially underestimated F sorption capacity, while the PD approach provided an accurate simulation of early F breakthrough (i.e., up to C/Cₒ of around 20%) but underpredicted F removal thereafter. One objective of this study was to resolve the discrepancy of whether the CD or PD RSSCT approach can provide an accurate simulation of F sorption by bone char through column testing, as well as kinetic tests to quantify the relationship between F intraparticle diffusivity and bone char particle size.

The second objective of this study was to evaluate a mass transfer modeling approach for predicting F removal in bone char columns. If reliably accurate, the use of model-based methods to simulate different treatment system design and performance scenarios could provide additional savings of time and experimental resources.

Sorption models are based on equilibrium parameters (e.g., Freundlich isotherm coefficients Kₑ and 1/n) as well as external and internal mass transfer coefficients describing film diffusion (kₒ) and pore (Dₚ) and/or surface (Dₛ) intraparticle diffusion. One model that has been used to describe sorption in fixed-bed contactors is the homogeneous surface diffusion model (HSDM), for example, arsenate sorption by GFH (Badruzzaman et al., 2004a; Sperlich et al., 2008) and organic micropollutant adsorption by GAC or biochar (Joshua Kearns et al., 2020; Piazzioli and Antonelli, 2018). Surface diffusion might be an apt conceptualization of intraparticle transfer of arsenate, which forms weak inner-sphere complexes with sorption sites on the GFH surface and is hypothesized to “hop” from site to site as it diffuses through the pore network (Badruzzaman et al., 2004a; Dale et al., 2016). Analogies between the arsenate-GFH and F-bone char systems include a hydrated anion sorbate forming weak inner-sphere interactions with sorbent surface sites. F sorption by bone char is believed to occur by electrostatic interaction and ion exchange, and has been demonstrated to be reversible (Abe et al., 2004; N. A. Medellin-Castillo et al., 2007; N. A. Medellin-Castillo et al., 2014). Therefore, a similar “site-hopping” mechanism of surface diffusion could govern intraparticle mass transfer of F in bone char, which suggests that the HSDM might accurately represent this system.

This study compared an empirical approach to simulating F removal from groundwater by full-scale bone char contactors using RSSCTs and pilot column testing with a hybrid approach that used the HSDM with experimentally determined equilibrium and kinetic parameters as model inputs. A sensitivity analysis was performed on the individual HSDM input parameters to inform the practicality and precision of the hybrid approach. The Fixed-Bed Adsorption Simulation Tool (FAST 2.1) (Schimmelpfennig and Sperlich, 2011) was used as a convenient freeware user interface for solving HSDM calculations. The motivation for this research is to provide water treatment practitioners with a simplified, economical workflow for conducting fixed-bed bone char contactor design and operational scenarios.

Materials and methods

Model groundwater

A model groundwater was prepared for all experiments using lab-grade salts (CaCl₂•2H₂O, NaF, MgCl₂•6H₂O, KCl, Na₂SO₄) and deionized (DI) water to obtain the following approximate ion concentrations: Ca²⁺ 12 mg/L, Mg²⁺ 1.2 mg/L, Na⁺ 34 mg/L, K⁺ 10 mg/L, Cl⁻ 37 mg/L, SO₄²⁻ 51 mg/L, F⁻ 7.5 mg/L. Previous work established that chloride and sulfate anions present at these concentrations are unlikely to compete for F sorption on bone char (N. A. Medellin-Castillo et al., 2014). The model groundwater was prepared following a representative groundwater report from Alto Río Laja Aquifer in Guanajuato State, Mexico (Knappett et al., 2018). Ion concentrations were verified by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis (Perkin Elmer ICP-OES Model 8000 Dual View, Waltham, MA) in the Environmental and Analytical Testing Services Laboratory (North Carolina State University, Raleigh, NC). Model groundwater pH was adjusted to pH 8.4 using 1 M sodium hydroxide solution and monitored before and after column tests by a Thermo Scientific™ Orion™ 3-Star pH Meter at room temperature (23°C).

Bone char preparation

Bone char samples used in this study were produced at the Caminos de Agua field laboratory (San Miguel de Allende, Mexico) as described previously (J. Kearns et al., 2018). In brief, cow bones were cut into pieces, sun dried for several days, and loaded into a 95 L (25 gal) lidded steel drum retort. The retort was heated to reach an internal temperature of 570 °C over a two-hour period (4.5 °C/min heating rate), held at approximately 570 °C for 45 min, then cooled rapidly with water to handling temperature. Textural characteristics of bone char produced by this method, including elemental content, surface area, and scanning electron micrography, were reported previously (J. Kearns et al., 2018).
Bone char pieces were ground by hand with a mortar and pestle and wet-sieved to collect the fractions retained between #8 and #30 US Standard sieves (log-mean particle diameter 1.29 mm), #60 and #100 (log-mean particle diameter 0.196 mm), and #100 and #200 (log-mean particle diameter 0.108 mm) for use in experiments.

**Bottle-point isotherm testing**

Pseudo-equilibrium F sorption properties of bone char were determined from bottle-point isotherm batch tests. Bone char samples were oven dried overnight at 105°C and cooled in a desiccator prior to weighing into 50 mL falcon tubes (VWR). Mass of bone char to be added was based on an estimated sorption capacity of 1.8 mg F/g BC (Leyva-Ramos et al., 2016; N. A. Medellin-Castillo et al., 2014). Individual tubes were dosed at 0.0, 0.9, 1.6, 2.2, 2.9, and 3.6 gs per liter of the different bone char size fractions with 20% duplicate vials. Initial F concentration was 8 mg/L. Isotherm vials were placed on a tumbler at ambient laboratory temperature (23°C) and F uptake was quantified after 14 days. Preliminary batch tests conducted for 18 days and 21 days showed no significant additional F uptake. Therefore 14 days was considered sufficient contact time for attaining pseudo-equilibrium conditions. Suspensions were filtered using 0.45 μm Whatman™ nylon syringe filters, and F was quantified in the filtrate using a portable Hach Colorimeter (DR850) following the SPADNS 2 reagent method.

**Kinetic testing**

To determine F sorption kinetics of the different sized bone char particles the same F test solution used in bottle-point isotherm tests was circulated through a differential column batch reactor from a completely mixed feed container (6.7 L). The DGBR apparatus (Figure S1) consisted of an 8 L glass carboy stirred continuously by a large polytetrafluoroethylene (PTFE) coated magnetic stir bar, transparent polypropylene (PP) tubing connected using 0.25-inch stainless steel fittings (Swagelok), a 1-inch (2.54 cm) inner diameter borosilicate glass chromatography column with Teflon end caps (DKW Life Sciences) packed with glass beads and glass wool to contain the bone char (6.7 g, bed volume 10 mL), and stainless steel pump head connected to a gear pump drive with RPM control (Cole-Parmer). The mass of bone char was chosen to result in approximately 50% F removal from the test solution over the duration of the experiment. Test solution was circulated at flow rate of 700 mL/min, corresponding to a loading rate of 83 m/hr. Samples (10 mL) were collected periodically over a two-week period. The total mass of F removed for analysis was kept below 2% of the initial mass in solution (Badruzzaman et al., 2004b).

**Column testing**

The pilot column test was designed based on a full-size bone char contactor made from a refillable cartridge (7.0 cm diameter, 18.0 cm bed depth) fitted into a filter housing and used for household point-of-use water treatment in central Mexico, as described previously (J. Kearns et al., 2018). The pilot column was comprised of a 1-inch (2.54 cm) diameter glass chromatography column filled with granular bone char (d_50 1.29 mm) to a depth (L) of 18 cm and with a bed density of 660 kg/m^3 and operated with a 30-minute EBCT. CD- and PD- RSSCTs were designed by equating the Reynolds numbers of the pilot and RSSCT columns and using Eq. (1) to determine small column loading rates (v_f (RSSCT)).

\[
\frac{EBCT_{RSSCT}}{EBCT_{pilot}} = \frac{d_5_{RSSCT}}{d_5_{pilot}}^{1-X} \cdot \left(\frac{v_f_{pilot}}{v_f_{RSSCT}}\right)^{1-X} \tag{1}
\]

For CD, the diffusivity factor X was set to zero, whereas for PD it was set to one. Other inputs to the design of RSSCTs include bone char particle porosity, bed porosity, tortuosity, fluoride molar volume, fluoride liquid diffusivity, and film mass transfer coefficients. These inputs are summarized in Table 1. Inputs for bone char bed density, particle porosity, bed porosity, and tortuosity were obtained from other studies (J. Kearns et al., 2018; Leyva-Ramos et al., 2010). The effective molar volume of a hydrated fluoride anion was adjusted until its liquid diffusivity value matched closely with literature values (Haynes et al., 2016; Leyva-Ramos et al., 2010; Ribeiro et al., 2010). Film mass transfer coefficients were calculated using the Gnielinski correlation (J. C. Crittenden et al., 2012) and correspond closely with other reported values (Leyva-Ramos et al., 2010).

**Results and discussion**

Comparison of CD- and PD- RSSCT for pilot column simulation

Fig. 1 shows F breakthrough data for the pilot column, CD-, and PD-RSSCT experiments. Strong correspondence was observed between F removal in the PD-RSSCT and pilot columns from the onset of breakthrough until around 500 bed volumes (BV) corresponding to F relative breakthrough (i.e., C/C_0) of around 40%. Thereafter, F breakthrough from the PD-RSSCT traced a steeper pattern than the pilot column. In contrast, F removal by the CD-RSSCT traced a “flatter” pattern with an earlier onset of breakthrough compared with the PD-RSSCT and pilot column. The CD-RSSCT simulated the effective F uptake capacity of the pilot column (i.e., the number of BV to a relative F breakthrough of 50%) well, but overestimated F removal at longer service times. The CD-RSSCT reached the WHO drinking water Guideline Value of 1.5 mg/L F in the column effluent with a bed lifecycle of around 370 BV, whereas the PD-RSSCT and pilot columns reached this level with a bed lifecycle of around 450 BV. These results are comparable to the experiments of Kennedy and coworkers (Kennedy Anthony and Arias-Paic, 2020). For a 30-minute EBCT, 450 BV corresponds to a service time of around 9.5 days.

**Table 1**

| Parameter                      | units          | Pilot column | PD-RSSCT | CD-RSSCT |
|-------------------------------|---------------|--------------|----------|----------|
| Q Flow rate                   | ml/min        | 3.04         | 1.27     | 2.81     |
| d_5 Particle diameter         | mm            | 1.29         | 0.108    | 0.196    |
| L Bed density                 | kg/m^3        | 660          | 660      | 660      |
| L Bed depth                   | cm            | 18.0         | 18.0     | 2.74     |
| L Bed diameter                | cm            | 2.54         | 0.476    | 0.953    |
| v_f Loading rate              | m/hr          | 0.360        | 4.28     | 2.36     |
| EBCT Empty bed contact time   | s             | 30 min       | 152 s    | 42 s     |
| τ Particle porosity           |               | 0.46         | 0.46     | 0.46     |
| ε Bed porosity                |               | 0.37         | 0.37     | 0.37     |
| τ Tortuosity                  |               | 2.1          | 2.1      | 2.1      |
| V_0 Fluoride molar volume     | cm^3/mol      | 53           | 53       | 53       |
| D_f Fluoride liquid diffusivity| cm^2/sec      | 1.39e-5      | 1.39e-5  | 1.39e-5  |
| k_f Film mass transfer coeff. | m/sec         | 1.17e-5      | 1.39e-4  | 7.66e-5  |
| Re Reynolds number            |               | 0.37         | 0.37     | 0.37     |
| Bi Biot number                |               | 25           | 25       | 25       |
The results of this study, corroborated by the work of Kennedy et al. (2020) (Kennedy Anthony and Arias-Paic, 2020), indicate that the PD-RSSCT can provide an accurate simulation of fixed-bed bone char contactors when high-to-moderate levels of F removal (i.e., for relative removals of greater than 60 to 70% of F in the influent) are required. If the treatment objective is to keep F levels below the WHO Guideline Value of 1.5 mg/L, based on observations in this study the PD-RSSCT is expected to provide an accurate simulation for treating waters with F concentrations of around 4 mg/L or greater. For treating waters with F concentrations below 4 mg/L, the PD-RSSCT can provide a conservative estimate of bone char contactor performance.

In order to further examine the robustness of the RSSCT approach and interrogate the hypothesis of non-constant diffusivity, equilibrium and kinetic parameters were measured experimentally and inputted into the HSDM to obtain model fits to RSSCT and pilot column F breakthrough data, as discussed in the following sections.

Bottle-point isotherm tests

Fig. 2 displays F uptake in bottle-point isotherm tests using bone char samples with different particle sizes used in pilot column and RSSCT experiments, respectively. The Freundlich isotherm model (Eq. (2)) was used to fit pseudo-equilibrium adsorption data and obtain Freundlich parameters ($K_F$, 1/$n$). The Freundlich model was selected for two reasons. One, the Freundlich model provided slightly better fits to isotherm data than the Langmuir model. Freundlich $R^2$ values ranged from 0.94 to 0.99, whereas Langmuir $R^2$ values ranged from 0.92 to 0.98. Second, this study made extensive use of sorption data from other studies to validate our approach (discussed in later sections), and Freundlich isotherm values are the most commonly reported. The smallest bone char particle size showed slightly higher F sorption capacity as indicated by the respective Freundlich capacity terms (i.e., $K_F$ values). The $+$/− values associated with Freundlich parameters shown in Fig. 2 represent 95% confidence intervals based on fits of the Freundlich model to batch test data.

$$q_e = K_F C^{1/n}$$  \(2\)

In Eq. (2), $q_e$ is the pseudo-equilibrium F solid phase concentration in mg/g, $C_e$ is the pseudo-equilibrium liquid phase concentration in mg/L, $K_F$ is the Freundlich capacity term in (mg/g)(L/mg)$^{1/n}$, and 1/$n$ is the unitless sorbent heterogeneity term.

Freundlich isotherm parameters obtained in this study compare favorably with other bottle-point isotherm studies. For sorption of F from water at circum-neutral pH using unmodified cow bone char generated at around 600 °C, reported Freundlich parameters typically range from $K_F$ 1.8 to 3.2 (mg/g)(L/mg)$^{1/n}$ and 1/$n$ values range from 0.28 to 0.43 (Brunson and Sabatini, 2014; Leyva-Ramos et al., 2010; N. A. Medellin-Castillo et al., 2007; N. A. Medellin-Castillo et al., 2014; Nigri et al., 2017; Rojas-Mayorga et al., 2013). This study, similar to work by Leyva-Ramos et al. (2010) (Leyva-Ramos et al., 2010), found F sorption capacity to increase modestly with decreasing bone char particle size.

Kinetic tests

Pseudo-equilibrium F sorption parameters determined from bottle-point isotherm tests were used as guides for fitting F sorption kinetics data obtained from DCBR experiments with different-sized bone char particles (Fig. 3). The FAST 2.1 software interface (Schimmpelfennig and Sperlich, 2011) was used to iteratively solve the HSDM while adjusting inputs ($K_F$, 1/$n$, $D_C$) in order to obtain good visual model fits to DCBR data. Due to the high hydraulic loading rate used in DCBR tests (83 m/hr) it was assumed that F concentration at the outer particle surface was approximately equal to its concentration in the bulk liquid, thereby minimizing film mass transfer resistance (Hand et al., 1983). Accordingly, the $k_t$ term was omitted from HSDM fits to DCBR data.

In the case of $d_p$ 0.108 mm it was necessary to reduce $K_F$ to 3.00 (mg/g)(L/mg)$^{1/n}$, which is below the 95% confidence interval range obtained from bottle-point isotherm tests (3.55 $+$/− 0.12 (mg/g)(L/mg)$^{1/n}$) to obtain a good visual fit of F kinetic data. In the cases of $d_p$ 1.29 and 0.196 mm, the $K_F$ values used to fit kinetic data fell within the 95% confidence interval ranges obtained from bottle-point isotherm tests. For
all particle sizes $1/n$ values used to fit kinetic data fell within the 95% confidence interval range obtained from bottle-point isotherm tests. Diffusivity values obtained from HSDM fitting of DCBR data were $1.5 \times 10^{-13}$ m$^2$/sec for $d_p 1.29$ mm, $2.5 \times 10^{-14}$ m$^2$/sec for $d_p 0.196$ mm, and $1.0 \times 10^{-14}$ m$^2$/sec for $d_p 0.108$ mm, indicative of non-constant diffusivity.

The bone char particle scaling factor (i.e., $d_p$ piloc/$d_p$ RSSCT) was 11.9 while the ratio of the largest and smallest $D_s$ values obtained from model fits was 15, suggesting approximately linear proportional diffusivity.

**HSDM fitting to column data**

Pseudo-equilibrium ($K_F$, $1/n$) and kinetic ($D_s$) parameters obtained from bottle-point and DCBR experiments were used as guides for HSDM inputs to obtain model fits to PD-RSSCT and pilot column F breakthrough data (symbols) and HSDM model fits (dashed lines) using the parameter inputs shown. “INF” signifies influent F concentration.
breakthrough data. Fig. 4 displays F breakthrough data, HSDM model fits, and the pseudo-equilibrium and kinetic parameter inputs used to obtain the fits. In order to obtain a good visual model fit to RSSCT breakthrough data it was necessary to tune $K_F$ and 1/n inputs slightly compared with values obtained from bottle-point and DCBR tests. A good visual fit to pilot column breakthrough data was obtained using $K_F$, and 1/n inputs consistent with those obtained from bottle-point and DCBR tests. $D_p$ values obtained from fitting DCBR data for the three particle sizes were used unchanged as inputs to the HSDM in fitting column breakthrough data. This lends further support to the hypothesis of non-constant diffusivity in fixed-bed bone char contactors. However, to obtain better visual fits to breakthrough data, particularly for the early portion of F breakthrough, it was necessary to invoke increased film mass transfer resistance. This was accomplished by decreasing the film mass transfer coefficients ($k_f$ model inputs) relative to the calculated values listed in Table 1.

To further evaluate the robustness of these observations, literature data were obtained from column studies that used different sized bone char particles. Brunson and Sabatini (2014) (Brunson and Sabatini, 2014) conducted bottle-point isotherm and column tests using bone char with particle sizes approximately 0.54 mm and 0.29 mm. Good visual fits of the HSDM to their column data were obtained using Freundlich parameters near or within range of their batch test data and $D_p$ values falling between those used to fit column data in the present study (Fig. 5 panels a and b). Similar to this study it was necessary to invoke additional film mass transfer resistance (by lowering $k_f$ model inputs below calculated values) to obtain good visual fits to the early portion of F breakthrough curves. F breakthrough data were also obtained from pilot ($d_p=0.92$ mm) and PD-RSSCT ($d_p=0.108$ mm) column experiments performed by Kennedy and Arias-Paic (2020) (Kennedy and Arias-Paic, 2020). Bottle-point isotherm data are not available for their bone char and groundwater. However, visual fits of the HSDM to their column data were obtained by inputting interpolated $D_p$ values as guides and adjusting them along with Freundlich parameters (Fig. 5 panels c and d). Once again, for obtaining good visual fits to early breakthrough it was necessary to invoke additional film mass transfer resistance via reduced $k_f$ inputs.

It is not surprising that film mass transfer resistance played a small but noticeable role in the shape of F breakthrough data observed in this study and those of Kennedy and Arias-Paic (2020) and Brunson and Sabatini (2014). The Biot number expresses the relative contributions of external (i.e., film) and internal mass transfer resistance. By convention, film mass transfer resistance can be considered negligible for Biot numbers greater than 30 (Hand David et al., 1984), although other researchers consider film mass transport to be important at Biot numbers up to 100 (Traegner and Suidan, 1989). The Biot numbers for pilot and PD-RSSCT columns in this study were 25, and were 31 and 29 for pilot and PD-RSSCT column experiments, respectively, conducted by...
Kennedy and Aria-Paic (2020). Biot numbers for the column tests carried out by Brunson and Sabatini (2014) were 16 ($d_p$ 0.54 mm) and 21 ($d_p$ 0.29 mm). In their study of arsenate sorption by GFH particles of different sizes (and Biot numbers ranging from 19 to 190), Badruzzaman et al. (2004) (Badruzzaman et al., 2004a) also found it necessary to invoke additional film mass transfer resistance by reducing $k_f$ values used in HSDM model fits by around one order of magnitude, and noted that this phenomenon had also been observed for organic compound adsorption by GAC.

Additional $D_f$ values for F sorption by bone char were obtained by fitting the HSDM to kinetic data extracted from the literature. Nigri et al. (2017) (Nigri et al., 2017) obtained F sorption kinetic data by analyzing water samples from agitated batch reactors containing bone char particles with average diameter of 1.32 mm at prescribed time intervals ranging from approximately one to 96 h. Leyva-Ramos et al. (2010) (Leyva-Ramos et al., 2010) used a rotating basket apparatus reactor to obtain F sorption kinetics data for bone char at two particle sizes – 1.29 mm and 0.79 mm. Freundlich parameters obtained from bottle-point isotherm data as reported by Nigri et al. (2017) and Leyva-Ramos et al. (2010) were used as inputs to the HSDM, obtaining good visual fits of the model to sorption kinetics data by modulating $D_f$ inputs (Fig. 6 panels a-c). $D_f$ values obtained using these literature datasets ranged from $2.0 \times 10^{-13}$ m$^2$/s to $3.3 \times 10^{-13}$ m$^2$/s. These values are similar but slightly larger than $D_f$ values obtained in the present study $(1.5 \times 10^{-13}$ m$^2$/s) and by Kennedy and Arias-Paic (2020) $(0.9 \times 10^{-13}$ m$^2$/s) for bone char particles that are around 1 mm in diameter.

Fig. 7 displays $D_f$ values obtained by fitting the HSDM to kinetic and column experiment data collected in the present study and from the literature (Brunson and Sabatini, 2014; Kennedy Anthony and Arias-Paic, 2020; Leyva-Ramos et al., 2010; Nigri et al., 2017) as a function of bone char particle size ($d_p$). The relationship between intraparticle diffusivity and particle size is suggested to be somewhat greater than linear proportionality as indicated by the slope factor of 1.2 shown in the power law regression fit to the data. The 95% confidence intervals of the power law fit to the data are shown in parenthesis – note that this interval encompasses a slope factor of 1.0. Additional kinetic experiments with a wider range of bone char particles are recommended to increase the precision of this relationship, for example to determine possible linear proportional diffusivity. However, the data in Fig. 7 do provide robust support for non-constant, approximately linear proportional diffusivity of intraparticle mass transport of F in bone char sorbents. For the arsenate-GFH system, Badruzzaman et al. (2004) (Badruzzaman et al., 2004a) observed an analogous nonlinear (slope factor 1.4) proportional diffusivity.

**HSDM input parameter sensitivity analysis**

For practitioners who design and operate water treatment systems using bone char to remove excess fluoride it is helpful to have an understanding of the merits and limitations of conducting modeling scenarios using the HSDM. The sensitivity of the HSDM output (i.e., predicted F breakthrough curves) to equilibrium and kinetic input parameters can underscore important limitations on the reliance on modeling over empirical approaches to predicting and assessing fixed-bed bone char contactor performance.

As an illustrative exercise, consider a hypothetical contactor using granular bone char with an average particle diameter of 1 mm used to treat water containing 8 mg/L F at a 15-minute EBCT with the objective to produce water below the WHO Guideline Value of 1.5 mg/L F. A base-case and ranges of equilibrium ($K_F$, $1/n$) and parameters ($K_F$, $1/n$, $D_f$) parameter inputs to the HSDM were selected from consideration of the experimental values obtained in this study and from the literature to reflect typical, expected values. The base-case inputs, with outer ranges shown in parenthesis, were as follows: $D_f$ 1.2 $\times 10^{-13}$ m$^2$/s (0.7 $\times 10^{-13}$ to 3.0 $\times 10^{-13}$ m$^2$/s), $k_f$ 5.0 $\times 10^{-6}$ m$^2$/s (2.0 $\times 10^{-6}$ to 20 $\times 10^{-6}$ m$^2$/s), $K_F$ 3.0 (mg/g)(L/mg)$^{1/n}$ (2.0 to 4.0 (mg/g)(L/mg)$^{1/n}$), $1/n$ 0.4 (0.3 to 0.5).

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**Fig. 6.** F sorption kinetic data for bone char with different particle sizes (symbols). HSDM fits (dashed lines) were obtained by inputting Freundlich parameters ($K_F$, $1/n$) and adjusting $D_f$ to obtain good visual correspondence with data. Panel (a) data were taken from Nigri et al. (2017) (Nigri et al., 2017). Panels (b) and (c) data were taken from Leyva-Ramos et al. (2010) (Leyva-Ramos et al., 2010). Bottle point isotherm values from the same studies are shown for comparison with the inputs used to obtain model fits to kinetic data.
Fig. 8 displays base-case and outer-range HSDM predicted F breakthrough curves for the hypothetical bone char contactor. Equilibrium and kinetic model inputs were varied individually to obtain predicted F breakthrough scenarios. Bed lifecycle, defined as the predicted number of bed volumes treated until the effluent F concentration reached 1.5 mg/L (BV$_{1.5}$), is used for comparing the different modeling scenarios. In the base-case scenario the BV$_{1.5}$ is 337 BV. BV$_{1.5}$ values for outer-range model inputs varied from 251 to 441 BV for $D_s$, 304 to 349 BV for $k_f$, 182 to 585 BV for $K_F$, and 268 to 415 BV for $1/n$. Thus, under these modeling scenarios, HSDM output sensitivity, defined as the breadth of predicted BV$_{1.5}$ values between outer-range inputs, increased in the order $k_f < 1/n < D_s < K_F$.

A treatment objective of 1.5 mg/L for a source water containing 8 mg/L F represents a relative ($C/C_0$) breakthrough of just under 20%. It is important to note that the HSDM output sensitivity to the different inputs can vary for lower or higher levels of relative F breakthrough. The change in model sensitivity to $K_F$ input is low across a wide range of F $C/C_0$ values, which is expected since $K_F$ represents effective sorption capacity and its modulation mainly shifts predicted breakthrough curves left or right. Model sensitivity to $K_F$ is the highest of the four parameters under nearly all scenarios, however – underscoring the importance of experimental accuracy and precision necessary for using this parameter as a model input. Model sensitivity to $D_s$ follows a decreasing trend but remains significant up to F $C/C_0$ ~60%, whereas sensitivity to $k_f$ is significant only at F $C/C_0$ values below ~20%. Model sensitivity to $1/n$ is significant and varies modestly across much of the range of likely $C/C_0$ values. These observations are expected as $D_s$, $k_f$, and $1/n$ affect F sorption kinetics and therefore breakthrough curve shape.

**Workflow recommendations for fixed-bed bone char contactor design**

Studies have demonstrated that bone char preparation conditions, including animal species of bone, bone pretreatment prior to pyrolysis, pyrolysis conditions, and post-pyrolysis bone char treatment (e.g., exposure to acid(s)) can exert profound effects on F uptake capacity (Alkurdi et al., 2019; Brunson and Sabatini, 2009; Chatterjee et al., 2018; Kawasaki et al., 2009; Nahum Andres Medellin-Castillo et al., 2016; Rojas-Mayorga et al., 2013). Likewise, background water characteristics such as pH and the presence of DOM and/or competing sorbates also influences F sorption capacity (Brunson and Sabatini, 2014; N. A. Medellin-Castillo et al., 2007; N. A. Medellin-Castillo et al., 2014).

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| $D_s$ ($10^{-13}$ m$^2$/s) | BV$_{1.5}$  |
|---------------------------|------------|
| 0.7                       | 251        |
| 1.2                       | 337        |
| 3.0                       | 441        |

| $k_f$ ($10^6$ m$^3$/s) | BV$_{1.5}$ |
|------------------------|------------|
| 2.0                    | 304        |
| 5.0                    | 337        |
| 20                     | 349        |

| $K_F$ (mg/g)(L/mg)$^{1/n}$ | BV$_{1.5}$ |
|---------------------------|------------|
| 2.0                       | 182        |
| 3.0                       | 337        |
| 4.5                       | 585        |

| $1/n$ | BV$_{1.5}$ |
|-------|------------|
| 0.3   | 268        |
| 0.4   | 337        |
| 0.5   | 415        |
Therefore, experiments to quantify F sorption using the specific bone char and source water combination of interest should be used to obtain treatment system design inputs. Representative experimental water sample(s) should be obtained to match source water background characteristics as well as expected F levels.

One approach to obtaining treatment system design specifications would be to conduct (pseudo-)equilibrium and kinetic tests of F uptake using the bone char and water combination of interest. These experiments would provide input parameters (K, D) to the HSDM for generating predicted breakthrough curves used to design and operate treatment units. A second approach would be to conduct a PD-RSSCT experiment using the bone char and water combination of interest and use the results directly as a guide to treatment system design and operation specifications. Comparison of Fig. 1 and Fig. 8 suggests that the latter approach is more reliable for predicting treatment system performance with precision.

Conclusions

This study compared CD- and PD- RSSCT methods for simulating F removal from model groundwater in granular bone char pilot columns. F removal by the PD-RSSCT closely matched pilot breakthrough on a scaled service time basis up to around 500 BV, corresponding to a relative breakthrough (C/C0) of around 40%, and provided a slightly conservative indicator of F removal thereafter. The CD-RSSCT closely matched the effective F sorption capacity of the pilot column (i.e., the number of BV at 50% breakthrough), but did not capture F sorption kinetics, tracing a “flatter” breakthrough profile than the pilot column. 

Pseudo-equilibrium (Freundlich K, n) and kinetics (k, D) parameters describing F sorption by bone char were obtained from batch experiments. K and n values measured in this study ranged from approximately 3.0 to 3.6 (mg/g)/(L/mg)1/n, and 0.36 to 0.46, respectively, and compared well with other studies of F uptake by unmodified cow bone char generated at around 600 °C. Bone char intraparticle surface diffusion coefficients (D) values were obtained from HSDM fits to DCBR data for bone char particle sizes ranging from 0.108 to 1.29 mm and ranged from 1 × 10−14 to 1.5 × 10−13 m²/s, indicative of approximately linearly proportional (i.e., non-constant) diffusivity with increasing bone char particle size. Literature data used to obtain additional pseudo-equilibrium and kinetic data provided corroborating evidence of near-linearly proportional diffusivity as a function of bone char particle size.

Obtaining the best visual fits of the HSDM to PD-RSSCT and pilot column breakthrough data using measured K, D, and n values required the invocation of film mass transfer resistance exceeding values calculated by the common Gnielinski method for “borderline” Biot numbers around 30. This effect is most consequential for treatment objectives that fall within early breakthrough (C/C0 < 20%). A sensitivity analysis of HSDM inputs revealed increasing sensitivity in the order k < 1/n < D < K. For a given water-bone char combination, the number of BV that could be treated to an effluent F concentration of 1.5 mg/L varied substantially over the ranges of values that are typical for 1/n, D, and K, and even over the ranges of precision with which these parameters can be determined experimentally. Accordingly, it is preferable to use PD-RSSCT experiments to simulate full-scale treatment system performance rather than a hybrid approach of predicting F breakthrough using the HSDM with inputs obtained from batch experiments.

This study advances savings in time, labor, and experimental resources in support of implementation of decentralized water treatment in low-resource settings.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.wroa.2021.100108.

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