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Application of the Homogeneous Surface Diffusion Model for the prediction of the breakthrough in full-scale GAC filters fed on groundwater

Andrea Piazzoli, Manuela Antonelli*

Politecnico di Milano, Department of Civil and Environmental Engineering (DICA), Environmental Section, Piazza Leonardo da Vinci 32, 20133, Milano, Italy

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ABSTRACT

Homogeneous Surface Diffusion Model (HSDM) has been widely used to simulate the breakthrough of organic micropollutants in fixed-bed adsorbers, but its practical applicability in real-scale conditions is not fully established. In this study we proposed a validated methodology to support the assessment of full-scale GAC adsorbers, providing a sound framework for a sustainable management. Specifically, we predicted the breakthrough of volatile organic compounds by the HSDM applied to full-scale granular activated carbon (GAC) adsorbers treating a complex groundwater matrix. Isotherm and short bed adsorber (SBA) tests were conducted to obtain equilibrium and mass-transfer coefficients for two contaminants (chloroform and perchloroethylene, PCE) and two GACs. Isotherm data were well described by Freundlich and Langmuir models, showing that single-component isotherms can be also used in complex water matrices, indirectly taking into account competition phenomena into the estimated parameters. The fitting of SBA data by HSDM was effective for chloroform, while PCE results were not well described, indicating that the combination of isotherm and SBA experiments to estimate HSDM parameters is not always effective, but it can depend on the characteristics of the adsorbate. Breakthrough data from the monitoring of two full-scale adsorbers were finally used to validate HSDM parameters for chloroform: its breakthrough was effectively simulated, without introducing any competition effect in HSDM equations. The model well reproduced also the release of the contaminant (resulting in chromatographic effect) by considering the variation of its influent concentration over time.

1. Introduction

Contamination by organic micropollutants affects groundwater sources in many industrialized areas of the world (Luo et al., 2014; Williams et al., 2002). Many of these compounds, including volatile organic compounds (VOCs), trihalomethanes and pesticides, are proven to be hazardous for human health and are regulated by national drinking water regulations (Register, 1989).

Adsorption onto granular activated carbon (GAC) was designated by the United States Environmental Protection Agency (US-EPA) as the best available technology for the treatment of many regulated organic pollutants (Sotelo et al., 2012; Westerhoff et al., 2005); thanks to its removal effectiveness, relative low cost and management simplicity, it is the most widespread technology in drinking water treatment plants (Oxenford and Lykins, 1991).

A fundamental step for the design and the management of a GAC system is the prediction of breakthrough profile, that is particularly important for estimating the operating costs (Kennedy et al., 2015; Yu et al., 2009). Different alternative methods to predict breakthrough profile were proposed in literature (*inter alia*, Anumol et al., 2015; Crittenden et al., 1991; Worch, 2008), but a general procedure has not yet been established and the problem must be faced in each specific case (Pełech et al., 2006a).

Rapid Small Scale Column Tests (RSSCTs) are a suitable choice for testing GAC performances and many studies showed their accuracy in simulating full-scale data for several adsorbents and mixtures of contaminants (*inter alia*, Anumol et al., 2015; Corwin and Summers, 2011; Knappe et al., 1997; Morley et al., 2005; Summers et al., 2013; Westerhoff et al., 2005). However, RSSCTs display some limitations: first, experimental trials can be too much time consuming and expensive, especially when tests are planned for simulating large-scale GAC systems (Jarvie et al., 2005); in addition, scaled-up results often do not accurately fit real breakthrough profiles, due to an improper choice of the design approach (constant or pro-

* Corresponding author.
E-mail address: manuela.antonelli@polimi.it (M. Antonelli).

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portional diffusivity) or to NOM interference on the adsorption of trace-organic contaminants (Corwin and Summers, 2010; Knappe et al., 1997).

An alternative approach involves the use of mathematical models (Jarvie et al., 2005). The most widely used models couple the description of the hydrodynamic transport through a fixed-bed filter with the description of the solute adsorption, considering a two-step diffusion mass transfer: through the external liquid-film and into the adsorbent grains. Depending on the description of diffusion mechanisms inside grains, different classes of models were developed (*inter alia*, Pore Diffusion Model and Pore Surface Diffusion Model) and, among these, the Homogeneous Surface Diffusion Model (HSDM) is one of the most widely referred to (*inter alia*, Ho and Newcombe, 2010; Knappe et al., 1999; Pérez-Foguet et al., 2012; Richard et al., 2010; Rossner and Knappe, 2008; Schideman et al., 2006; Zhang et al., 2009). Despite being less time-consuming than pilot-scale tests or RSSCTs, the use of HSDM for breakthrough prediction in full-scale GAC systems is rather poor and mostly limited to specific research applications (Heijman and Hopman, 1999; Worch, 2008). So far, the main aspects to be faced regards the estimation of model parameters and the model adaptation to not-ideal working conditions (such as complex water mixture, time-varying flow rates and influent concentrations), typical of large-scale systems (Heijman and Hopman, 1999; Knappe et al., 1999; Richard et al., 2010; Worch, 2008).

In the case of HSDM, the correct determination of site-specific equilibrium and mass-transfer coefficients is a key-point (Worch, 2008). Equilibrium parameters are commonly estimated by the determination of adsorption isotherms (Moreno-Castilla, 2004). Despite many isotherm models were proposed for describing single-solute adsorption (Foo and Hameed, 2010), a proper description of competitive adsorption mechanisms in multi-component systems is an issue so far. In fact, the application of the main models proposed in literature (i.e. IAST model, Extended Langmuir model) is often not suitable for describing competitive adsorption in real water, requiring a high number of experiments and parameters to be determined (Erto et al., 2011; Najm et al., 1991), but anyway leading to not accurate and reliable results (Ebie et al., 2001; Newcombe et al., 2002). Mass-transfer coefficients, being external and intraparticle mass-transfer coefficients, can be estimated by empirical correlations and relatively easy bench-scale experiments. As for external mass-transfer coefficient, many semi-empirical correlations were proposed with some dimensionless parameters, such as Reynolds (Re), Schmidt (Sc), and Sherwood (Sh) numbers (*inter alia*, Williamson et al., 1963; Wilson and Geankoplis, 1966; Yoshida et al., 1962). However, these correlations are rarely accurate, strongly depending on the characteristics of the adsorbent grain and the case-specific hydrodynamic conditions (Richard et al., 2010). As for intraparticle mass transfer coefficient, different experimental procedures were proposed based on batch kinetic studies, such as Crank, Vermeulen and Reichenberg methods (Cotoruelo et al., 2009; García-Mateos et al., 2015). However, the application of coefficients obtained in this way remains limited to the study of adsorbent surface properties and there are only few works in literature in which they were used to simulate breakthrough of a fixed-bed adsorbent (García-Mateos et al., 2015).

Despite their relative higher complexity, Short Bed Adsorber tests (SBA) (Knappe et al., 1999; Weber and Liu, 1980) are the most widely referred method for experimentally determining both mass transfer coefficients in GAC systems. Many papers showed the effectiveness of SBA tests in estimating model parameters and simulating breakthrough profiles for several contaminants (*inter alia*, Ho and Newcombe, 2010; Knappe et al., 1999; Richard et al., 2010; Rossner and Knappe, 2008); however, practical applicability of SBA tests for full-scale adsorbers or real water media is not fully established, since most of the works dealt only with single-component adsorption and reported experimental results obtained under controlled conditions (synthetic solutions, stable experimental parameters).

The validation of the predictive model with large-scale data is another fundamental step for assessing its reliability. Simulation results are usually verified in pilot-scale columns, allowing to reproduce full-scale systems in a less time-consuming way. Model validation with full-scale data is rarely reported in literature; however, it represents the most effective way to verify model accuracy, since model sensitivity to the adopted parameters and the initial assumptions can vary with the scale of the GAC system (Knappe et al., 1999). Secondly, the variation of the operating parameters over time (i.e. flow rate, influent concentrations), usually occurring during full-scale operations, but not during short-lasting pilot-scale experiments, is an important aspect to be considered, since it can affect the adsorption process.

Finally, the HSDM sensitivity to the parameters is an important aspect to be evaluated, being strictly related to the interpretation of SBA data and to the accuracy of breakthrough predictions. Previous studies (Knappe et al., 1999; Richard et al., 2010) investigated the role of some model parameters (e.g. equilibrium and mass-transfer coefficients, adsorbent particle size), but general conclusions cannot be easily derived from the literature. In fact, parameters do not act independently to determine model outputs and the model sensitivity to all the parameters must be evaluated in each specific case, to test possible parameter interactions.

In this paper, the problem of the prediction of breakthrough profiles was faced for full-scale GAC adsorbers treating groundwater contaminated by a mixture of organic micropollutants (4 chlorinated solvents and 7 pesticides). HSDM was used to simulate the breakthrough profiles of the contaminants: equilibrium parameters were derived from isotherm determination, while mass-transfer coefficients were determined by SBA tests. All the experiments were performed on groundwater samples and the study was carried out for two kinds of commercial GAC, differing for the physical-chemical characteristics. First the ability of the tested methods to accurately estimate model parameters in a complex multi-component solution was assessed, validating results with data collected from the full-scale GAC adsorbers in 21 month monitoring. Then, the criteria for the application of HSDM to multi-component real water solution were defined, accounting also for variations of contaminant influent concentrations. In conclusion, we proposed a validated methodology to support the assessment of full-scale GAC adsorbers, providing a sound framework for a sustainable management.

2. Materials and methods

2.1. Adsorbents

Two commercial granular activated carbons (Chemviron) were used: GAC-1240 (GAC-M) and Acticarbone NCL 1240 (GAC-V), being, respectively, of mineral (coal-based) and vegetal (coconut-based) origin. Apparent density (ρ_b) of the carbons in full-scale filters was measured according to ASTM D2854-89; apparent density of GAC bed during SBA tests was calculated as the ratio between the carbon mass and the bed volume; both in full-scale filters and SBA tests, the bed porosity (ε_b) was calculated assuming a GAC particle density (ρ_p) of 2100 kg m^{-3} (Crittenden et al., 2012). Apparent density and bed porosity values are reported in Table 1. Grain size distribution of the GACs was determined by a mechanical sieve (Giuliani, I), using 7 different mesh sizes between 10 and 70. Results were used to determine average and median particle diameters (d_P). The granulometric curves are reported in Supporting Information (S.I.1), while calculated d_P median values are reported in