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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 h of experimental data from the small-scale column experiments were found to provide sufficient information to predict the performance of the large-scale filters for up to three months.

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 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

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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_o)
N_o	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)

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:

$$ln\left(\frac{C_O}{C_b}-1\right)=ln\left[exp\left(k_{BA}N_O\frac{Z}{U}\right)-1\right]-k_{BA}C_Ot_b \quad (1)$$

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:

$$ln\left(\frac{C_O}{C_b}-1\right)=k_{BA}N_O\frac{Z}{U}-k_{BA}C_Ot_b \quad (2)$$

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