Research article

Adsorption of pharmaceuticals onto activated carbon fiber cloths — Modeling and extrapolation of adsorption isotherms at very low concentrations

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ARTICLE INFO

ABSTRACT

Activated carbon fiber cloths (ACFC) have shown promising results when applied to water treatment, especially for removing organic micropollutants such as pharmaceutical compounds. Nevertheless, further investigations are required, especially considering trace concentrations, which are found in current water treatment. Until now, most studies have been carried out at relatively high concentrations (mg L^{-1}), since the experimental and analytical methodologies are more difficult and more expensive when dealing with lower concentrations (ng L^{-1}). Therefore, the objective of this study was to validate an extrapolation procedure from high to low concentrations, for four compounds (Carbamazepine, Diclofenac, Caffeine and Acetaminophen). For this purpose, the reliability of the usual adsorption isotherm models, when extrapolated from high (mg L^{-1}) to low concentrations (ng L^{-1}), was assessed as well as the influence of numerous error functions. Some isotherm models (Freundlich, Toth) and error functions (RSS, ARE) show weaknesses to be used as an adsorption isotherms at low concentrations. However, from these results, the pairing of the Langmuir-Freundlich isotherm model with Marquardt's percent standard of deviation was evidenced as the best combination model, enabling the extrapolation of adsorption capacities by orders of magnitude.

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1. Introduction

The contamination of aquatic systems by pharmaceutical residues is widely reported and constitutes a growing concern and risk for the environment and human health (Das et al., 2014; Gamarra et al., 2015; Huerta-Fontela et al., 2011). For instance, Loos et al. (2009) detected diclofenac in 83% of their samples in European rivers. The maximum concentration was 11 ng L^{-1} (de Jesus Gaffney et al., 2015). Likewise, carbamazepine and acetaminophen were identified and quantified at concentrations of 200 ng L^{-1} in surface waters (Segura et al., 2011). Exposure to environmentally concentrations of pharmaceutical residues (Carbamazepine, Diclofenac and Acetaminophen) could alter biomarkers and biochemical processes of C. *fluminea* and duckweed plants (Chen et al., 2014;

Kummerová et al., 2016). However, risks for human health were considered negligible by Webb et al. (2003).

Adsorption processes are recognized among the most efficient, promising and widespread water treatments for the removal of pharmaceuticals (Foo and Hameed, 2009). In practice, granular activated carbon (GAC) and/or powdered activated carbon (PAC) are used to eliminate organic pollutants. According to (Rigobello et al., 2013; Sotelo et al., 2014), the adsorption capacities of diclofenac onto granular activated carbon are about 230 mg g^{-1} for a residual aqueous concentration of 40 mg L^{-1}. For carbamazepine, Cai and Larese-Casanova (2014) found capacities of 200 mg g^{-1} onto granular activated carbon for a concentration of 0.5 mg L^{-1}. For a residual concentration of 500 ng L^{-1}, (Yu et al., 2008) found capacities of 1 mg g^{-1}. More recently, activated carbon fiber cloths (ACFC) have also been studied for water treatment (Faur-Brasquet et al., 2002). The advantages of such textiles are their high specific surface areas, predominantly microporous texture and large adsorption capacities (Ayranci and Hoda, 2005). Therefore, ACFC were more efficient in terms of adsorption rate and selectivity than granular activated carbon for the removal of phenols (Dabrowski et al., 2005). However, to our knowledge, few studies have dealt

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with the adsorption of pharmaceutical residues onto ACFC (Ayranci and Duman, 2006; Bayram and Ayranci, 2012; Guedidi et al., 2014).

The design of the adsorption process is generally based on the equilibrium data for the particular system: adsorbent vs. adsorbate. Thus, relevant and accurate models for the sorption equilibrium are critical to predict the performances of the treatment. Adsorption isotherms (relationship between the amount adsorbed at equilibrium and the residual aqueous concentration for a given temperature) are usually reported for a narrow range of concentrations. Moreover, high aqueous concentrations (about mg L^{-1}) (Brasquet et al., 1996) of pollutants are commonly considered since trace concentrations are hardly achievable unless a complex and costly analytical strategy is carried out. The question is whether the adsorption capacities obtained at high concentrations can be easily transposed to realistic trace conditions. As mentioned above, in aquatic compartments, the concentrations of pharmaceutical residues are very low (in the ng L^{-1} range) and the determination of adsorption isotherms at such environmental concentrations is difficult, requiring powerful analytical tools such as liquid chromatography coupled to mass spectrometry and time-consuming sample preparation (solid phase extraction).

The accuracy of the extrapolation is greatly dependent on the isotherm model considered as well as the adjustment procedure used for the optimization of the isotherm parameters. In the literature, numerous isotherm models are available, starting from the Freundlich and Langmuir models, which have been widely used and validated to describe equilibrium relationships between various adsorbents and adsorbates (Ho, 2004; Nam et al., 2014; Sotelo et al., 2014; Yu et al., 2008). Nam et al. (2014) have shown a better fit of adsorption onto granular activated carbon with the linear form of the Langmuir model, compared to the Freundlich model, for acetaminophen adsorption. These authors used concentrations of pollutants between 20 and 500 ng L^{-1}, with a mass of granular activated carbon of 1 mg L^{-1}. Regarding diclofenac, (Nam et al., 2014) have shown a better fit with the Freundlich model while, for carbamazepine, (Yu et al., 2008) have shown better results with the Freundlich model, for an equilibrium concentration of 10—800 ng L^{-1}. Over the years, a wide variety of equilibrium isotherm models have been developed while considering various assumptions (heterogeneity of the surface energy, multilayer adsorption, etc.). These isotherm models can be classified as two-parameter (Langmuir, Freundlich, Temkin, Elovich, Dubinin-Radushkevich) or three-parameter models (Redlich-Peterson, Toth, Langmuir-Freundlich, Sips, Radke-Prausnitz). (Limousin et al., 2007; Rouquerol et al., 1999; Ruthven, 1984; Worch, 2012).

In combination with the selection of the relevant model, various options are possible to determine the model parameters: linearization of the equations with a simple least-square regression or a non-linear regression method. This latter approach has generally been preferred since it provides the most accurate description of experimental data (Foo and Hameed, 2010). Moreover, some models cannot be linearized and the determination of parameters is necessarily based on minimizing an error function, which corresponds to the deviation between the experimental data and the predicted value from the model. The optimized parameters for the isotherm model thus strongly depend on the selected error function. It should be noted that the choice of the error function influences the accuracy of the modeled data, since this function promotes a better fit of isotherms at low or high concentration with different weights for the experimental data.

Recent studies have compared several error functions in combination with the usual isotherm models (Allen et al., 2003; Chan et al., 2012; Foo and Hameed, 2010). Normally, error functions are used to minimize or maximize the error distribution between the experimental equilibrium data and the predicted isotherms,

according to the definition of the error function. Although the method of least squares is one of the most widely used techniques with the maximum coefficient of determination, r^2, some studies have pointed out that other error functions are more relevant, such as the hybrid fractional error function (HYBRID), Marquardt's percent standard of deviation (MPSD), the average relative error (ARE), the sum of the absolute errors (EABS) etc. According to Chan et al. (2012), the hybrid error function provided the best overall results. For this study, the Sips model performed the best prediction only if the model was adjusted using the hybrid method with the experimental data.

Most investigations have been carried out for the adsorption of organic compounds at high concentrations (at the mg L^{-1} scale) (Sotelo et al., 2014). Only recently, research programs have focused on the modeling of adsorption isotherms at lower concentrations (μg L^{-1} or less) with the development of analytical tools (Al Mardini and Legube, 2010; Matsui et al., 2003). This trend is more consistent with the emerging pollutants encountered in the environment and should be generalized to achieve a better understanding of the adsorption process used for the production of drinking water. However, at trace concentrations, experimental results are more difficult and more expensive to obtain. In order to avoid this problem, the extrapolation of the isotherm model from high to low concentrations would be an interesting option. In fact, if the model is fitted at high concentrations, the prediction outside the range of measurements (to trace contents) could give relevant results. As previously mentioned, the selection of the isotherm model and the error function plays a key role in predicting adsorption capacities.

This study focused on the relevance and reliability of the extrapolation of adsorption isotherms from high to low concentrations, with the aim of evaluating the ability of numerous isotherm model/error function pairs to achieve this change of scale. For this purpose, three emerging pollutants were chosen and their isotherms of adsorption were determined for one ACFC. Two sets of experiments were carried out at low and high concentrations. Then, the combinations between 13 models and 8 error functions were evaluated.

2. Materials and methods

2.1. Materials

2.1.1. Organic compounds

The targeted compounds — acetaminophen, carbamazepine and diclofenac - were all purchased from Sigma—Aldrich (purity > 98%). The physicochemical properties and molecular structures of the compounds are listed in Table 1. Stock solutions (10 mg L^{-1}) were prepared by dissolving the commercial standard in ultrapure water (UPW) provided by an ElgaPureLab System (18.2 MΩ cm). Two sets of experiments were carried out. The first was conducted at high concentrations of pollutant (0.1—20 mg L^{-1}). The second set was achieved at low concentrations (0.1—2 μg L^{-1}), which is the range closer to the levels observed in surface waters (Petrie et al., 2014).

For the high range of concentrations, analyses were performed by Ultra Performance Liquid Chromatography (UPLC) using a Waters ACQUITY H-class system (Waters Assoc., Milford, MA) equipped with a photodiode array detector (PDA). Detection was carried out at 243, 272, 276 and 280 nm with a PDA eλ detector (Waters) for acetaminophen, diclofenac and carbamazepine, respectively. 5 μL of sample was injected onto a BEH C18 column (100 $\times$ 2.1 mm $\times$ 1.7 μm, Waters) thermostated at 35 °C. The binary gradient consisted of a mixture of acetonitrile as mobile phase A, and acetonitrile/water/formic acid (10:90:0.1, v/v/v) as mobile phase B. The separation was initiated at a constant flow of 0.4 ml/min with 90% B for 1 min, followed by a decrease in B to 10% within 7 min. This composition