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Predicting the propagation of concentration and saturation fronts in fixed-bed filters

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**Abstract**

The phenomenon of adsorption is widely exploited across a range of industries to remove contaminants from gases and liquids. Much recent research has focused on identifying low-cost adsorbents which have the potential to be used as alternatives to expensive industry standards like activated carbons. Evaluating these emerging adsorbents entails a considerable amount of labor intensive and costly testing and analysis. This study proposes a simple, low-cost method to rapidly assess the potential of novel media for potential use in large-scale adsorption filters. The filter media investigated in this study were low-cost adsorbents which have been found to be capable of removing dissolved phosphorus from solution, namely: i) aluminum drinking water treatment residual, and ii) crushed concrete. Data collected from multiple small-scale column tests was used to construct a model capable of describing and predicting the progression of adsorbent saturation and the associated effluent concentration breakthrough curves. This model was used to predict the performance of long-term, large-scale filter columns packed with the same media. The approach proved highly successful, and just 24-36 hours of experimental data from the small-scale column experiments was found to provide sufficient information to predict the performance of the large-scale filters for up to three months.

**Keywords:** Low-cost adsorbents, adsorption, phosphorus, wastewater treatment
Nomenclature

a Time constant in Eqn. 6/Eqn. 13
a* Time constant in Eqn. 7/Eqn. 14
a** Time constant in Eqn. 8/Eqn. 15
A Constant of proportionality in Eqn. 12 (mg g\(^{-1}\))
B Constant of system heterogeneity in Eqn. 12
C Sorbate concentration in bulk solution (mg L\(^{-1}\))
C\(_b\) Breakthrough concentration (mg L\(^{-1}\))
C\(_e\) Sorbate concentration of filter effluent (mg L\(^{-1}\))
C\(_o\) Sorbate concentration of filter influent (mg L\(^{-1}\))
k\(_{BA}\) Bohart-Adams rate constant (L mg\(^{-1}\) min\(^{-1}\))
M Mass of adsorbent (g)
N Residual sorption capacity of bed (mg L\(^{-1}\))
N' Fractional residual sorption capacity (N/N\(_0\))
N\(_0\) Sorption capacity of bed at equilibrium (mg L\(^{-1}\))
N\(_t\) Time dependent sorption capacity of bed (mg L\(^{-1}\))
Q Filter loading rate (L min\(^{-1}\))
q\(_e\) Equilibrium sorbate concentration per unit mass of adsorbent (mg g\(^{-1}\))
q\(_t\) Time dependent sorbate concentration per unit mass of adsorbent (mg g\(^{-1}\))
t Service time/operating time of bed (min)
t\(_b\) Service time/operating time of bed at breakthrough (i.e. when C\(_e\) = C\(_b\)) (min)
U Flow velocity of solution past adsorbent (cm min\(^{-1}\))
V Volume of solution filtered (L)
V\(_B\) Empty bed volumes of solution filtered
V\(_x\) Filter-bed volume to a bed depth of ‘x’ (L)
Z Filter bed depth (cm)
1. Introduction

Adsorbents are used to remove contaminants from gases and liquids across a diverse range of industries including manufacturing, agriculture, mining, and the treatment of both drinking water and municipal wastewater (Dąbrowski, 2001). These industries are naturally interested in achieving optimum treatment efficiency with minimal investment, and there has been a growing interest in 'low-cost adsorbents', which are emerging as alternatives to more expensive and well-established adsorbents such as activated carbons (Babel and Kurniawan, 2003; Crini, 2006). The term ‘low-cost adsorbent’ can be used to describe any abundantly available natural material, industrial byproduct, or waste material which, with minimal processing, has suitable physical and chemical properties to allow for its use in the adsorption of some contaminant of interest (Bailey et al., 1999). Such media often display lower adsorption affinities and saturation capacities than well-established adsorbents, like activated carbons and synthetic resins, but they can nonetheless replace these ostensibly 'better' media with the introduction of minor modifications to adsorption treatment processes (Brown et al., 2000; Reddad et al., 2002) - for example, increasing the hydraulic residence time of a filter bed or increasing the adsorbent dose in a batch reactor. Therefore, despite the fact that low-cost adsorbents often display less favorable adsorption characteristics, their use is nonetheless a highly attractive option because of their ability to ultimately achieve equal treatment efficacy to established adsorbents, but at a greatly reduced cost.

The interaction between an adsorbent material and a dissolved contaminant is a highly complex one, influenced by a multitude of factors such as the physicochemical properties of the adsorbent and target adsorbate (Bockris et al., 1995), the composition and pH of the solution matrix (Faust and Aly, 1998), and the contact mechanism (i.e. batch or through-flow) between adsorbent and adsorbate (Goel et al., 2005). The complexity of these
interactions makes characterizing the adsorptive properties of a medium for a given contaminant a vital first step in assessing its suitability for any intended treatment process. As low-cost adsorbents are often derived from locally sourced natural materials, industrial by-products, and waste materials, there is an inherent variability in their physical structure and chemical composition; no two low-cost adsorbents are exactly alike, and consequently, no two adsorbents will display identical adsorption characteristics. This problem is exacerbated by the fact that there is equal variability in waste streams, and hence there results an unavoidable necessity to characterize and assess every low-cost medium with respect to every potential use.

This poses a significant challenge to researchers, as there is a substantial amount of work involved in characterizing an adsorptive medium prior to its utilization in a real world application. Batch studies, capable of providing a rough approximation of a medium's adsorptive properties, are a common first step in media characterization, and these are an attractive option by virtue of their being cheap and easy to perform, with experimental methods being well established and results being easy to interpret (Crini and Badot, 2008). The primary disadvantage is that batch experimental conditions are radically different to through-flow conditions in real world filter-beds. These studies are, for this reason, unable to provide sufficient information to allow for the design of full-scale adsorption filters (Søvik and Kløve, 2005). Accordingly, when media are to be used in filter-beds, large-scale field studies are widely considered to be the most reliable method of assessing their potential (Pratt et al., 2012). Such tests provide excellent insight into the behavior of real-world adsorption systems; however, the propriety of conducting such large-scale and costly investigations is questionable when using untested and unproven materials. The limitations of both batch studies and large-scale column studies have made rapid small-scale column tests (RSSCTs), of the kind proposed by Crittenden et al. (1986, 1987), an ideal option for initial media
characterization, and it has been repeatedly demonstrated that such tests can provide excellent predictions as to the performances of real-world filter units (Crittenden et al., 1991). RSSCTs involve the use of scaling equations to select media particle sizes, hydraulic loading rates, and empty bed contact times (EBCT, defined as the empty bed volume divided by the flow rate) which will ensure exact similarity of operation between small- and large-scale adsorption filters. Providing exact similitude is achieved, the breakthrough curve (BTC) observed when operating a small-scale filter column should match that of a large-scale filter almost exactly. The advantages of RSSCT type experiments are numerous; they are fast and inexpensive to perform, they require minimal quantities of both adsorbent and adsorbate solution, and perhaps most importantly, they investigate the interaction between adsorbent and adsorbate under through-flow conditions which are representative of intended field conditions, providing insight into both adsorption capacity and kinetics simultaneously. The primary drawback of RSSCTs is that they only make reliable predictions for the very specific case for which they were designed; a single RSSCT corresponds to only one large-scale filter operated in an exactly similar manner (in terms of loading rate and empty bed contact time etc). Also, while it is easy to obtain different particle sizes of activated carbon (the material for which the RSSCT methodology was originally proposed), it may not be possible to scale down many low-cost media due to their physical characteristics.

Mathematical models provide a means by which to make theoretical predictions for any fixed-bed system, and there are a great many mathematical models which have been developed in an attempt to predict the breakthrough behavior of adsorptive media. Xu et al. (2013) summarized some of the most widely used of these in a recent review, listing, amongst others, the Thomas model (Thomas, 1944), the Bohart-Adams (B-A) model (Bohart and Adams, 1920), and the Bed Depth Service Time (BDST) model (Hutchins, 1973). It is interesting to note that the B-A model is often erroneously referred to as the Thomas model;
this has caused considerable confusion (Chu, 2010), even though the former predates the latter by a considerable margin. The B-A model is also the basis of the popular BDST model proposed by Hutchins (1973), which is, essentially, just a simplified rearrangement of the B-A model. It therefore seems reasonable to assert that the B-A model is quite possibly the most popular fixed-bed sorption model in current use. The basic form of the B-A model is as follows:

\[ \ln \left( \frac{C_o}{C_b} - 1 \right) = \ln \left[ \exp \left( k_{BA} N_o \frac{Z}{U} \right) - 1 \right] - k_{BA} C_o t_b \]  

(1)

Where \( C_o \) is the influent concentration, \( C_b \) is the effluent breakthrough concentration at any time, \( t_b \); \( k_{BA} \) is a kinetic constant associated with the B-A model, \( N_o \) is the adsorptive capacity of the medium per unit volume of the bed, \( Z \) is the depth of medium in the filter bed, and \( U \) is the linear flow velocity.

In practice, \( \exp(K_{BA}N_oZ/U) \) is often much larger than one (Al-Degs et al., 2009), and the equation can therefore be simplified by ignoring the unity term on the right hand side of Eqn.1 to yield:

\[ \ln \left( \frac{C_o}{C_b} - 1 \right) = k_{BA} N_o \frac{Z}{U} - k_{BA} C_o t_b \]  

(2)

As stated earlier, Hutchins’ BDST model is based on a rearrangement of the simplified B-A equation (Eqn.2), and proposes a linear relationship between filter-bed depth and filter service time to a given breakthrough concentration. The time to any breakthrough concentration is found by rearranging Eqn. 2 into form \( t=mx+c \), to yield Hutchins’ BDST equation (Hutchins, 1973) as follows:

\[ t_b = \frac{N_o}{C_o U} Z - \frac{1}{K_{BA} C_o} \ln \left( \frac{C_o}{C_b} - 1 \right) \]  

(3)
Mathematical modelling offers more versatility in terms of predicting a wide range of potential fixed-bed arrangements, though this is arguably at the cost of the certainty and reliability that predictions based on experimental observations provide. It would therefore seem logical that a combination of both experimental observation and mathematical modelling would hold promise - providing the versatility of mathematical modelling as well as the certainty associated with experimental results. The BDST modeling approach is a widely implemented example of such a procedure. The BDST approach to filter design involves using experimental data from a number of filter columns to determine the coefficients $N_0$ and $K_{BA}$ in Eqn. 3. The BDST model then allows for designers to use interpolation and extrapolation to make predictions as to the behavior of adsorption systems with different flow rates, bed depths, and influent concentrations to those used to obtain the model coefficients.

The BDST model does not attempt to predict full BTCs, but instead predicts the time at which a certain breakthrough concentration will occur for a given filter depth and flow rate. Were the BDST equation rearranged in an attempt to predict the entire BTC, a sigmoidal function would be obtained, i.e. Eqn. 2. Therefore, the BDST model may fit experimental data at a single breakthrough point, but if extrapolations are made to different breakthrough concentrations, predicted BTCs may vary significantly from observed BTCs. This is particularly true in relation to low-cost adsorbents, which often produce BTCs that deviate significantly from the ideal symmetrical sigmoidal shape predicted by formulae such as that used in the BDST model.

Naturally, with the addition of enough modifying constants, a model can achieve an almost perfect fit to any dataset, but this detracts from the purpose of creating a model; a model should be simple enough to be of practical use, allowing for its easy application by those in industry, but sophisticated enough that the predictions it offers will be of practical use.
Creating a model which adheres to these criteria will necessitate the adoption of various simplifications and assumptions, and depending on the assumptions made, the resultant model will almost certainly only be suitable for only certain adsorption systems (Xu et al., 2013). This is not a limitation, per se, rather just an unavoidable reality, one that necessitates the use of different models for different systems. Striving to create a ‘perfect’ model at the expense of its ever being practically utilized is a wholly academic pursuit if its complexity is such that very few can effectively implement it. This is reflected by the popularity of the simple B-A model, which assumes a rectangular isotherm, while the Thomas model, which assumes a more realistic Langmuir isotherm, and often offers a better fit to experimental data, has seen much less use; Chu (2010) compared the Thomas model to the B-A model and described the former as being “computationally intractable”.

In a recent paper, Callery et al. (2016) found that the long-term performance of large-scale filters packed with low-cost adsorbents could be predicted mathematically using a simple model, which was constructed using 24 hr of experimental data obtained from small-scale column tests. The methods used didn’t require the use of scaling equations, as is generally the case with RSSCTs. Similitude was achieved by using the same media particle sizes and hydraulic loading rates in both the large and small-scale filters. In this way, the small columns were not so much scaled-down versions of large-scale filters, rather they could be considered cylindrical longitudinal-sections of hypothetical large-scale filter-beds. The BTCs obtained from these small-scale filters could be modeled, and extrapolations could be made to predict the performance of large-scale filters using the same media.

While dispensing with the necessity for scaling equations made this method simpler than the RSSCT approach, the advantages of RSSCTs were retained. So too was the disadvantage that there needed to be exact similarity between the small- and large-scale tests. For this reason, there is a necessity to develop this method further before it is capable of predicting the
performance of filters with any bed depth operated at any loading rate, and this need is addressed by this study.
Theory

In through-flow adsorption systems, the mass of adsorbate retained by a filter medium is a function of the contact time between the adsorbent medium and the adsorbate solution. This means that having an understanding of an adsorbent’s kinetic performance is of paramount importance when attempting to design any such system (Qiu et al., 2009). Changing the bed depth of a filter-bed (or adjusting the hydraulic loading rate) will affect the EBCT (used as a measure of the contact time between the adsorbent and the adsorbate solution) which will in turn affect the system’s performance. The BDST model supposes that the relationship between bed depth (and therefore EBCT) and service time – the filter operating time to some defined breakthrough concentration - is a linear one (Hutchins, 1973). This assumption, while often reasonable, was quickly shown to not be valid for all systems (Poots et al., 1976a, 1976b). Curved plots of bed depth vs. service time are not uncommon, and intraparticle diffusion can cause tailing of BTCs (Deokar and Mandavgane, 2015), and non-linear BDST plots which deviate from those predicted by Hutchins’ BDST model (Ko et al., 2000, 2002).

Internal diffusion of adsorbate molecules often becomes a significant factor as a medium’s surface becomes increasingly saturated, or as a result of lengthy filter EBCTs. Hutchins’ BDST model is based on the assumption that intraparticle diffusion and external mass resistance are negligible (Ayoob and Gupta, 2007); this is rarely the case in real-world adsorption systems, where adsorption is seldom controlled solely by surface chemical reactions between the adsorbent and adsorbate (Crini and Badot, 2010). This limitation has been noted before, and attempts have been made to modify the BDST model to make it more universally applicable (Ko et al., 2000, 2002).

In deriving their fixed-bed model, Bohart and Adams (1920) made the assumption that the rate of the adsorption reaction in a fixed bed filter is proportional to the fraction of the
medium’s adsorption capacity which is still retained, and the concentration of adsorbate in
the solution being filtered. They described this relationship as follows:

$$\frac{\partial N}{\partial t} = -kNC \quad (4)$$

$$\frac{\partial C}{\partial Z} = -\frac{k}{U}NC \quad (5)$$

Where $C$ is the adsorbate concentration of the solution being filtered, $t$ the time, $Z$ the filter
bed depth, $U$ the flow velocity of the solution past the adsorbent, and $k$ is a reaction rate
constant; $N$ is the residual adsorption capacity which is assumed to be some fraction, $N'$, of
the adsorptive capacity of the adsorbent, $N_o$ (i.e. $N'=N/N_o$, or $N=N_oN'$).

Eqns. 4 and 5 are based on the assumption that the filter bed has a definite sorption
maximum, $N_o$, which is independent of bed contact time and the duration for which the filter
has operated; at equilibrium Eqn. 4 reduces to a rectangular sorption isotherm (highly
favorable, irreversible adsorption) (Chu, 2010). In reality, it is known that filter-bed
adsorption capacity does change depending on the fluid residence time in the bed (Ko et al.,
2000, 2002) and the duration of filter operation. Increases in bed depth, and consequent
increases in EBCT and service time, allow adsorbate molecules to diffuse deeper into the
adsorbent particles resulting in a consequent increase in bed capacity. To account for this, Ko
et al. (2000, 2002) proposed that a time dependent bed capacity term, $N_t$, could replace the
standard bed capacity term of the BDST model, $N_o$, and presented two possible equations
with which to determine this value:

$$N_t = N_o(1 - e^{-\alpha t}) \quad (6)$$

$$N_t = N_o(1 - e^{-\alpha^*\sqrt{F}}) \quad (7)$$

Where $\alpha$ and $\alpha^*$ are first order and diffusional kinetic rate parameters respectively.
Regardless of the solid-liquid contact mechanism employed (i.e. batch or fixed bed), the equilibrium and kinetic characteristics of an adsorption system remain unchanged (Chu, 2010). With this in mind, just as Eqn. 6 is based on Lagergren’s (1898) pseudo first-order model, following the work of Liu (2008), another possible expression for \( N_t \) is proposed, based on Ho and McKay’s (1999) pseudo second-order model:

\[
N_t = N_o \frac{t}{t + a^{**}} \tag{8}
\]

Where \( a^{**} \) is a fitting parameter associated with second order kinetics; the full derivation of Eqn. 8 can be found accompanying Figure S1 of the supplementary information. It is worth noting that (given the interdependence of bed depth, EBCT, and service time), with different values for the constants \( a, a^*, \) and \( a^{**} \), EBCT could be used in the place of service time, \( t \), in Eqns. 6 - 8. The primary advantage of this being that EBCT is an easily calculable property of a filter, whereas service time must be experimentally determined. This point is also expounded in Figure S1 of the supplementary file accompanying this text.

When \( N_t \) (as defined by one of Eqns. 6, 7 or 8, to be selected on the basis of best fit to the system in question) is substituted for \( N_o \) in Eqn. 3, a modified form of the BDST equation (one which can describe a non-linear relationship between bed depth and service time) is obtained:

\[
t_b = \frac{N_o}{C_o U} - \frac{1}{k_{BA} C_o} \ln \left( \frac{C_o}{C_b} - 1 \right) \tag{9}
\]

This equation can also be rearranged in the form of a modified BA equation to describe sigmoidal breakthrough curves:

\[
\ln \left( \frac{C_o}{C_b} - 1 \right) = \frac{k_{BA} N_o t Z}{U} - k_{BA} C_o t_b \tag{10}
\]
Ko et al. (2000, 2002) demonstrated the utility of this modified BDST model (Eqn. 9), using Eqns. 6 and 7 to determine values for \( N_t \) (to the best of our knowledge, Eqn. 8 has not yet been used for this purpose), however, once the model is rearranged in the form of Eqn. 10 an inherent limitation becomes apparent: the model describes only sigmoidal curves, and is therefore poorly suited to the description of linear to convex BTCs which are commonly observed in fixed-bed studies using low-cost adsorbents.

To address this limitation, Callery et al. (2016) proposed the following model in a recent study:

\[
C_e = C_o - \frac{q_e M}{V_B} \quad (11)
\]

Where \( C_e \) and \( C_o \) are the filter effluent and influent contaminant concentrations respectively, \( M \) is the mass of filter medium, \( V \) is the volume of solution loaded on to the filter, \( B \) is a model constant, and \( q_e \) is the mass of adsorbate adsorbed per unit mass of filter medium, as modeled by:

\[
q_e = AV_B^{\left(\frac{1}{6}\right)} \quad (12)
\]

where \( A \) is a model constant and \( V_B \) is the number of bed volumes of solution filtered.

Callery et al. (2016) found that Eqns. 11 and 12 were well suited to the modeling of non-sigmoidal BTCs, though a limitation of this model is that it does not provide any information regarding the bed depth service time relationship. It is hypothesized that this may be easily addressed; just as Ko et al. (2000, 2002) replaced \( N_o \) with \( N_t \) to modify the B-A/BDST model, \( q_e \) in Eqn. 11/12 could be replaced with an analogous time dependent parameter, \( q_t \). Mirroring Eqns. 6-8, the following expressions for \( q_t \) are obtained:

\[
q_t = q_e \left(1 - e^{-at}\right) \quad (13)
\]
$$q_t = q_e(1 - e^{-a\sqrt{t}}) \quad (14)$$

$$q_t = q_e \frac{t}{t+a^{**}} \quad (15)$$

Again, a, a*, and a** are model constants associated with first order, diffusional, and second order kinetics respectively. Their value in the above equations will depend on whether service time or EBCT is used in the place of t; EBCT will be used in this study.

The adsorbate solution’s concentration will reduce as it travels through the filter bed and, if the flow rate is constant, we can assume that at any depth within the filter, the pore concentrations will depend on the contact time that has elapsed between the solution and the filter medium, (as well as the duration for which the filter has been loaded). The solution adsorbate concentration at any filter depth (i.e. after any EBCT), $C_t$, as opposed to the filter effluent concentration, $C_e$, can be found by substituting $q_t$ for $q_e$ in Eqn 11/12:

$$C_t = C_o - \frac{q_t M}{V_B} \quad (16)$$

Given the linear relationship between filter depth and EBCT, Eqn. 16 can be used to calculate the filter pore concentrations of the adsorbate solution at any depth within the filter-bed after any filter loading, V, and can therefore describe the propagation of concentration fronts within the filter-bed.

Eqn. 16 can also be rearranged to yield a function with similar utility to Hutchins’ BDST model, i.e. one that describes the relationship between bed depth and volume of solution treated to any breakthrough concentration, $C_t$, of interest:

$$V = \frac{q_t M}{B(C_o-C_t)} \quad (17)$$
The filter service time can be found from Eqn. 17 by dividing the volume treated, $V \text{ (L)}$, by the loading rate ($L \text{ s}^{-1}$).

In summary, sigmoidal BTCs and corresponding plots of bed depth vs. service time may be described by Eqns. 10 and 9 respectively, while linear to convex BTCs and corresponding plots of bed depth vs. service time may be described by Eqns. 17 and 16 respectively.
Materials and Methods

Preparation of filter columns

The low-cost adsorbents utilized in this study were aluminum water treatment residual (dried at 105°C for 24 hr and ground to pass a 0.5 mm sieve) and two grades of crushed concrete ("fine", ground to pass 0.5 mm sieve, and "coarse", ground to pass a 1.18 mm sieve but retained by a 0.5 mm sieve). Small bore filter columns of lengths 0.1, 0.15, 0.2, 0.3, and 0.4 m were constructed using HDPE tubing with an internal diameter of 0.0094 m. These columns were packed with each of the aforementioned media, with care being taken to ensure that an equal bulk density was achieved in each filter. Endcaps, consisting of PE syringe barrels packed with a small quantity of glass wool, were fastened by means of a friction fit to the ends of the filter columns, and silicone tubing was connected to the tip of these syringe barrels to provide inlet and outlet lines to the filter columns. Large bore filter columns of length 0.65 m were then constructed in triplicate using uPVC piping with an internal diameter of 0.104 m. These columns were packed to a bed depth of 0.4 m using the same media and same packing density as was used in the small-bore filters. Again, care was taken to ensure that an equal bulk density was achieved in each filter for each medium. Sampling ports were installed through the walls of the large-bore filter columns at bed depths of 0.05, 0.1, 0.18, and 0.25 m from the filter surface. Water samples could also be collected from the outlet at the base of each column.

Operation of filter units

A synthetic wastewater was produced by dissolving $K_2HPO_4$ in tap water to obtain a $PO_4$-P concentration of 1 mg L$^{-1}$ [similar to forest drainage water (Finnegan et al., 2012)]. A peristaltic pump was used to supply this wastewater to the small-bore filter units at consistent flow rates of between 134 and 259 mL hr$^{-1}$ [hydraulic loading rates similar to those found in
high rate trickling filters (Spellman, 2013) or activated carbon adsorbers (Chowdhury, 2013)]

to achieve a variety of filter bed contact times. The small-bore filters were operated
intermittently, in 12 hour on/off cycles, and were fed from the bottom of the vertically
oriented filters to preclude any incidence of wastewater bypassing the filter media. The
effluent from the small-bore columns was collected in 2 hr aliquots using an auto-sampler.
The large-bore filter columns were manually loaded 2-3 days per week with 28 L of the same
synthetic wastewater as used in the small-bore filters. Water samples were collected from the
sampling ports at various intervals, and the effluent from each loading event was collected in
large HDPE containers.

**Data collection and analysis**

Collected effluent samples were passed through 0.45 µm filters and analyzed with a Konelab
nutrient analyzer in accordance with the standard methods (Eaton et al., 1998). With the
influent and effluent PO$_4$-P concentrations determined, medium saturation, $q_e$, was
calculated. Graphs of $q_e$ vs V and $C_e$ vs V were plotted, and Eqn.15 and Eqn.16 were fit to
these experimental data by non-linear regression, using Microsoft Excel’s solver add-in to
minimize the sum of the squares of the errors (ERRSQ):

$$\sum_{i=1}^{n_p} (q_{e,calc} - q_{e,meas})^2 = \text{(18)}$$

Where $q_{e,calc}$ is the model predicted equilibrium solid phase PO$_4$-P concentration and $q_{e,meas}$ is
the measured equilibrium solid phase PO$_4$-P concentration.

**Predicting large-scale filter performance**

With the coefficients A, B, and $a^{**}$ determined from the small-scale column tests, Eqn. 16
was used to predict effluent concentrations and pore water concentrations at multiple depths
within the large-scale filter columns. $V_x$, the volume of the large-scale filter to a depth of ‘x’
was calculated by multiplying ‘x’ by the area of the filter column (i.e. $\pi D^2/4$, where $D$ is 0.104m, the internal diameter of the large-scale filter column). After some filter loading, $V$, the pore concentration at a filter-bed depth of ‘x’ (if predicting effluent concentration, $x=Z$, the full filter-bed depth), was predicted by inputting the following values into Eqn. 16: $V_B = V/V_x$, $M = \rho V_x$ (where $\rho$ is the bulk density of the media in the filter column; this should be the same as used in the small-scale tests), and $t = V_x/Q$ (where $Q$ is the loading rate applied to the large-scale filter).

**Validation of model using independent data**

To validate and further support the modelling strategy applied in this study, a literature review was carried out to identify column studies which utilized low-cost adsorbents and observed BTCs which tended towards a convex to linear shape, rather than the sigmoidal curve predicted by other models. The BTCs published in these studies were downloaded as raster images and converted to vector graphics, the ordinates of which could be exported as a text file. The text files were imported into Microsoft Excel as x and y coordinates, which could then be processed in the same fashion as the experimental data. This method was validated using known data points, and it was found that the mean absolute percentage error between actual values and data points obtained in this manner was 0.18%.

Figure 1 shows a step-by-step schematic of the data collection and modelling procedure employed in this study.
4. Results and Discussion

Predicting medium saturation in RSSCTs

Figure 2 shows plots of filter loading versus phosphorus retained by filter columns of various lengths. As can be seen, the relationship between filter loading and medium saturation could be accurately described by Eqn. 15. The ERRSQ function was used as a metric for goodness of model fit, with average ERRSQ values of 0.074, 0.057, and 0.008 obtained for small-scale filter columns containing Al-WTR, fine concrete, and coarse concrete, respectively. As described previously, $q_t$ can be calculated in a number of ways; Figure S2 in the supplementary file compares graphs of the three functions from which a value for $q_t$ may be obtained. Comparing the shapes of these functions, it can be seen that Eqn. 14, originally proposed by Ko et. al (2000, 2002) to account for diffusional adsorption, appears to very closely match the curve produced by Eqn. 15, based on second-order kinetics. This would seem to indicate that both functions might have similar utility, however the differences between the two can be considerable when the two are compared on a local scale, as can be seen from the inset in Figure S2. In constructing Figure 2, attempts were made to fit the experimental data from the small-scale column tests to each of Eqns.13, 14 and 15. As can be seen from Table 1, which compares ERRSQ values obtained using each of these equations, Eqn. 15 was found to be optimal for each of the media studied. As it provided the best fit to these initial data (and because Ko et al. (2000, 2002) have already explored the use of Eqns. 13 and 14), Eqn. 15 was used for the remainder of this study when fitting Eqns. 16 and 17 to experimental data.

Predicting pore concentrations at multiple depths in large-scale filter columns

Once it was established that Eqn.15 was capable of describing and predicting the progression of medium saturation in small-scale filter columns of various lengths, it was hypothesized
that Eqn. 16 would also be able to predict pore \( \text{PO}_4\text{-P} \) concentrations at any bed depth within the filter bed of a large-scale column. To test this hypothesis, Eqn. 16 (with \( q_t \) determined using Eqn. 15) was fit, using the ERRSQ method, to the data obtained from depth samples taken from various depths within the large-scale filter columns. Figure 3(a) shows the fit of Eqn. 16 to these experimental data, and the associated ERRSQ values are shown in Table 2. Average ERRSQ values of 0.026, 0.011, and 0.005 were obtained for large-scale filter columns containing Al-WTR, fine concrete, and coarse concrete, respectively. It can be seen that the slight day-to-day variances in influent concentration had a marked influence on the shape of the observed BTCs. While Eqn.16 was initially proposed to be accurate with the assumption of constant influent concentration, it appeared to display good resilience to these fluctuations, and was nonetheless able to make accurate pore and effluent concentration predictions. With it established that the model could describe the performance of both small- and large-scale filter columns, it was further hypothesized that the coefficients determined from the small-scale columns could also be used to predict the performance of the large-scale filter columns. With these coefficients, the performance of small-scale filters of any depth operated at any HLR could be predicted, and equivalent loadings for large-scale columns subjected to the same HLR were calculated by scaling filter throughput based on the ratio of the small- and large-scale filter areas. Figure 3(b) shows data from the large-scale column tests fit to models created using data from the small-scale column tests, and the associated ERRSQ values are shown in Table 2. While not fitting quite as closely as when modeled directly on the large-scale column data, the level of precision achieved was still very good, with average ERRSQ values of 0.062, 0.054, and 0.008 obtained for filter columns containing Al-WTR, fine concrete, and coarse concrete, respectively. For practical purposes of preliminary filter design, this level of accuracy was considered more than sufficient, and it allowed for prediction of the adsorptive performance of the large-scale filter columns for the
entire duration of their operation. It could reasonably be expected that loading the large-scale filters with a wastewater whose chemical composition was significantly different from that of the wastewater applied to the small-scale filters (in terms of pH, concentration of target contaminant, competing compounds etc.) would invalidate any model predictions of large-scale performance based on the small-scale experiments; a more complex modeling approach would be required to take account of such variations.

Validation of model using independent data

To further verify the validity and utility of Eqn. 16, it was fit to BTCs published in a number of independent studies. The results of this are shown in Figure 4, and it can be seen that the model fit these data very well. Poots (1976b) was the first author who attempted to apply Hutchins’ (1973) BDST model to experimental results (according to the Web of Science citation index), and found that it was a poorly suited to describing the relationship between bed depth and service time in peat filters designed to remove Telon blue from aqueous solution. However, as can be seen in Figure 4(a), Eqn. 16 was able to describe the breakthrough behavior of Telon blue at all filter depths, accurately describing the non-linear relationship between bed depth and service time described by the BTCs. A recent study on phosphate adsorption (Nguyen et al., 2015) recorded BTCs from filters packed with a low cost adsorbent (zirconium loaded okara) using phosphate concentrations an order of magnitude higher than those used in the present study; as can be seen from Figure 4(b), Eqn. 16 was well suited to the description of these curves. Finally, Han et al. (2009) investigated the ability of iron oxide-coated zeolite as an adsorbent for the removal of copper (II) from aqueous solution in filter beds of various depths, and, as shown in Figure 4(c), the BTCs obtained these can be suitably modeled by Eqn. 16.

Description of sigmoidal curves
Although Eqn. 15 can describe many of the linear to convex BTCs commonly observed from fixed-bed studies using low-cost adsorbents, it is not suitable for the description of sigmoidal curves. This is perhaps the most commonly observed BTC shape observed in fixed-bed sorption studies (Gupta et al., 2000), and so, an attempt was made to model curves of this shape by modifying the B-A model (Eqn. 2) to obtain Eqn. 10, as described previously.

Using Eqn. 8 (letting t in Eqn. 8 be EBCT) to determine a value for $N_t$, Eqn. 10 was fit to a number of independent data sets, as shown in Figure 5. In the B-A model, $N_o$ serves a similar function to $q_e$ in Eqn. 11, as both represent the sorption capacity of the media. The B-A model assumes a rectangular sorption isotherm (highly favorable, irreversible adsorption) and a definite sorption maximum, which is independent of the contact time and the duration for which the filter has operated. However, in reality, it is known that filter-bed adsorption capacity does change depending on contact time (Ko et al., 2002) and duration of operation.

Eqn. 11 assumes that there is an exponential distribution of adsorption sites and energies, meaning that adsorption energies become exponentially weaker with increasing duration of filter operation and associated medium saturation; the bed’s capacity increases with operating time and, though there is no defined maximum capacity, there are adsorption maxima for any given filter runtime. Making bed capacity dependent on empty bed contact time, i.e. substituting $q_t$ for $q_e$, proved to be very successful, and similar success was found modifying Eqn. 2 by replacing $N_o$ with $N_t$. This can be seen in Figure 5, in which Eqn. 10 (with $N_t$ determined from Eqn. 8) has been fit to six independent data sets. Ko et al. (2000, 2002) also implemented a similar approach, using Eqn. 6 and Eqn. 7 to modify the BDST model, which is itself derived from the B-A model.

**Prediction of BDST relationship**

The relationship between bed depth and service time is not necessarily a linear one; greater bed depths result in longer EBCTs, which in turn allow for increased adsorption due to
increased intraparticle diffusion of adsorbate molecules. Figure S3 of the supplementary file shows some hypothetical BTCs, comparing a linear relationship between bed depth and service time, as proposed by Hutchins’ arrangement of the the B-A equation (Figure S3a), and a non-linear relationship between bed depth and service time as predicted by Eqn. 10, the B-A equation modified with Eqn. 8 (Figure S3b). The non-linear relationship between bed depth and service time as predicted by Eqns. 16 and 17 is also shown in Figure S3b, illustrating that the BDST plot doesn’t necessarily provide any information regarding the shape of the BTC; though the BTCs predicted by Eqn. 10 and Eqn. 16 are very different, both yield the same curved BDST plot.

Ko et al. (Ko et al., 2002) modified the BDST model using Eqn. 6 and Eqn. 7, and this made it possible to describe non-linear BDST plots. However, as can be seen in Figure 6, the BTCs observed in their study were not sigmoidal, and so, the B-A model on which the modified BDST model is based would not be appropriate for the description of entire BTCs. Eqn. 16 was fit to the data from this study, and, as can be seen in Figure 6, it was capable of describing not only the non-linear BDST relationship, but also the entire BTC for each filter-bed depth investigated. Eqn. 17 can therefore, in this case, be used to predict the BDST relationship at any breakthrough concentration of interest, as well as at any flow rate of interest, as demonstrated in Figure 6b.
Conclusions

This study described a testing and modelling methodology which uses results from short-term small-scale column tests to predict the long-term performance of large-scale fixed-bed filters.

- The proposed methodology was used to describe the adsorptive performance of small-scale and large-scale filter columns, successfully modelling medium saturation, as well as filter-pore and effluent concentration data.
- Predictions of large-scale filter performance based on small-scale filter performance were highly accurate.
- Two three-parameter models were investigated, and these allowed for the description and prediction of sigmoidal or convex breakthrough curves for multiple filters containing the same media, as well as concentration profiles across multiple depths within single filters.
- The proposed models also allow for the description of non-linear relationships between filter-bed depth and service time, as is commonly observed in fixed-bed systems which take a long time to reach equilibrium.
- The proposed modelling approach was applied to multiple independent data sets and was found to suitably describe the adsorption of various solutes including dyes, phosphate, metals (copper, cadmium, and zinc), fluoride, and arsenic.

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Figures

Figure 1. Step-by-step schematic of the data collection and modelling procedure employed in this study.

Figure 2. Phosphorus retained by filter media (y-axis) vs. filter loading (x-axis) for small scale filter columns of various lengths and predictions made by Equation 15.

Figure 3. PO$_4$-P concentration (y-axis) vs. filter loading (x-axis) for large scale filter columns, showing (a) Equation 16 fit directly to large scale column data, and (b) predictions made by Equation 16 with model coefficients determined from small-scale column tests.

Figure 4. Equation 16 fit to independent data sets of normalised pore/effluent contaminant concentration (y-axis) vs. filter loading/operating time (x-axis).

Figure 5. Equation 10 fit to independent data sets of normalised pore/effluent contaminant concentration (y-axis) vs. filter loading/operating time (x-axis).

Figure 6. (a) Equation 16 fit to an independent data set of normalised effluent contaminant concentration (y-axis) vs. filter operating time (x-axis) for various filter-bed depths, and (b) plots of filter service-time (y-axis) vs. filter-bed depth (x-axis) compared to predictions made by Equation 17 using the same model coefficients

Tables

Table 1. ERRSQ values obtained using Equations 13, 14, and 15 to model phosphorus retained by filter media vs. filter loading for small-scale filter columns of various lengths.

Table 2. Comparison of model coefficients and ERRSQ values obtained when (a) fitting Equation 16 directly to concentration data from the large-scale column experiments and (b) when fitting Eqn. 16 to concentration data from the large-scale column experiments using model coefficients determined from small-scale column tests.
Figure 1

Sample Collection

Collect samples of low-cost media and wastewater of interest

Small-Scale Column Tests

Pack columns of various lengths with low-cost media, and load with wastewater of interest to obtain breakthrough curves (BTCs)

Characterise Breakthrough Curves (BTCs)

Sigmoidal BTCs

Linear/Convex BTCs

Fit Appropriate Model to ETC Data

Eqn. 9 & Eqn. 10

Eqn. 16 & Eqn. 17

Model media performance

Use model to make service time predictions for filter columns of any depth and design hydraulic loading rate (HLR)

Predict performance of full-scale filter subjected to equivalent loading by scaling throughput based on filter area

Design Full-Scale Filter Bed
Figure 2

Al-WTR

Finely Crushed Concrete

Coarsely Crushed Concrete

PO₄-P Adsorbed (mg)

Filtered Volume (L)

Measured:

Modeled:
Figure 3

(a) Model fit using coefficients determined from large-scale column tests

(b) Model fit using coefficients determined from small-scale column tests

Al-WTR

Finely Crushed Concrete

Coarsely Crushed Concrete

PO₄-P Conc. (mg L⁻¹)

Filtered Volume (L)

Measured:

Modeled:
Figure 4

(a) Adsorption of Telon Blue Dye on Peat (Poots et al., 1976b)

(b) Adsorption of Phosphate on Zirconium Loaded Okara (Nguyen et al., 2015)

(c) Adsorption of Copper on Iron Oxide Coated Zeolite (Han et al., 2009)
Figure 5

(a) Adsorption of Fluoride on Kanuma Mud (Chen et al., 2011)

(b) Adsorption of Copper on Immobilized Chitosan (Futalan et al., 2011)

(c) Adsorption of Fluoride on MnO$_2$ Coated Alumina (Maliyekkal et al., 2006)

Adsorption of Cadmium on Treated Rice Husk (Kumar and Bandyopadhyay, 2006)

Adsorption of Arsenic on Iron-Oxide Coated Cement (Kundu and Gupta, 2005)

Adsorption of Copper on Modified Rice Husk (Wong et al., 2003)
Figure 6 – Data from (Ko et al., 2002)

Breakthrough Curves at Different Bed Depths

Zinc Ion-Bone Char System

Average ERRSQ = 0.035
Flow rate = 100 ml min⁻¹

AB80-Activated Carbon System

Average ERRSQ = 0.052
Flow rate = 30 ml min⁻¹

Bed Depth: 5cm 10cm 15cm 20cm 25cm

Experimental: Model Prediction:

Bed Depth Service Time Plots

Bone Char

AB80-ActivatedCarbon

Flow rate (ml min⁻¹): 50 75 100

Experimental: Model Prediction:
### Table 1.

| Equation                                                                 | Al-WTR | Fine Conc. | Coarse Conc. |
|------------------------------------------------------------------------|--------|------------|--------------|
| \( q_e = q_e(1 - e^{-at}) \)                                          | 0.0762 | 0.0687     | 0.0080       |
| \( q_e = q_e(1 - e^{-a\sqrt{\pi t}}) \)                                | 1.0534 | 0.0873     | 0.1028       |
| \( q_e = q_e \frac{t}{t + a^{**}} \)                                    | 0.0737 | 0.0568     | 0.0078       |

### Table 2.

| Model Parameters | Model parameters determined from Large Column Data | Model parameters determined from Small Column Data |
|------------------|---------------------------------------------------|----------------------------------------------------|
|                  | Al-WTR | Coarse Concrete | Fine Concrete | Al-WTR | Coarse Concrete | Fine Concrete |
| A                | 0.0105 | 0.0062          | 0.0058        | 0.0163 | 0.0071          | 0.0124        |
| B                | 1.2370 | 1.6385          | 1.3733        | 1.3692 | 1.7606          | 1.7054        |
| a**              | 10.6786| 9.1300          | 1.3525        | 10.1007| 9.2322          | 1.2134        |

| Filter Depth | Model ERRSQ values | Model ERRSQ values |
|--------------|--------------------|--------------------|
|              | Al-WTR | Coarse Concrete | Fine Concrete | Al-WTR | Coarse Concrete | Fine Concrete |
| 5cm          | 0.0245 | 0.0028          | 0.0038        | 0.0210 | 0.0048          | 0.0026        |
| 10cm         | 0.0328 | 0.0012          | 0.0027        | 0.1540 | 0.0011          | 0.0282        |
| 18cm         | 0.0472 | 0.0032          | 0.0105        | 0.0596 | 0.0034          | 0.1034        |
| 25cm         | 0.0209 | 0.0106          | 0.0144        | 0.0291 | 0.0189          | 0.0641        |
| 40cm         | 0.0038 | 0.0074          | 0.0228        | 0.0463 | 0.0100          | 0.0735        |
| µ:            | 0.0259 | 0.0050          | 0.0108        | 0.0620 | 0.0076          | 0.0544        |