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Evaluating the long-term performance of low-cost adsorbents using small-scale adsorption column experiments

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Abstract

This study investigated a novel method of predicting the long-term phosphorus removal performance of large-scale adsorption filters, using data derived from short-term, small-scale column experiments. The filter media investigated were low-cost adsorbents such as aluminum sulfate drinking water treatment residual, ferric sulfate drinking water treatment residual, and fine and coarse crushed concretes. Small-bore adsorption columns were loaded with synthetic wastewater, and treated column effluent volume was plotted against the mass of phosphorus adsorbed per unit mass of filter media. It was observed that the curve described by the data strongly resembled that of a standard adsorption isotherm created from batch adsorption data. Consequently, it was hypothesized that an equation following the form of the Freundlich isotherm would describe the relationship between filter loading and media saturation. Moreover, the relationship between filter loading and effluent concentration could also be derived from this equation. The proposed model was demonstrated to accurately predict the performance of large-scale adsorption filters over a period of up to three months with a very high degree of accuracy. Furthermore, the coefficients necessary to produce said model could be determined from just 24 hours of small-scale experimental data.

Keywords: adsorption, column, phosphorus, low-cost adsorbent, modeling
1. Introduction

Adsorption and surface precipitation are fast, cost-effective, and therefore highly attractive water treatment techniques that are applicable to the removal of a broad range of contaminants. In particular, there is considerable interest in low-cost adsorbents, which may be suitable for use in the treatment of water contaminated by pollutants such as heavy metals, industrial dyes, and nutrients (Demirbas, 2008; Vohla et al., 2011; Yagub et al., 2014). Natural materials, as well as industrial and agricultural wastes, are ideal in this regard, due to their low cost, local availability, and the added economic value associated with avoiding disposal routes such as landfill and incineration (Babel and Kurniawan, 2003; Crini, 2006).

When assessing the suitability of a potential filter medium, batch adsorption experiments are the most commonly utilized test, favored by researchers for their convenience and low cost (Crini and Badot, 2008). In fact, a large proportion of studies (arguably erroneously) rely solely on batch experiments to make inferences as to the behaviour of media in real-world filters (Ali and Gupta, 2007). The data from these batch adsorption tests are used in the construction of adsorption isotherms - curves that describe the removal of a contaminant from a mobile (liquid or gaseous) phase by its binding to a solid phase, across a range of contaminant concentrations. The determination of these isotherms is considered a critical step in the design and optimization of any adsorption process (Behnamfard and Salarirad, 2009; Hamdaoui and Naffrechoux, 2007), and there are a multitude of models describing these equilibrium curves.

Whilst important in the characterisation of potential adsorptive materials, it has been noted that batch adsorption tests have a number of potential shortcomings. Data obtained from batch studies are heavily influenced by factors such as initial solution concentration (Drizo et al., 2002), pH (Cucarella and Renman, 2009), and contact time (McKay, 1996), as well as by
experimental conditions which are sometimes very different to real world applications - for example the use of unrealistic solid-to-solution ratios, and the agitation of batch samples (Ádám et al., 2007; Søvik and Kløve, 2005).

Adsorption isotherms may also be determined using flow-through experiments, and the utilization of such methodologies, while not offering a ‘solve-all solution’, may help to address many of the shortcomings associated with batch studies. Buergisser et al. (1993) note that the solid-to-liquid ratio used when determining sorption isotherms with flow-through experiments is much closer to ratios that might be found in real-life systems where the adsorption of contaminants plays an important role in the treatment of contaminated waters (e.g. wastewater filtration units, constructed wetland substrates, and riparian buffer zones). Grolimund et al. (1995) also highlighted a number of other advantages of flow-through methodologies, such as the ease of prewashing the media under investigation, the reduced cost of the equipment necessary to perform the analysis, and the mitigation of experimental errors caused by the shaking motions used in batch experiments. A question still remains, however, regarding the applicability of the obtained isotherm to real-world situations. The isotherm alone provides no useful information regarding the longevity of a system (Seo et al., 2005), and when considering potential practical applications, predicting the lifespan of a given filter media is of paramount importance (Johansson, 1999).

Pratt et al. (2012) argue that the only reliable method of predicting the long-term performance of a filter media is full-scale field testing. While this may be true, it is obviously impractical to conduct such a study with an unproven material, and it is therefore desirable to perform short-term, laboratory-based experiments prior to undertaking any such large-scale study. Therefore, to address the question of adsorbent longevity, flow-through experiments in large-
scale, laboratory-based columns are the most commonly utilised method, though Crittenden et al. (1991) demonstrated that rapid small-scale column tests (RSSCTs) could also be used to predict the performance of pilot-scale adsorption columns.

There are a number of models commonly used to describe column adsorption, among the most popular of which are the Thomas model (Thomas, 1944), the Clark model (Clark, 1987), the Yoon-Nelson model (Yoon and Nelson, 1984), and the bed depth service time (BDST) model developed by Hutchins (Hutchins, 1973), based on an earlier model proposed by Bohart and Adams (Bohart and Adams, 1920). All of these models attempt to predict the performance of a filter column by studying the relationship between filter loading and effluent concentration, though in full-scale filters this relationship can be far from ideal.

When a filter is intermittently loaded, as might be the case, for example, in sub-surface vertical flow constructed wetlands (Healy et al., 2007; Pant et al., 2001), intermittent sand filtration systems (Rodgers et al., 2005), or indeed even riparian buffer zones (Ulén and Etana, 2010; Vidon et al., 2010), the relationship between effluent concentration and running time can be strongly affected by pauses in filter loading. It has been noted by a great many researchers that such breaks in the continuity of loading potentially allows for the diffusion of adsorbate molecules further into the adsorbent particles, thus resulting in a rejuvenation of the adsorbent surface prior to the next loading cycle (Ouvrard et al., 2002; DeMarco et al., 2003; Greenleaf and SenGupta, 2006; Sengupta and Pandit, 2011). This results in a non-uniform evolution of column effluent concentration with successive loadings, and means that the relationship between effluent concentration and loading is unlikely to follow one of the ideal breakthrough curves described by any of the aforementioned models. For example, the BDST model predicts an S-shaped curve, which is often not observed in laboratory studies, experimental data instead producing concave or linear curves associated with less ideal...
adsorption (Malkoc et al., 2006; Walker and Weatherley, 1997). Furthermore, this model is best suited to columns containing ideal adsorbents with continuous flow-through rates that are low enough to allow adsorptive equilibrium to be reached (Jusoh et al., 2007) – conditions which are not necessarily representative of real world conditions.

Considering that the ability to predict the point at which the effluent from an adsorptive filter exceeds a pre-defined contaminant concentration (i.e., the breakthrough point) is the principal objective of any column service time model (Deliyanni et al., 2009), the purpose of the current study was to develop a model capable of predicting filter breakthrough, while addressing the difficulties of modelling effluent concentration from an intermittently loaded filter. The proposed model works under the hypothesis that, if the relationship between filter media saturation and filter loading can be accurately described for an intermittently loaded filter, then effluent concentration can be obtained implicitly for any given influent concentration, and in the case of an intermittently loaded media, this approach is likely to be more successful than attempting to simply model the effluent concentration directly. To the best of our knowledge, this approach to predicting filter longevity has not been attempted before.

The proposed model was developed from rapid small-scale column tests, and its accuracy was confirmed using large-scale, laboratory-based filters which, in terms of media mass and loading, were two orders of magnitude larger than the experiment from which the model was derived. To test the model’s adaptability to variations in operating conditions such as 1) removal of contaminants, 2) continuous loading, 3) treatment of complex sample matrices, 4) variations in contaminant concentration, and 5) variations in filter hydraulic retention time
(HRT), the proposed model was fit to published data from a previous study (Claveau-Mallet et al., 2013).

The speed and ease with which the proposed experimental procedure may be performed, as well as the low costs associated with equipment and analysis, make this methodology an attractive complement to batch tests, as it provides an estimate of filter longevity in a similarly short timeframe to batch tests’ provision of estimates of filter capacity. As is the case with the RSSCTs proposed by Crittenden et al. (1991), the proposed model makes rapid predictions of filter longevity without the need for any preceding kinetic or isotherm studies, and only a small volume of sample wastewater is required for collection of the experimental data necessary to construct the model. In contrast with RSSCTs, the proposed model focuses on filter media subject to intermittent loading, modelling media saturation instead of filter effluent concentration. Predictions of filter performance are greatly simplified by virtue of the proposed model’s empirical nature, which circumvents the need to consider mechanistic factors such as solute transport mechanisms and intraparticle diffusivities.
2. Theory

Where a wastewater is loaded onto an adsorptive filter column, and the effluent collected in a number of containers, the relationship between the total volume of wastewater filtered and the mass of a contaminant adsorbed per unit mass of filter media is described by:

\[ q_e = \sum_{i=1}^{n} \frac{(c_o-c_{ei})V_i}{m} \]  \hspace{1cm} (1)

where \( q_e \) is the cumulative mass of contaminant adsorbed per gram of filter media, \( n \) is the number of containers in which the total volume of effluent \( (\sum V_i) \) is collected, \( c_o \) is the influent contaminant concentration, \( c_{ei} \) is the effluent contaminant concentration in the \( i^{th} \) container, \( V_i \) is the volume of effluent contained in the \( i^{th} \) container, and \( m \) is the mass of filter media contained in the filter column.

The Freundlich adsorption isotherm (Freundlich, 1906) is an empirical model describing the relationship between the adsorption of a contaminant from a mobile phase to a solid phase across a range of contaminant concentrations. The equation is as follows:

\[ q_e = K_f C_e^{\frac{1}{n}} \]  \hspace{1cm} (2)

where \( q_e \) is the cumulative mass of contaminant adsorbed per gram of filter media, \( C \) is the contaminant concentration of the supernatant at equilibrium, and \( K_f \) and \( n \) are the Freundlich constants. The Freundlich equation assumes that the heat of adsorption decreases in magnitude with increasing extent of adsorption, and that this decline in the heat of adsorption is logarithmic, thus implying an exponential distribution of adsorption sites and energies (Sheindorf et al., 1981; Thomas and Crittenden, 1998). There is much experimental evidence that the real energy distributions, while perhaps not being strictly exponential, are indeed roughly of this sort (Cooney, 1998). Being a characteristic of the media, the assumption of
exponential distribution remains equally valid, regardless of whether the saturation of the media is due to batch or through-flow exposure to adsorbate molecules. In the case of a batch experiment, the mass of adsorbate bound to the surface of a filter media increases with increasing solute concentration. In the case of a column experiment, the mass of adsorbate bound to the surface of the media increases as more solution is passed through the filter. Column effluent concentration, $C_e$, increases as progressively more wastewater is passed through the adsorptive media in a filter column, and therefore $C_e$ is a function of $V$, the volume treated by the filter. If that function of $V$ were modeled after Eqn. 2, it could reasonably be hypothesized that there would be some values of $A$ and $B$ such that the following equation might hold true:

$$q_e = AV^B$$  \hspace{1cm} (3)$$

where $B$ is a dimensionless constant of system heterogeneity, just as $n$ is a heterogeneity factor in the Freundlich equation (Allen et al., 2004), and $A$ is a constant of proportionality with units (mg/g)(L)$^{-1/B}$. Eqn. 3 should only be considered valid for $B>1$, as values of $B<1$ would imply that a greater adsorbate concentration in the filter media serves to enhance the free energies of further adsorption. If this were the case, it would contradict the earlier assertion that the heat of adsorption decreases in magnitude with increasing extent of adsorption. Eqn. 3 can be validated in the same manner as the Freundlich equation is validated for batch tests, i.e. by constructing a plot of experimental data and comparing it to the linearized version of the equation:

$$\ln(q_e) = \ln(A) + B^{-1}\ln(V)$$  \hspace{1cm} (4)$$

If Eqn. 3 describes the experimental data, the plot of $\ln(q_e)$ versus $\ln(V)$ would then be linear, meaning the model constants could be determined from the plot as follows: $A=\exp(\text{intercept})$, and $B = (\text{slope})^{-1}$. Should the linear plot have a coefficient of determination, $R^2$, close to
unity, it would indicate that Eqn. 3 is a suitable empirical model to describe the relationship between filter loading and filter media saturation.

Were all the filter column effluent collected in a single container, the average effluent concentration up to any volume, \( V \), would be given by substituting Eqn. 1 into Eqn. 3 to yield:

\[
C_{e_{\text{avg}}} = C_o - AmV^{(\frac{1}{\hat{b}} - 1)}
\] (5)

If, however, the effluent were collected in a number of sequentially filled containers, the theoretical concentration of a given effluent aliquot collected at any time over the duration of operation of a filter may be calculated using:

\[
C_{e_{\Delta V}} = C_o - \frac{\Delta q_e M}{\Delta V}
\] (6)

where \( \Delta V \) is the volume the filter effluent collected in a container between some arbitrary volumes \( V_a \) and \( V_b \), \( C_{e_{\Delta V}} \) is the theoretical concentration of the filter effluent volume \( \Delta V \), and \( \Delta q_e \) is the theoretical change in the mass of contaminant adsorbed per unit mass of filter media from \( V_a \) to \( V_b \).

Assuming Eqn. 3 fits the experimental data with acceptable accuracy, \( \Delta q_e \) between \( V_a \) and \( V_b \) can be calculated as follows:

\[
\Delta q_e,\text{mod} = AV_b^{\frac{1}{\hat{b}}} - AV_a^{\frac{1}{\hat{b}}}
\] (7)

Substituting Eqn. 7 into Eqn. 6, and letting \( V_a \) equal \( V_b - \Delta V \) therefore gives the following:

\[
C_{e_{\Delta V}} = C_o - \frac{AM[V_b^{\frac{1}{\hat{b}} - (V_b - \Delta V)^{\frac{1}{\hat{b}}}]}}{\Delta V}
\] (8)
The concentration of effluent at a given cumulative flow-through volume, \( V \), as opposed to the average concentration, as given by Eqn. 5, can then be estimated by obtaining the concentration across an infinitesimally small \( \Delta V \) as follows:

\[
C_{eV} = \lim_{\Delta V \to 0} \left( C_o - \left( \frac{AM[V^{\frac{1}{B-1}}(V - \Delta V)^{\frac{1}{B}}]}{\Delta V} \right) \right)
\]  

(9)

This yields the following:

\[
C_{eV} = C_o - \frac{AMV^{(\frac{1}{B-1})}}{B}
\]  

(10)

Thus, to determine \( V_b \), the volume at which any given breakthrough concentration, \( C_{eb} \), is reached, Eqn. 10 can be rearranged as follows:

\[
V_b = \left( \frac{(C_o-C_{eb})B}{AM} \right)^{\frac{B}{B-1}}
\]  

(11)

Eqn. 11 describes the breakthrough curve for all breakthrough effluent concentrations in the range \( 0 < C_{eb} < C_o \), though it is important to note in Eqn. 10 that \( V^{1/B-1} \to 0 \) as \( V \to \infty \), meaning the model will only asymptotically approach total breakthrough, \( C_{eb} = C_o \). This should not pose a limitation at concentration ranges of practical interest, i.e. \( 0 < C_{eb} < 0.9(C_o) \). Above this range filter media are commonly thought to have reached exhaustion (Han et al., 2006; Netpradit et al., 2004), and caution should be exercised when trying to utilise the model to predict effluent concentrations past this exhaustion point. The volume at which initial breakthrough occurs, \( V_{b,0} \), is found by letting \( C_e \), in Eqn. 11 equal to 0 mg L\(^{-1}\). Inputting a value less than \( V_{b,0} \) into Eqn. 10 would result in a negative \( C_e \) (as \( V^{1/B-1} \to -\infty \) as \( V \to 0 \)) which should simply be taken as zero. Breakthrough curves can easily be predicted for any filter subjected to equivalent loading by simply multiplying Eqn. 11 by a scaling factor, \( M_2/M_1 \), where \( M_1 \) is the mass of the filter from which the data to derive Eqn.11 was obtained,
and $M_2$ is the mass of the filter of interest. Eqn. 10 can also be rearranged to yield following linear relationship between $C_e$ and $V$:

$$ln(C_o - C_e) = \left(\frac{1}{b} - 1\right)lnV + ln\frac{AM}{B}$$  \hspace{1cm} (12)

With Eqn. 12, the coefficients $A$ and $B$ can theoretically be obtained from the slope and intercept of a plot of $ln(C_o-C_e)$ vs $ln(V)$ as follows: $A = B(exp(\text{intercept})/(M))$, and $B = (\text{slope}+1)^{-1}$. However, as discussed previously, for an intermittently loaded filter column, it is hypothesized that attempting to model the saturation of the filter media would prove more successful than attempting to directly model column effluent concentration. To complement the explanations given in this section, Figure S1 shows the derivation of the breakthrough curve (Eqn. 11) from a mass balance analysis of a filter system.
3. Materials and Methods

3.1 Preparation of small bore adsorption columns

Small bore adsorption columns were prepared using polycarbonate tubes with an internal diameter of 0.94 cm and lengths of 10, 15, 20, 30, and 40 cm. Sets of tubes (comprising one tube of each length without replication) were packed with four different adsorbent media. These media comprised mixtures containing (1) aluminium sulfate drinking water treatment residual (Al-WTR; oven dried for 24 h at 105 °C and ground to pass a 0.5 mm sieve) (2) ferric sulfate drinking water treatment residual (Fe-WTR; oven dried for 24 h at 105 °C and ground to pass a 0.5 mm sieve) (3) fine crushed concrete (pulverized with a mortar and pestle and ground to pass a 0.5 mm sieve), and (4) coarse crushed concrete (pulverized with a mortar and pestle and ground to pass a 1.18 mm sieve, but retained by a 0.5 mm sieve); these will henceforth be referred to as media A, B, C, and D, respectively. In a preliminary experiment (not reported here), the relationship between dry bulk density and hydraulic conductivity was studied for each media, and the polycarbonate tubes used in this study were packed with media at a dry bulk density such that each of the columns had a saturated hydraulic conductivity of 0.14 cm s\(^{-1}\). The physical characteristics of the different media were such that this value could be achieved for all four media, and this value of hydraulic conductivity is comparable to that found in constructed wetland substrates (Brix et al., 2001) and slow sand filters (Mauclaire et al., 2006; Rodgers et al., 2004). Plastic syringes with an internal diameter equal to that of the polycarbonate tubes’ outside diameter were fastened, by friction fit, to either end of the columns, and a small quantity of acid-washed glass wool was placed at the top and bottom of each column to retain the filter media within the tube. Flexible silicone tubing was attached to the syringe ends to provide influent and effluent
lines, and the columns were attached to a frame to maintain a stable vertical orientation throughout the duration of the experiment.

### 3.2 Operation of small bore adsorption columns

A peristaltic pump with a variable speed motor was used to pump influent water, with an ortho-phosphorus (PO$_4$-P) concentration of 1 mg L$^{-1}$, into the base of each small-bore adsorption column at an approximate flow rate of 202±30 ml hr$^{-1}$. The combination of using a low flow rate in up-flow mode, and the high ratio of the column diameter to adsorbent particle diameter was considered sufficient to preclude any channeling effects (Vijayaraghavan et al., 2004). The influent was prepared by adding a small quantity of K$_2$HPO$_4$ to tap water, with the resulting solution having a pH of 8.09±0.37. The simple makeup of the influent precluded interfering chemical interactions, and phosphorus (P) was selected as an excellent example of a contaminant commonly targeted by adsorption filters; its precise quantification is also relatively simple and inexpensive. The pump was operated in twelve hour on/off cycles to achieve loading periods of 24 to 156 hours. The effluent from each column was collected in two-hour aliquots in separate containers using an auto-sampler. The effluent in each container was analyzed for dissolved PO$_4$-P using a nutrient analyzer (Konelab20, Thermo Clinical Lab systems, Finland) after APHA (1998) and the cumulative mass of P adsorbed by the filter media was calculated using Eqn. 1. The limit of detection was determined, after McNaught and Wilkinson (1997), to be 0.009 mg L$^{-1}$.

### 3.3 Preparation of full-scale filter units

The media which showed the highest and the lowest absorbencies in the small-bore column experiments – media A and media D, respectively – were studied in 0.65 m-deep laboratory filters with an internal diameter of 0.104 m. These filters were constructed in triplicate and were packed with filter media to a depth of 0.4 m from the bottom of each column. The free-
board of 0.25 m in each column was to allow water to be poured onto the surface without spillage. As was the case in the small bore columns, the mass of media in each column was varied to achieve a packing density such that each of the columns had an approximate hydraulic conductivity of 0.14 cm s\(^{-1}\).

3.4 Operation of full-scale filter units

The filter units were operated in a temperature-controlled room at 10\(^{\circ}\)C, and were subjected to repeated synthetic wastewater loadings over one to three months. The synthetic wastewater influent contained a PO\(_4\)-P concentration of 1 mg L\(^{-1}\), and was loaded manually onto a baffle at the top of the filter media. Columns containing filter media D were loaded with 28 liters of synthetic wastewater per loading event 10 times over the course of one month. Columns containing filter media A were loaded with 28 liters of synthetic wastewater 17 times, and were subsequently loaded nine times with 56 liters, in order to hasten the P saturation of the media. This loading was carried out over the space of three months. For both media, each loading event took place over a period of 1.5 hours, and there was a minimum of one day’s rest between each loading event.

3.5 Processing of experimental data

During each loading event, the effluent from the filter units was collected in large HDPE containers and was analyzed for PO\(_4\)-P using a nutrient analyzer (Konelab20, Thermo Clinical Lab systems, Finland) after APHA (1998). The mass of phosphorus adsorbed per unit mass of filter media was calculated using Eqn. 1, and a graph of cumulative q\(_e\) versus cumulative collected effluent volume, V, was constructed. The observed values of q\(_e\) were then compared to values predicted by models created using coefficients calculated from the data collected during small-scale adsorption column experiments.
3.6 Verification of model’s adaptability to variances in operating conditions

In their 2013 paper, “Removal of phosphorus, fluoride and metals from a gypsum mining leachate using steel slag filters”, Claveau-Mallet et al. (2013) provided a supplementary file containing concentration and pH data for effluents from columns which were being used to treat reconstituted gypsum mining leachate. In the study, a total of ten columns were operated as five sets of two columns connected in series. These were continuously loaded with leachate for a period of 145-222 days, and effluent concentrations of fluoride (amongst other contaminants) were measured twice per week. Four of the columns were loaded with a low concentration leachate (L1), while the remaining six were fed with a higher concentration leachate (L2). The effluents of those columns fed with leachate L2 showed variations in pH of 4.15±2, while those of columns fed with leachate L1 showed variations of 1.29±0.67. Due to the effect that the large fluctuations in the pH of effluent from columns fed with leachate L2 had on the data, the model proposed in the current study was fit to the effluent fluoride concentration data from the columns fed with leachate L1. The columns were loaded continuously with an influent that had a fluoride concentration of 9 mg L⁻¹. Effluent fluoride concentrations were measured twice weekly, and using these data, averages of effluent concentration were used to determine the amount of fluoride removed by the filter media (qₑ).

Given that the columns were loaded at a continuous rate by a peristaltic pump, the volume of leachate filtered (V) was taken to be analogous to the time (T) for which the columns were running (as V= αT, where α is the flow rate in L day⁻¹), and a plot of qₑ versus V was developed from which the model coefficients, A and B, were computed from plots of Eqn. 4, as described previously. The difficulties of modeling non-ideal breakthrough curves was discussed in detail by Sperlich et al. (2005), and to further validate our proposed model, a supplementary Excel file has been made available with this paper demonstrating our model’s ability to describe and predict (using RSSCT data) the breakthrough curves observed in that
study. The Excel file also contains a template to facilitate the fitting of our proposed model to other experimental data.

### 3.7 Determination of model error

The hybrid error function (HYBRID), developed by Porter et al. (1999), is a non-linear error function often employed when using non-linear regression methods to predict isotherm parameters. Chan et al. (2012) analyzed data relating to the adsorption of acid dyes onto charcoal, and of the five non-linear error functions studied, concluded that the HYBRID function was the most effective in determining isotherm parameters for the six isotherm equations used in their study. The HYBRID function was used in the current study as a metric for the comparison of the goodness of model fit to experimental data. The function is:

$$\frac{100}{n-p} \sum_{i=1}^{n} \frac{(q_{e,i,meas} - q_{e,i,calc})^2}{q_{e,i,meas}}$$ (12)

where $n$ is the number of experimental data points, $p$ is the number of constants in the proposed model, $q_{e,i,meas}$ is the value of $q_e$ obtained from Eqn. 1, and $q_{e,i,calc}$ is the value of $q_e$ obtained from Eqn. 3. The mean percentage error (MPE) was also calculated to provide an easily comparable metric by which to assess the model’s goodness of fit and its bias toward either over- or underestimation of predicted values compared to observed values. The MPE was calculated thus:

$$MPE = \frac{100}{n} \sum_{i=1}^{n} \frac{q_{e,i,meas} - q_{e,i,calc}}{q_{e,i,meas}}$$ (13)

where $n$, $q_{e,i,meas}$, and $q_{e,i,calc}$ are the same as given for Eqn. 12. A negative MPE indicates that the model predictions tend to underestimate experimentally observed adsorption, whereas a positive error indicates an overestimation.
4. Results and Discussion

4.1 Verification of theory at bench scale.

For all four of the media studied, the relationship between filter loading and the mass of P adsorbed per unit mass of filter media, $q_e$, could be estimated with a very high degree of accuracy by the proposed model (Eqn.3). Figure 1 shows the goodness of fit of model predictions made using 36 hours of experimental data. The model coefficients, along with the $R^2$ values of the linear plots from which they were determined, are shown in Table S1. The experimental data fitted the linear expression of the model with a very high degree of accuracy, and the average linear regression coefficients observed for media A, B, C, and D were 0.997, 0.991, 0.963 and 0.997, respectively.

A column containing media A was loaded for 68 hours to study the effect of experimental runtime on the accuracy with which model coefficients could be determined. Revised estimates of model coefficients were determined from experimental data collected at two-hour increments, and a model using these coefficients was fitted to experimental data for the entirety of the period for which the filter was loaded. Figure S2a shows the HYBRID error of these models, against the time at which the model coefficients were determined. After an initial sharp drop-off in model error, there was little improvement in model fit past the 24-hour mark. Figure S2b shows the goodness of fit to experimental data of models using coefficients determined after 24 and 36 hours of data aggregation, demonstrating that there was little benefit to be gained from experimental run times in excess of 24 hours.

To study the accuracy with which effluent concentration, average daily effluent concentration, and total P loss could be predicted, a small-bore adsorption column containing media A was operated for an extended period of 156 hours. All filter effluent was collected in two hour aliquots, and it was possible, using Eqn. 9, to predict the P concentration of any one
of these aliquots at any given time. There were 12 hour rest-periods in between loading cycles, and these cessations in filter loading appear to have allowed the filter media to replenish some of its adsorptive potential. Increased P uptake at the beginning of each loading phase resulted in the effluent concentrations producing the cyclical 6-point pattern seen in Figure 2a, and this strongly suggests that intraparticle diffusion of P, driven by the concentration gradient within the media particles, resulted in rejuvenation of the media surface; this has also been observed by many others (DeMarco et al., 2003; Greenleaf and SenGupta, 2006; Sengupta and Pandit, 2011; Song et al., 2011). Model predictions of $C_e$ describe the general trend of increasing effluent concentration with increasing volume well, though the model does not describe the cyclical pattern described previously. However, as can be seen in Figure 2b, it was possible to produce highly accurate model predictions of average daily effluent concentration; these values could be forecast with a mean error of just 0.59% ± 10.54%. Average daily effluent concentration is, arguably, a more useful metric for assessing the long-term performance of a filter media, and, as seen in Figure 2c, predictions of cumulative P loss made using predicted average daily effluent concentration had a mean error of just 3.74% ± 8.31%.

To ensure the results of the small-bore column experiments were replicable, 20 cm columns packed with media A were operated in triplicate for a period of 24 hours, and the model coefficients calculated from each column were compared. As can be seen in Figure S3a, the experimental data from each of the three columns fit the linear expression of the proposed model with a coefficient of determination, $R^2$, of 0.996±0.001. The model coefficients were determined as $A = 0.109±0.003$ and $B = 1.480±0.043$. Figure S3b demonstrates the effect of this variability in coefficients on the models produced. After 24 hours of operation, at which 0.5 liters of effluent had been collected, the mean $q_e$ predicted by substituting $V=5$ litres into
Eqn. 3 was $0.320 \pm 0.017$ mg g$^{-1}$. The variability of model predictions being so slight would indicate that this method of determining model coefficients is highly replicable.

### 4.2 Verification of theory at filter-scale.

Figure 3 shows the experimental data from large-scale experiments overlain by predictions made using models created from the small-bore adsorption column data. In the case of filter media A, the model obtained from the 24 hour small-bore adsorption study predicted the performance of the full-scale filter unit over three months with a very high degree of accuracy. Predicted values of $q_e$ differed from observed values by just $2.94\% \pm 4.31\%$, and the model fit the observed values with a HYBRID error of just 0.074. In the case of filter media D, predicted values of $q_e$ differed from observed values by $8.08\% \pm 11.49\%$, and the model fit the observed values with a HYBRID error of just 0.070. It was thus demonstrated that, in terms of media mass and loading, scaling the experiment up by approximately two orders of magnitude had very little negative impact on the ability of the model to predict filter performance, appearing to confirm the hypothesis that a small-scale, 24-hour experiment could be used to accurately predict large-scale filter performance over a much greater period. To further validate this assertion, RSSCT data from a study conducted by Sperlich et al. (2005) was used to construct a model which was then used to successfully predict the performance of a lab-scale filter that was over 700 times larger than the RSSCT in terms of filter media mass. This model and the data used in its construction can be found in the supplementary Excel file which has been made available with this paper.

### 4.3 Adaptability of model to varying conditions

Figure 4 shows the model proposed by this study fit to fluoride removal data published by Claveau-Mallet et al. (2013). As can be seen, the model described the evolution of fluoride concentrations in the filter effluent well for both those filters fed with a constant fluoride
concentration of 9 mg L\(^{-1}\) (Figure 4, ‘A’ Columns), and those fed with a variable concentration from the effluent of the preceding filter in a series (Figure 4, ‘B’ Columns). This would appear to confirm the model’s applicability to contaminants other than P, as well as to filter media other than those examined by this study. The complexity of the wastewater’s composition did not appear to have a negative impact on the model’s ability to describe the observed data, nor did continuous loading of the columns. Columns 1A, 1B, 4A, and 4B (Figure 4) had HRTs of 14.2, 18.2, 4.8, and 4.3 hours, respectively, though these variations in HRT appear to have had no significant impact on the goodness of model fit. Columns 1A and 4A were both loaded using wastewater with a constant fluoride concentration of 9 mg L\(^{-1}\), while columns 1B and 4B were loaded with the effluents from columns 1A and 4A, thus receiving an influent with fluoride concentrations ranging from 0.85-7.66 and 5.86-8.63 mg L\(^{-1}\), respectively. In general, higher MPEs were recorded for models fit to data from columns fed by an influent of varying concentration, and a greater variance in influent concentration resulted in a larger MPE. This would seem to indicate that variation in influent concentration had a negative impact on model fit, though with a maximum recorded MPE of 12.35% (Figure 5b), the model appeared to cope well with this variability nonetheless.

4.4 Practical implications

To be of the greatest utility, a method of filter media characterisation must be easy to use, quick to execute, and should replicate the performance of a field-scale system as closely as possible (Limousin et al., 2007). Many field-scale adsorption systems are loaded intermittently, and it was hypothesized that for such a system, a model which attempted to describe and predict filter media saturation would be more successful than a model which attempted to model filter column effluent directly. The model proposed by this study can be linearized in two ways, and the coefficients required to produce the model can be determined from linear plots of \(q_e\) or \(C_e\) data using linear plots of \(lnq_e\) vs \(lnV\) (method 1) and \(ln(C_o-C_e)\) vs
\ln V \text{ (method 2), respectively. The former attempts to model media saturation, while the later attempts to model column effluent directly. The suitability of an equation to model an adsorption system can be judged by the } R^2 \text{ correlation coefficient of its linear plot, and when there are multiple methods of linearizing an equation to obtain model coefficients (e.g. as with the Langmuir isotherm) the } R^2 \text{ can be used to determine the better method (Behnamfard and Salarirad, 2009). As can be seen in Figure 5, plots of } \ln q_e \text{ vs } \ln V \text{ produced graphs with higher linearity than plots of } \ln(C_o - C_e) \text{ vs } \ln V \text{ in all cases, suggesting that method 1 may be preferable to method 2. To further confirm this hypothesis, graphs of experimental data from small-bore columns containing filter media A were modeled using model coefficients determined using method 1 and method 2, respectively. Figure 6 shows the comparison of these models and their goodness of fit to values of } q_e \text{ and } C_e \text{ obtained experimentally. As can be concluded from analysis of Figure 6, coefficients determined using method 1 and method 2 described the evolution of filter effluent with similar accuracy, though method 2 gave marginally better accuracy. In contrast, method 1 was significantly better for producing accurate models of the evolution of filter saturation. This appears to confirm the hypothesis that to predict the performance of an intermittently loaded filter, modeling media saturation is a more successful approach than attempting to model filter effluent concentrations directly.}
5. Conclusions

This study proposed a model capable of describing the non-ideal (i.e. non s-shaped, linear to convex) breakthrough curves often described by data from column experiments using low-cost adsorbents and soils.

- It was demonstrated that the model could be used to describe and predict the performance of multiple low-cost filter media, which were intermittently loaded with a wastewater containing 1 mg L$^{-1}$ of PO$_4$-P.

- The model was fit to data from two independent studies, demonstrating its ability to describe the removal of contaminants other than phosphorus (fluoride and arsenate), and its adaptability to continuous loading conditions, complex wastewater compositions, and variations in HRT.

- It was shown that model parameters could be determined experimentally from both filter effluent data and media saturation data, with the latter approach being more successful when modelling intermittently loaded filters.

- The model was successfully used to predict the performance of lab-scale filter columns which were intermittently loaded over the course of a number of months.

- The model parameters required to predict the performance of the lab-scale filters were determined using data aggregated over a 24 hour period using small-scale column tests.

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Figure 1.
Figure 1. Filter media P adsorption (y-axis) vs. filter loading (x-axis), showing observed progressions of media saturation and the goodness of model fit for each media and column length.
Figure 2.

(a) Effluent Concentration

(b) Effluent Concentration (24 hour mean)

(c) Total P Loss

Experimental Values

Predicted Values
Figure 2. (a) Comparison of predicted and observed progressions of effluent concentration (y-axis) vs. cumulative filter loading (x-axis), with predictions and observations made on a bi-hourly basis.

Figure 2. (b) Comparison of predicted and observed daily mean effluent concentrations (y-axis) vs. cumulative filter loading (x-axis).

Figure 2. (c) Comparison of predicted and observed cumulative P loss in effluent (y-axis) vs. cumulative filter loading (x-axis).
Figure 3. Comparison of predicted and observed $q_e$ values (y-axis) vs. filter loading (x-axis), demonstrating the ability of the proposed model to predict large-scale filter performance.
Figure 4.

(a) Experimental $q_e$ vs modeled $q_e$

(b) Experimental $C_e$ vs modeled $C_e$

(c) Experimental $q_e$ vs modeled $q_e$

(d) Experimental $C_e$ vs modeled $C_e$

MPE:

- 0.29%
- 5.28%
- 0.15%
- 0.72%

MPE:

- 12.35%
- 0.60%
- 0.33%
Figure 4. (a-d) Goodness of model fit to fluoride removal data reported by Claveau-Mallet et al. (2013).
Figure 5.

Ln\(q_e\) vs Ln\(V\)

\[ R^2 = 0.9953 \]

Ln\((C_0 - C_e)\) vs Ln\(V\)

\[ R^2 = 0.7341 \]

Ln\(q_e\)

\[ R^2 = 0.9982 \]

Ln\((C_0 - C_e)\)

\[ R^2 = 0.8813 \]

Ln\(q_e\)

\[ R^2 = 0.9976 \]

Ln\((C_0 - C_e)\)

\[ R^2 = 0.8732 \]

Ln\(q_e\)

\[ R^2 = 0.9962 \]

Ln\((C_0 - C_e)\)

\[ R^2 = 0.8833 \]
**Figure 5.** Comparison of the linearity of plots of \( \ln(q_e) \) (left y-axis) vs. \( \ln(V) \) (x-axis), and \( \ln(C_0-C_e) \) (right y-axis) vs. \( \ln(V) \) (x-axis). These plots are used to determine model coefficients by analysis of filter saturation or filter effluent concentration respectively.
Figure 6.

Experimental $q_e$ vs modeled $q_e$

- MPE: Method 1: - 0.04%
- Method 2: - 42.03%

- MPE: Method 1: - 0.02%
- Method 2: - 65.28%

- MPE: Method 1: - 0.03%
- Method 2: - 50.86%

- MPE: Method 1: - 0.06%
- Method 2: - 38.65%

- MPE: Method 1: - 0.06%
- Method 2: - 27.53%

Experimental $C_e$ vs modeled $C_e$

- MPE: Method 1: - 3.96%
- Method 2: - 1.39%

- MPE: Method 1: - 6.45%
- Method 2: - 1.07%

- MPE: Method 1: - 10.43%
- Method 2: - 1.25%

- MPE: Method 1: - 18.79%
- Method 2: - 3.26%

- MPE: Method 1: - 134.32%
- Method 2: - 104.46%
Figure 6. Plots of $q_e$ (left y-axis) and $C_e$ (right y-axis) vs. filtered volume (x-axis), demonstrating the effect that the method of coefficient determination (i.e., analysis of filter saturation or analysis of filter effluent concentration) has on model accuracy.