Water Research 101 (2016) 429–440

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

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

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ARTICLE INFO

Article history:
Received 21 March 2016
Received in revised form
5 May 2016
Accepted 30 May 2016
Available online 31 May 2016

Keywords:
Adsorption
Column
Phosphorus
Low-cost adsorbent
Modeling

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 h of small-scale experimental data.

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;

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http://dx.doi.org/10.1016/j.watres.2016.05.093
0043-1354/© 2016 Published by Elsevier Ltd.

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 pre-washing 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 linear to convex 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 modeling 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, modeling 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:

$$q_e = \sum_{i=1}^{n} \frac{(C_o - C_{e_i})V_i}{m} \tag{1}$$

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 ($\sum Vi$) is collected, C_o is the influent contaminant concentration, $C_{e,i}$ is the effluent contaminant concentration in the