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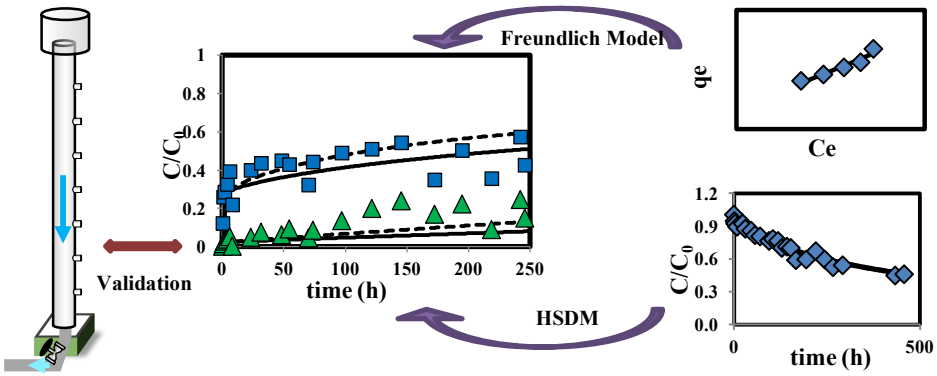

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Upscaling fixed bed adsorption behaviors towards emerging micropollutants in treated natural waters with aging activated carbon: model development and validation

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Abstract

A scale-up procedure was assessed in this study to predict the fixed bed adsorption behaviors with aging granular activated carbon (GAC) for various micropollutants (pesticides, pharmaceuticals). Two assumptions of this upscaling methodology (*i.e.*, involving equal adsorption capacities and surface diffusivities between the batch test and the fixed bed) were studied for the first time to investigate the aging effect on the adsorption capacity and kinetics of carbon at full scale. This study was conducted in natural waters (the Seine River) treated by Veolia Eau d'Ile de France in Choisy-Le-Roi, a division of Syndicat des Eaux d'Ile de France, aiming to monitor real industrial conditions. The isotherms showed that the adsorption capacity for most compounds was significantly affected by aging. For the mass transfer coefficients (*i.e.*, as determined by the homogeneous surface diffusion model (HSDM)), different patterns of adsorbate/adsorbent behaviors were observed, suggesting different competition mechanisms. The model predictions (*i.e.*, HSDM) performed with all parameters obtained during the batch tests tended to overestimate the full-scale pilot adsorption performance. This overestimation could be compensated for by applying a scaling factor. Finally, an empirical pseudo-first order function was used to model the impact of the GAC service time on the characteristic adsorption parameters. Thus, our scale-up procedure may enable the prediction of long-term fixed bed adsorption behaviors and increase the model efficiency for practical implementation.

Key words: Adsorption; prediction; fixed bed; granular activated carbon; micropollutants; treated natural waters

1. Introduction

Adsorption on activated carbon is recognized as an efficient technology for emerging organic micropollutant (MP) removal in drinking water treatment plants (DWTPs) (Katsigiannis et al., 2015; Kennedy et al., 2015). The most common MP removal process is the application of a fixed bed reactor using granular activated carbon (GAC), where the carbon grains remain in place for several months or years. To optimize the industrial design and maintenance, numerical modeling is a useful tool to predict the MP removal efficiency. Among all the descriptive models, the homogeneous surface diffusion model (HSDM) is commonly used in number of studies to simulate adsorption processes at different scales (Bakir et al., 2014; Capelo-Neto and Buarque, 2016; Hand et al., 1997; Kim et al., 2016; Schideman et al., 2006a, 2006b; Zhang et al., 2009).

However, the estimation of HSDM parameters (*i.e.*, adsorption capacity and kinetics) in real industrial situations is complicated by the presence of natural organic matter (NOM) in waters not only due to its direct competition but also because of its preloading effect, mainly resulting in GAC aging. Number of previous researches have assessed the NOM preloading effect, showing a reduction in the adsorption capacities and kinetics with increasing NOM preloading time (Ding et al., 2006; Li et al., 2003; Schideman et al., 2006a, 2006b). Furthermore, these studies emphasized an accurate prediction of long-term fixed bed adsorption requisites by incorporating the NOM preloading effect into the modeling process.

Nevertheless, these studies have some limitations. First, all of studies used artificially in-lab preloaded GAC, which may not be representative of real full-scale GAC aging, especially regarding biofilm development. Second, some of the studies were conducted with a relatively high concentration of pollutants ($mg \cdot L^{-1}$), whereas the pollutant concentration in treated water (DWTP) ranges from $ng \cdot L^{-1}$ to $\mu g \cdot L^{-1}$. The adsorption behavior might be different for these

different concentrations. To date, few modeling studies have attempted to provide insight into the effect of real fixed bed aging on pollutant adsorption at low concentrations for practical industrial implementation.

Various methodologies can be used to estimate the two essential HSDM parameters. Pilot-scale studies are the most accurate approach (Kennedy et al., 2015), but they are time-consuming and expensive. To overcome their disadvantages, scale-down technologies such as discontinuous tests (*i.e.*, perfectly mixed batch reactor (PMBR), differential column batch reactor (DCBR)) and short-bed column tests (SBCTs) have been investigated (Hand et al., 1984). Carter and Weber Jr. (1994) predicted the breakthrough curve of trichloroethylene in a small-scale pilot using adsorption results in batch-scale studies. Their studies demonstrated the feasibility of the upscaling method to predict fixed bed behavior; however, the studies are restricted by high pollutant concentrations, the use of artificially preloaded GAC and a relatively small-scale pilot verification.

Recent studies have attempted to simulate or predict full-scale pilot adsorption behavior with pollutant concentrations of $ng \cdot L^{-1}$ or $\mu g \cdot L^{-1}$. Scharf et al. (2010) evaluated the adsorption capacity with ground activated carbon particles in batch tests to simulate on-site pilot test data over a two-year period. This approach is suitable for modeling but not for prediction. Later, Capelo-Neto and Buarque (2016) applied all the adsorption parameters in batch studies to predict the behavior of a hypothetical GAC filter, but the prediction results were not verified by a full-scale pilot study. Regrettably, neither study considered the NOM preloading effect in the modeling process, although the other experimental conditions approached the real DWTP conditions.

Hence, our study was conducted under conditions that are representative of real DWTP conditions by ensuring the same water quality as that used in real filters and ensuring a

pollutant concentration of $ng \cdot L^{-1}$ to $\mu g \cdot L^{-1}$. In contrast to all previous studies using artificially in-lab preloaded GACs, in this study, the GAC samples were collected through local coring filters of various service times (from several months to years) at three different depths; thus, these samples represent the actual GAC spatial and temporal aging process over most of its service life.

The primary objective of this research is to develop and validate an upscaling methodology to predict GAC fixed bed adsorption behaviors subject to the GAC aging effect. To achieve this aim, the study is separated into three steps: (1) investigation of the GAC aging effect on the adsorption capacity and kinetics using batch tests; (2) validation of the upscaling prediction by full-scale industrial pilot tests; and (3) assessment of an empirical function of the aging effect for practical implementation.

2. Materials and methods

2.1 Experimental methodology

The choice of scale-down approaches aims to guarantee an accurate determination of adsorption parameters under controlled conditions. Adsorption isotherms were achieved using ground and mixed GAC particles in PMBR according to Capelo-Neto and Buarque (2016) and Scharf et al. (2010), with the assumption that the adsorption capacity determined by mixing GACs from three depths can approximate the overall capacity of the fixed bed. Recent works by Corwin and Summers (2010) and Kennedy et al. (2017) showed that the adsorption kinetics of MPs (*i.e.*, as for pesticides) with GAC was dominated by intraparticle diffusion (pore diffusion and surface diffusion). The external mass transfer resistance was negligible in both small-scale and pilot-scale column tests over the long term. Therefore, a differential

column batch reactor (DCBR) was employed here to determine the intraparticle diffusivity for uncrushed aged GAC grains. This approach can minimize the external mass transfer influence and enhance the accuracy of intraparticle diffusivity determination (Baup et al., 2000; Hand et al., 1983).

Finally, an *in-situ* pilot-scale test was used to validate the proposed prediction methodology. Uncrushed GACs from three depths were loaded in the same arrangement into pilot columns to approximate the real spatial variation of local filters. The columns were fed with deozonated water from the plant, spiked with a set of MPs.

2.2 Water quality

Pretreated surface water from the DWTP of Choisy-Le-Roi (France, supplying 1.8 million people for the region of Ile de France) was used for all adsorption experiments. The influent water for the pilot test was collected after the ozonation-deozonation step to maintain the same water quality as that in the GAC filters in the DWTP. The water used for the batch tests was collected at one time during the pilot test to minimize temporal fluctuations of influent water. In addition, 30 $mg \cdot L^{-1}$ of sodium azide was added to the batch experiments to inhibit biological activities. Carter and Weber Jr. (1994) showed that the addition of sodium azide did not affect the adsorption process. Sodium azide was not added to the pilot tests to represent real industrial conditions. Previous study (Kennedy et al., 2015) also emphasized that the removal of MPs was governed by adsorption in similar conditions. Over the test period (approximately 3 weeks), the water quality was almost stable, with an average total organic carbon of approximately 2.3 $mg \cdot L^{-1}$ and a pH value close to 7.9.

2.3 Target MPs

Seventeen emerging organic MPs, including seven pharmaceutical compounds and ten pesticides, were selected for this adsorption study in view of the MP occurrence in surface and drinking water (Gasperi et al., 2009; Vulliet et al., 2011; Vulliet and Cren-Olivé, 2011) and their removal efficiency by activated carbon (Bunmahotama et al., 2017, 2015; Mailler et al., 2016). These MPs cover a wide range of physio-chemical properties, such as molar mass, polarity and solubility to evaluate the robustness of our approach over a broad range of properties for potential targets. The detailed information is provided in Supplementary Material A (See **Table SA.1**). All compounds were of analytical purity and purchased from Sigma-Aldrich (France).

The selected molecules were analyzed by ultra-high-pressure liquid chromatography (UHPLC) coupled with tandem mass spectrometry (MS/MS) (Acquity, Waters, Quattro Premier, Micromass, USA) following an online solid phase extraction (SPE) (Waters 2777). The complete analytical procedure was previously described by Bazus et al. (2016) and was adapted in this study to the target compounds by a slight modification of the elution gradient. Briefly, separation was achieved within 13 minutes using an Acquity BEH C18 (2.1 x 100 mm – 1.7 μm) column and with a linear elution gradient achieved by increasing the proportion of acetonitrile at a constant flow rate of 0.4 $mL \cdot min^{-1}$. The chromatographic conditions and multiple reaction monitoring (MRM) transitions are reported in **Table SA.2** in Supplementary Material A.

2.4 Activated carbon

To investigate the influence of GAC aging on the adsorption capacities and kinetics, a virgin GAC, namely, Aquasorb 1200 (Jacobi, France), was used as the reference for virgin GAC filters, and three aged GACs were collected from local filters at three depths (0.5 m, 1 m and 2 m) from the DWTP of Choisy-Le-Roi, France. The GACs were in service for 6, 17.4 and 35 months with a treated bed volume of 20930, 56000 and 102000, respectively. The four GACs were renamed C-0, C-6, C-17 and C-35, where the number represents the months of service of the GAC.

For the batch tests, all GAC samples were first washed with pure water to remove fines and dried at 60 °C to avoid destruction or modification of the NOM adsorbed on the GAC surface. Then, for the equilibrium isotherm test, the same amount of GAC from the three depths was mixed, crushed and sieved to obtain small-sized grains between 80 µm and 100 µm (the specific areas of the GACs are shown in **Table SA.3**) to minimize the equilibrium time and reduce the risk of degrading the target compounds. Patni et al. (2008) showed that crushed GAC had the same specific area and micropore size volume fraction as the original GAC. For batch kinetics tests, the fraction of 800/1000 µm was used by sieving the dried GAC grains of each depth separately. However, the original GAC grains were used for pilot tests without any pretreatment, and they were packed in accordance with the spatial arrangement of local filters with the same amount of GAC from the three depths.

2.5 Isotherm tests and kinetics batch tests

Equilibrium adsorption capacities were evaluated using the bottle-point technique. A constant mass of crushed GAC (2 $mg \cdot L^{-1}$) was mixed using magnetic stirrers with MP concentrations ranging from 1 to 10 $\mu g \cdot L^{-1}$ in 10 L of water at room temperature (25°C). The equilibrium time was determined by following the adsorption kinetics in the middle concentration range,

and the kinetics evaluation showed that the adsorption reached equilibrium after 14 days. Initial and residual concentrations of each compound were measured by SPE-UPLC-MS/MS to determine the adsorption quantities according to **Eq. 1**:

$$q_e = \frac{(C_0 - C_e) \cdot V_R}{m_{GAC}} \quad \textbf{(Eq. 1)}$$

where q_e is the adsorbed quantity (nmol·g^{-1}), C_0 and C_e are the initial and equilibrium solute concentrations in the liquid phase, respectively (nmol·L^{-1}), V_R is the reactor volume and m_{GAC} is the quantity of GAC.

The kinetics studies were carried out in a DCBR with 100 mg of uncrushed GAC grains (approximately 33.3 mg for each depth). The 10 L solution (1 µg·L^{-1} for each pollutant), which was stored in a glass bottle equipped with a magnetic stirrer, was pumped with a constant flow (peristaltic pump; 1.5 L·h^{-1}) through a small plastic column (4.32 mm inner diameter) containing the GAC grains, and then the solution was returned to the tank (**Fig. SB.1** in Supplementary Material B).

2.6 Full-scale pilot design and experiments

The full-scale pilot was designed to be representative of the GAC filter units of the DWTP in Choisy-Le-Roi, France (**Figure 1**). This pilot allows studying the breakthrough curves in 4 parallel 2 m columns simultaneously fed with the same water quality. Within the plant, the water is withdrawn from the GAC feeding line into a mixing tank equipped with a back flow preventer. Since the adsorbent at the bottom of the column requires approximately the same amount of time for saturation as the GAC filters in the DWTP (typically many years), determining the complete breakthrough curve is not reasonable. Therefore, the columns were equipped with intermediate sampling points (every 25 cm) to determine the concentration-

depth profile at a given time or to determine the breakthrough curve at a given bed depth. The columns consist of a 50 mm internal diameter cylinder (the height of the GAC filling is approximately 1.2 m, which corresponds to an empty bed contact time of 7.2 minutes) of polycarbonate. To avoid any entry of air bubbles into the GAC filter, the columns are topped with a tank that is overflowing with water spiked with 1 $\mu g \cdot L^{-1}$ of each MP. An HPLC pump is used to add 1.6 $mL \cdot min^{-1}$ of a 1 $mg \cdot L^{-1}$ stock solution into the main water flow. A flow rate of 20 $L \cdot h^{-1}$ in each column was controlled at the outlet using a multichannel peristaltic pump. The contact time and linear velocity (10 $m \cdot h^{-1}$) corresponded to the common industrial conditions of Veolia in Paris. Moreover, to ensure both a continuous operation and a reliable comparison of the GAC performance between the pilot test and the real industrial fixed bed, a 2-hour backwash was applied for every 48-hour operation. Water samples were periodically collected from each column at different bed depths through sampling ports and analyzed by SPE-UPLC-MSMS.

2.7 Model description

Several modeling strategies have been proposed for the adsorption equilibrium of MPs in water containing NOM. Studies (Bunmahotama et al., 2017; Smith et al., 1987; Zietzschmann et al., 2014) have successfully shown the use of competition models that consider the NOM as an “equivalent background compound”. In the competition models, the optimized parameters are obtained by fitting the model parameters to experimental data associated with a defined error function. However, the application of the models is limited by common shortcomings. These models require at least mixed isotherms in NOM-free and NOM-containing water to obtain better fitting parameters. Furthermore, the fitting parameters are not transferable; hence,

for other water/GAC/MP system, complementary tests and fitting procedures are necessary to re-determine these parameters.

Another model is a single 'apparent' component model, which has already been employed in previous studies (Carter and Weber Jr., 1994; Scharf et al., 2010). In such a model, the parameters are directly fitted to experimental data of the target compounds obtained in NOM-containing water. Regarding the practical objective of our study, we limited ourselves to the latter approach. The adsorption equilibrium of each target molecule was modeled by the Freundlich model according to **Eq. 2**:

$$q_e = K \times C_e^{1/n} \quad \textbf{(Eq. 2)}$$

where q_e is calculated according to **Eq. 1**, K is Freundlich's coefficient ($nmol \cdot g^{-1}/[(nmol \cdot L^{-1})^{1/n}]$, and n is Freundlich's exponent (dimensionless). The logarithmic transformation allows the use of classical linear regression available in many spreadsheet software packages.

The HSDM was used to simulate batch kinetics and pilot breakthrough curves. The model equations for DCBR and fixed bed are presented in **Table SA.4**, and these equations were numerically solved using in-house software (Baup et al., 2000) that applied the orthogonal collocation method to convert the partial differential equations into ordinary differential equations with a function of approximation provided by Villadsen and Stewart (1967). The resolution began with nondimensionalization of the equations to simplify the influence of units. External mass transfer (characterized by the coefficient k_f) and surface diffusion (characterized by the surface diffusion coefficient D_s) are the two potentially limiting steps for adsorption kinetics. Their values can be determined by fitting experimental data. The optimization solver's fitting criteria are the sum of least squares of the absolute difference between the experimental and modeled concentrations at all sampling times. The Biot number (**Eq. 3**) is introduced to interpret the predominant limiting step. When the Biot number > 100,

the whole kinetics process is controlled by surface diffusion; when the Biot number < 0.1, the external mass transfer is predominant, and when the Biot number is between 0.1 and 100, the adsorption kinetics is influenced by the two mechanisms. More details of the model description can be found in many publications (Schideman et al., 2006a; Zhang et al., 2009).

$$Biot = \frac{k_f \cdot R_p \cdot C_0}{D_s \cdot \rho_p \cdot q_0} \quad \textbf{(Eq. 3)}$$

Here, R_p and ρ_p are the particulate radius and apparent density, respectively, and q_0 is the adsorption capacity of carbon at concentration C_0.

3. Results and discussion

3.1 Effect of GAC aging on the adsorption capacity

The effect of GAC aging on the adsorption capacity was evaluated using isothermal equilibrium tests with a virgin GAC (C-0) and three aged GACs (C-6, C-17 and C-35). The obtained Freundlich model parameters (K and 1/n) can be found in **Table SA.5**. The adsorption capacity of compounds (represented by q) is equal to the K value when the concentration is fixed to 1 nmol·L^{-1}. To facilitate the comparison of the aging effect for different compounds, the relative adsorption capacity was introduced. Instead of using the virgin GAC as a reference, we used q/q_{max} since some compounds have a higher q value with aged GAC than with virgin GAC.

Figure 2 shows that the GAC aging effect on MP adsorption differs. Four behaviors can be distinguished. For the pollutants of Group I, a continuous decrease in q is observed with increasing aging time. The q values diminish sharply (approximate 50%) after the initial 6 months of use and continue to decrease at a similar or slightly slower rate with increasing age.

Compounds of Group II have a similar severe reduction in q values (more than 50%) at the earlier aging stage. However, unlike Group I, the K values for these compounds remain stable afterward (between 6 and 35 months of service). The two behaviors of Groups I and II have been reported in previous studies (Carter and Weber Jr., 1994; Schideman et al., 2006a), noting that the NOM accumulated successively at the GAC surface reduced adsorption capacity due to pore blockage and pore competition.

For the compounds of Group III, a general reduction in q was observed for the three aged GACs compared to the virgin GAC. However, after a strong initial decrease, the q values of the three compounds increased with aging time. This irregular increase in adsorption capacity is difficult to explain with the current competition mechanisms. Changes in the nature of the biofilm might provide an explanation. Long-term studies of biofilm formation scare, but some data indicate an evolution of the morphology and composition of the biofilm (Batté et al., 2003; Gibert et al., 2013) during a long operation time, especially a reduction in the carbohydrate content from a fresh biofilm to an older biofilm. Thus, these changes in the biofilm nature might modify the affinity of GAC towards each molecule and contribute to the biodegradation of molecules.

In Group IV, the experimental isotherm plots (**Fig. SB.2**) show no significant difference in adsorption capacity between C-0 and C-6, whereas a serious reduction in adsorption capacity is observed after long-term use. The behavior of the compounds in this group is generally similar to the compounds of Group I but with a lag phase before the drop in the adsorption capacity. A competition mechanism mentioned by Yu et al. (2009) can explain this lag phase. At the initial preloading stage, the NOM with a low molecular weight diffuses rapidly into the adsorption sites of the outer layers of the GAC, resulting in a serious reduction in the adsorption potential of smaller molecules compared with larger molecules. As the molecules of Group IV have the highest molecular weight, they were less impacted at this initial phase

but could be seriously affected when the NOM diffused simultaneously into the GAC inner space during the later aging period.

3.2 GAC aging influence on the adsorption kinetics

The aging effect on the adsorption kinetics was first investigated by DCBR tests. Experimental kinetics data obtained using the DCBR setup that was operated at initial concentrations of 1 $\mu g \cdot L^{-1}$ in treated river water show no obvious difference from the aged GACs (**Fig. SB.3**). However, the observed kinetics are influenced by both the adsorption capacity and mass transfer. To separate these effects, the HSDM is applied using the equilibrium data obtained in the previous section. The kinetics parameters are then determined by fitting the external mass transfer coefficient (k_f) and internal surface diffusivity (D_s) to the experimental data (the results are collected in **Table SA.6**).

The experimental plots can be satisfactorily fitted by HSDM for all pollutants, despite the analytical uncertainties observed for some compounds at these low concentrations. Essentially, the DCBR is designed to accurately estimate internal diffusion by minimizing or controlling the influence of external diffusion. The parameter sensitivity for the model calibration is interpreted by employing the Biot number. Relatively high Biot numbers (>50) are observed for most molecules (**Table SA.6**), which suggests that the adsorption kinetics is indeed mainly dominated by D_s. Thus, the following discussions focus only on the influence of GAC aging on D_s. A relative surface diffusivity was introduced to simplify the presentation. The D_s/D_{smax} ratio was also used since most compounds appear to have a higher D_s value with aged GAC than with virgin GAC.

Table SA.6 shows that the aging effect on D_s is complicated and might be differentiated into two groups. As presented in **Figure 3**, Group I has the highest D_s value for virgin GAC; then, this value greatly decreases at the earlier aging stage and stabilizes during the later aging period, except for diuron, whose D_s values are not greatly impacted by the aging time. The behavior of Group I was expected and has already been observed in previous studies (Carter et al., 1992; Speth and Miltner, 1989). However, the behavior of Group II was observed for the majority of molecules in which the D_s values reach the maximum after several months of use followed by a decrease in the later stage. A hypothesis is presented to explain this phenomenon. The adsorbed NOM, mainly in the macropores and mesopores, might change the surface properties, thus reducing the affinity towards some compounds. Note that the HSDM is based on the assumption that surface diffusion is largely predominant over porous diffusion (Noll et al., 1991). A less attractive surface can increase the relative contribution of porous diffusion, resulting in an apparent increase in the D_s value obtained using HSDM fitting. Indeed, the measured diffusion coefficient is an apparent coefficient that represents the two phenomena. Later in the process, the diffusion in the micropores will limit the mass transfer process. These changes in the attractiveness of the surface might differentially affect the various molecules and could explain the differences observed for the fitted D_s values.

The range of D_s covers several orders, making it difficult to highlight some internal correlations. The logarithmic transformation ($pD_s = - Log_{10}(D_s)$) allows a better study of the possible correlations among the GACs; the results are shown in **Table SA.7**. It appears that the relationship of the pD_s values between the aged GACs and the virgin GAC is mostly insignificant (the p values are relatively high), whereas a strong linear correlation of pD_s values among aged GACs is observed (**Figure 4**). Thus, for practical implementation, it seems that extrapolation of the experimental results carried out on virgin GAC to explain the

adsorption kinetics on aged GACs would lead to erroneous results, while the extrapolation would be much more reliable with GAC that was already exposed to NOM.

3.3 Scale-up model development and validation

After investigating the aging effect on the adsorption capacity and kinetics in batch tests, a scale-up procedure was carried out to predict the influence of aging on the fixed bed adsorption behavior. The procedure assumes that the GAC in the fixed bed has the same adsorption capacity and surface diffusivity as those during the batch experiment; therefore, pilot breakthrough curves can be predicted by HSDM associated with these two parameters determined in batch-scale studies. The external mass transfer coefficient is calculated by empirical correlations from the literature because it is not scalable from batch-scale studies to pilot-scale studies due to changes in flow in the reactor. The prediction results are finally verified by full-scale pilot studies.

Only the breakthrough curves of atenolol at the upper two depths (approximately 12 and 37 cm) for 4 GACs are shown here (**Figure 5**) since the concentrations of samples taken at deeper sampling points are below the quantification limits. The results obtained for all molecules and GACs can be found in Supplemental Material B (**Fig. SB.4**). A 47% and 80% removal efficiency of atenolol was achieved for 12 cm and 37 cm depths, respectively, with virgin GAC after 250 hours of operation (**Figure 5 (a)**), corresponding to a throughput of 20833 and 6757 equivalent bed volumes (BVs), respectively. However, a slightly better removal efficiency is observed for C-6 (**Figure 5 (b)**), which achieves 58% and more than 90% removal at almost the same depths. Then, the removal efficiency decreased with aging time, showing 54% and 88% for C-17 (**Figure 5 (c)**) and 41% and 72% for C-35 (**Figure 5 (d)**) at the upper two depths, respectively.

371 The observed fixed bed behaviors of atenolol with the 4 GACs are consistent with the D_s
372 evolution in the batch kinetics tests; accordingly, the better removal performance of atenolol
373 with C-6 in the pilot tests is probably due to its faster mass transfer. The molecules penetrate
374 more rapidly into the pores of GAC, resulting in a lower molecular concentration in the outlet
375 flux (C/C_0). The good agreement between the GAC adsorption behaviors in the pilot test and
376 the D_s evolution in the batch test confirmed the feasibility of the proposed upscaling
377 prediction procedure if the pilot-scale studies are also controlled by surface diffusion.

378 Therefore, the prediction procedure was evaluated by estimating the external mass transfer
379 coefficient (k_f), which was initially estimated by several empirical correlations (Ohashi et al.,
380 1981; Ranz and Marshall Jr., 1952; Wakao and Funazkri, 1978; Wilson and Geankoplis, 1966)
381 (**Table SA.8**) and adjusted using, in particular, the first 20 hours of the breakthrough data. It
382 was intended to use empirical corrections for k_f; however, the model prediction with these
383 values underestimated the initial removal of compounds. The only adjustment of k_f improved
384 the predictions in the early stage, which also confirmed that the film diffusion controlled the
385 adsorption rate initially. The adjusted values (**Table SA.9**) are almost systematically 5-10
386 times greater than their estimations by the empirical correlations, possible because the
387 underlying assumption in the correlations is that particles are spherical, and no correction
388 factor is incorporated into the correlation formulas to compensate for the sphericity.

389 However, **Figure 5** shows that the predicted curves with equilibrium and surface diffusion
390 parameters obtained under batch conditions (represented by black continuous lines) are
391 generally located below the atenolol experimental data. This finding suggests an
392 overestimation of at least one of two “batch” parameters, either adsorption capacity or surface
393 diffusivity, or perhaps both. Several authors (Corwin and Summers, 2010; Kennedy et al.,
394 2017) have proposed introducing a scaling function of adsorption capacity or kinetics to
395 compensate for this overestimation for more accurate pilot modeling.

Accordingly, the first step was to determine an optimized modeling procedure for the pilot results while keeping as many "batch" parameters as possible. It was decided to first adjust the D_s value and to consider modifying the equilibrium parameters only in a second stage. The reason for this choice is that the uncertainty of the surface diffusivity obtained through the batch experiments is much larger than that of the isotherm parameters since the D_s value is obtained using K and n. Another reason is that the breakthrough curves are only observed over a relatively short period (nearly two weeks), while they are mostly kinetically driven. A schematic description of the upscaling prediction procedure is shown in **Fig. SB.5**.

The prediction results with optimized D_s for atenolol are plotted in **Figure 5** (represented by black discontinuous lines), showing a better agreement with the experimental data. The adjusted D_s values and Biot numbers for all GACs can be found in **Table SA.9**. Similar to batch kinetics, the Biot numbers for most molecules are relatively high, indicating that surface diffusion controls the mass transfer processes for the pilot tests. This finding is in accordance with a previous study (Kennedy et al., 2017).

Then, the correlation analysis considers only the fitted k_f values obtained when the Biot number is below 100 because k_f values are not significant when the Biot number is greater than 100; the results are reported in **Table SA.10** and **Figure 6 (a)**. Simultaneously, a correlation analysis is also conducted with the pD_s values of the four GACs (see **Table SA.11** and **Figure 6 (b)** for the results). The results show no significant correlations of k_f or D_s between the virgin GAC and the aged GACs, but good correlations are observed among the aged GACs. This result suggests that the extrapolation of k_f and D_s values for aged GACs is reliable when using GAC that was already preloaded with the NOM rather than using the virgin GAC.

Additionally, **Figure 7** shows that the behavior of surface diffusivity obtained by fitting fixed bed experiments is very close to that observed from batch kinetics experiments (**Figure 3**); their evolutions with GAC aging are similar, except for trimethoprim, ciprofloxacin and propranolol. The cross correlations of pD_s between batch and fixed-bed tests are further examined; however, no significant link between these tests was observed (**Figure 8**). **Figure 8** shows that the range of variation of surface diffusion coefficients is approximately one to one and a half orders of magnitude for the fixed bed, while it covers almost three orders of magnitude for the batch values. Nevertheless, many points are close to the first bisector line, indicating that for these compounds, the fixed bed D_s values can be easily obtained from the batch data, whereas for other compounds, a scaling factor (SF) is required.

The investigation of the SF was then conducted for every compound and GAC, using the ratio of the optimized pilot D_s value to the fitted DCBR D_s value. The results are summarized in **Table SA.12**, which shows that the individual SF differs for compounds and GACs. However, for several molecules, their individual SFs for the four GACs are very close, such as the SFs for atenolol and atrazine, and especially for chlortoluron and diuron, whose individual SFs for the four GACs are identical. Hence, a common SF for the four GACs was proposed by minimizing the sum of the square error according to **Eq. 4**.

$$\sum error = \sum\left(\frac{D_{s\,pilot} - D_{s\,DCBR} * common\ SF}{D_{s\,pilot}}\right)^2 \qquad \textbf{(Eq. 4)}$$

From **Table SA.12**, the 9 molecules (*i.e.*, atenolol, atrazine, chlortoluron, deisopropyl atrazine, diuron, roxithromycin, propazine, tebuconazol) can be successfully scaled by a single common SF ($\sum$Error < 1) (an example is shown in **Figure 9**), while a common SF cannot be derived for other molecules.

3.4 Application of the time-variable empirical function

The above studies are mainly dedicated to finding upscaling approaches for fixed bed prediction, while the relationships among the adsorption parameters and the aging time are not well understood. Indeed, the adsorption isotherm and kinetics tests show that the evolution of the adsorption capacity and rate with GAC aging time can be represented by a time-variable empirical function (Carter and Weber Jr., 1994; Jarvie et al., 2005).

In the study by Carter and Weber Jr. (1994), they considered up to only 4 weeks of preloading; hence, they proposed empirical functions having a generic form like **Eq. SA.1** (in the Supplementary Material A) or a single linear relation with preloading time. Such a model is not suitable here, as we have observed that most kinetics parameters exhibit a maximum value during their time evolution.

Moreover, several studies demonstrated that the adsorption parameters were related to the NOM surface loading rather than the preloading time since NOM preloading can be significantly impacted by hydraulic conditions (especially the flow velocity) (Li et al., 2003) and the NOM concentration. Corwin and Summers (2010) showed that mixing and repacking of GAC media did not disrupt the mass transfer zone of the NOM, and the NOM surface concentration of a given BV was identical. Therefore, the use of a BV for the time-variable empirical function can successfully avoid the interference of the preloading time.

Hence, we propose a slightly different generic expression (**Eq. 5**) that can reproduce most of the observed evolutions; an example of the fitted curves can be seen in **Figure 10**.

$$\frac{X(BV)}{X_0} = 1 - (a_X - b_X \cdot BV) \cdot \exp\left(-\frac{BV}{c_X}\right) \qquad \textbf{(Eq. 5)}$$

where X is any adsorption parameter (K, n, k_f or D_s) for a given BV, X_0 is the value for virgin activated carbon, and a_x, b_x and c_x are the empirical coefficients for parameter X. Nonlinear

regression analyses are carried out for all varying parameters with the defined function (**Eq. 5**), and the results are summarized in **Table SA.13 – SA.15**. All coefficients here are specific to the given adsorbate/adsorbent/matrix experimental conditions and are not to be extended to other cases, but the empirical functions give a relatively good prediction with low errors.

Therefore, the GAC aging effect on the adsorption capacity and kinetics in batch tests can be assessed by the application of a time-variable empirical function for all target molecules. However, this assessment is not enough for a pilot prediction since the breakthrough curves of fixed bed tests cannot be directly simulated by batch parameters without an SF. Thus, for further upscaling applications, the empirical function of D_s can be modified by the SF (**Eq. 6**):

$$\frac{D_s(BV)_{fixed-bed}}{D_{s_{0,batch}}} = SF \cdot \left[1 - \left(a_{D_s} - b_{D_s} \cdot BV\right) \cdot \exp\left(-\frac{BV}{c_{D_s}}\right)\right] \quad \textbf{(Eq. 6)}$$

where the D_s value for the fixed bed prediction can be estimated at a given BV. Unfortunately, while the values of the coefficients a_{Ds} and c_{Ds} from the DCBR data and the fixed bed data are close for many compounds, this cannot be considered a generally acceptable assumption. A smaller variation range of D_s values obtained from fixed bed data mainly affects the b_{Ds} values.

4. Conclusions

The scale-up methodology based on the HSDM was tested as a feasible approach to predict breakthrough curves of fixed beds with aged GAC. All the experiments, equilibrium, batch kinetics and fixed bed dynamics were performed with real water that was withdrawn from a drinking water treatment plant just before the GAC treatment unit and with the GAC sampled from the plant's GAC filters to maximally maintain the real conditions. Several conclusions can be drawn from this study:

- The adsorption capacities for MPs were well fitted by the Freundlich isotherm for both virgin and aged GACs in the presence of NOM. A global reduction in the adsorption capacity was observed for aged GACs compared to virgin GAC, which can be explained by pore blockage and direct competition mechanisms. While an irregular increase in the adsorption capacity was observed for three compounds with aged GACs, this result suggested that biofilm evolution modified the surface interactions towards these molecules.
- Adsorption kinetics in batch reactors and fixed bed reactors can successfully be described by HSDM for all GACs. The adsorption kinetics for both experimental scales was dominated by surface diffusion (D_s). Instead of a continuous reduction in the D_s values with aging time, the D_s reached a maximum after several months of use for more than half of the compounds in both reactor setups. A possible explanation for this result was that modification of the surface properties by a biofilm contributed to the porous diffusion, resulting in an apparent increase in the D_s value obtained using HSDM fitting.
- The feasibility of the upscaling prediction procedure was evaluated via the adsorption capacity and surface diffusivity obtained in batch-scale tests. This modeling approach was finally verified by comparing the predicted breakthrough curves with the real adsorption profiles in a real-scale fixed bed pilot test. The model prediction overestimated the pilot adsorption performance for the majority of compounds when the batch parameters were directly used. An SF for D_s could help to compensate for the overestimation. However, its value appeared to be compound dependent. The application of the above upscaling studies for fixed bed predictions, including the direct use of batch parameters and the use of batch parameters with an SF, was

restricted to a portion of molecules because no clear global relationship was found between the two scales used for the experimental tests.

- Finally, the aging effect on the adsorption capacities and kinetics was interpreted by a new form of an empirical function that enabled reproducing the different forms of the relative evolutions of equilibrium and kinetics parameters with aging time or bed volume throughput. Although the empirical function is still an adsorbent/adsorbate/matrix-dependent function, it provides insight into the aging effect on the adsorption parameters. Combining this function with the SF, the prediction for pilot adsorption behaviors is now possible. For industrial long-term implementation, this scale-up prediction methodology associated with empirical functions should facilitate the modeling approach.

This simulation approach remains interesting since all modeling parameters, such as adsorption capacities and surface diffusion coefficients, determined in relatively short-term economical batch tests could be used for fixed bed efficiency predictions. Although it is beyond the scope of this study, qualitative and quantitative structure-activity relationships should be considered to interpret the influence of the nature of the compounds, the GACs or the water quality on the SF or coefficients of the time-variable empirical functions. This methodology might offer a useful simulation approach for industrial design.

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Reference

Bakir, A., Rowland, S.J., Thompson, R.C., 2014. Transport of persistent organic pollutants by microplastics in estuarine conditions. Estuar. Coast. Shelf Sci. 140, 14–21. https://doi.org/10.1016/j.ecss.2014.01.004

Batté, M., Koudjonou, B., Laurent, P., Mathieu, L., Coallier, J., Prévost, M., 2003. Biofilm responses to ageing and to a high phosphate load in a bench-scale drinking water system. Water Res. 37, 1351–1361. https://doi.org/10.1016/S0043-1354(02)00476-1

Baup, S., Jaffre, C., Wolbert, D., Laplanche, A., 2000. Adsorption of pesticides onto granular activated carbon: Determination of surface diffusivities using simple batch experiments. Adsorption 6, 219–228. https://doi.org/10.1023/A:1008937210953

Bazus, L., Cimetiere, N., Wolbert, D., Randon, G., 2016. Development of on-line solid-phase extraction-liquid chromatography coupled with tandem mass spectrometry method to quantify pharmaceutical, glucuronide conjugates and metabolites in water. J. Chromatogr. Sep. Tech. 7, 1–10. https://doi.org/10.4172/2157-7064.1000337

Bunmahotama, W., Hung, W.-N., Lin, T.-F., 2017. Prediction of the adsorption capacities for four typical organic pollutants on activated carbons in natural waters. Water Res. 111, 28–40. https://doi.org/10.1016/j.watres.2016.12.033

Bunmahotama, W., Hung, W., Lin, T.-F., 2015. Predicting the adsorption of organic

pollutants from water onto activated carbons based on the pore size distribution and molecular connectivity index. Water Res. 85, 521–531. https://doi.org/10.1016/j.watres.2015.08.008

Capelo-Neto, J., Buarque, N.M.S., 2016. Simulation of saxitoxins adsorption in full-scale GAC filter using HSDM. Water Res. 88, 558–565. https://doi.org/10.1016/j.watres.2015.10.048

Carter, M.C., Weber Jr., W.J., 1994. Modeling adsorption of TCE by activated carbon preloaded by background organic matter. Environ. Sci. Technol. 28, 614–623. https://doi.org/10.1021/es00053a013

Carter, M.C., Weber Jr, W.J., Olmstead, K.P., 1992. Effects of background dissolved organic matter on TCE adsorption by GAC. J. Am. Work. Assoc. 84, 81–91. https://doi.org/10.1002/j.1551-8833.1992.tb07415.x

Corwin, C.J., Summers, R.S., 2010. Scaling trace organic contaminant adsorption capacity by granular activated carbon. Environ. Sci. Technol. 44, 5403–5408. https://doi.org/10.1021/es9037462

Ding, L., Mariñas, B.J., Schideman, L.C., Snoeyink, V.L., Li, Q., 2006. Competitive effects of natural organic matter: Parametrization and verification of the three-component adsorption model COMPSORB. Environ. Sci. Technol. 40, 350–356. https://doi.org/10.1021/es050409u

Gasperi, J., Garnaud, S., Rocher, V., Moilleron, R., 2009. Priority pollutants in surface waters and settleable particles within a densely urbanised area: Case study of Paris (France). Sci. Total Environ. 407, 2900–2908. https://doi.org/10.1016/j.scitotenv.2009.01.024

Gibert, O., Lefèvre, B., Fernández, M., Bernat, X., Paraira, M., Pons, M., 2013. Fractionation

and removal of dissolved organic carbon in a full-scale granular activated carbon filter used for drinking water production. Water Res. 47, 2821–2829. https://doi.org/10.1016/j.watres.2013.02.028

Hand, D.W., Crittenden, J.C., Hokanson, D.R., Bulloch, J.L., 1997. Predicting the performance of fixed-bed granular activated carbon adsorbers. Water Sci. Technol. 35, 235–241. https://doi.org/10.1016/S0273-1223(97)00136-4

Hand, D.W., Crittenden, J.C., Thacker, W.E., 1984. Simplified models for design of fixed-bed adsorption systerms. J. Environ. Eng. 110, 440–456. https://doi.org/10.1061/(ASCE)0733-9372(1984)110:2(440)

Hand, D.W., Crittenden, J.C., Thacker, W.E., 1983. User-oriented batch reactor solutions to the homogeneous surface diffusion model. J. Environ. Eng. 109, 82–101. https://doi.org/10.1061/(ASCE)0733-9372(1983)109:1(82)

Jarvie, M.E., Hand, D.W., Bhuvendralingam, S., Crittenden, J.C., Hokanson, D.R., 2005. Simulating the performance of fixed-bed granular activated carbon adsorbers: Removal of synthetic organic chemicals in the presence of background organic matter. Water Res. 39, 2407–2421. https://doi.org/10.1016/j.watres.2005.04.023

Katsigiannis, A., Noutsopoulos, C., Mantziaras, J., Gioldasi, M., 2015. Removal of emerging pollutants through granular activated carbon. Chem. Eng. J. 280, 49–57. https://doi.org/10.1016/j.cej.2015.05.109

Kennedy, A.M., Reinert, A.M., Knappe, D.R.U., Ferrer, I., Summers, R.S., 2015. Full- and pilot-scale GAC adsorption of organic micropollutants. Water Res. 68, 238–248. https://doi.org/10.1016/j.watres.2014.10.010

Kennedy, A.M., Reinert, A.M., Knappe, D.R.U., Summers, R.S., 2017. Prediction of full-

603 scale GAC adsorption of organic micropollutants. Environ. Eng. Sci. 34, 496–507.
604 https://doi.org/10.1089/ees.2016.0525

605 Kim, Y., Bae, J., Park, H., Suh, J.-K., You, Y.-W., Choi, H., 2016. Adsorption dynamics of
606 methyl violet onto granulated mesoporous carbon: Facile synthesis and adsorption
607 kinetics. Water Res. 101, 187–194. https://doi.org/10.1016/j.watres.2016.04.077

608 Li, Q., Mariñas, B.J., Snoeyink, V.L., Campos, C., 2003. Three-component competitive
609 adsorption model for flow-through PAC systems. 1. Model develepment and verification
610 with a PAC/membrane system. Environ. Sci. Technol. 37, 2997–3004.
611 https://doi.org/10.1021/es020989k

612 Mailler, R., Gasperi, J., Coquet, Y., Derome, C., Buleté, A., Vulliet, E., Bressy, A., Varrault,
613 G., Chebbo, G., Rocher, V., 2016. Removal of emerging micropollutants from
614 wastewater by activated carbon adsorption: Experimental study of different activated
615 carbons and factors influencing the adsorption of micropollutants in wastewater. J.
616 Environ. Chem. Eng. 4, 1102–1109. https://doi.org/10.1016/j.jece.2016.01.018

617 Noll, K.E., Gounaris, V., Hou, W.-S., 1991. Adsorption technology for air and water pollution
618 control. LEWIS PUBLISHERS, INC., Michigan, USA.

619 Ohashi, H., Sugawara, T., Kikuchi, K., Konno, H., 1981. Correlation of liquid-side mass
620 transfer coefficient for single particle and fixed-beds. J. Chem. Eng. Japan 14, 433–438.
621 https://doi.org/10.1252/jcej.14.433

622 Patni, A.G., Ludlow, D.K., Adams, C.D., 2008. Characteristics of ground granular activated
623 carbon for rapid small-scale column tests. J. Environ. Eng. 134, 216–221.
624 https://doi.org/10.1061/(ASCE)0733-9372(2008)134:3(216)

625 Ranz, W.E., Marshall Jr., W.R., 1952. Evaporation from drops - Part 1. Chem. Eng. Prog. 48,

141–148. https://doi.org/10.1016/S0924-7963(01)00032-X

Scharf, R.G., Johnston, R.W., Semmens, M.J., Hozalski, R.M., 2010. Comparison of batch sorption tests , pilot studies , and modeling for estimating GAC bed life. Water Res. 44, 769–780. https://doi.org/10.1016/j.watres.2009.10.018

Schideman, L.C., Mariñas, B.J., Snoeyink, V.L., Campos, C., 2006a. Three-component competitive adsorption model for fixed-bed and moving-bed granular activated carbon adsorbers. Part I. Model development. Environ. Sci. Technol. 40, 6805–6811. https://doi.org/10.1021/es060603w

Schideman, L.C., Mariñas, B.J., Snoeyink, V.L., Campos, C., 2006b. Three-component competitive adsorption model for fixed-bed and moving-bed granular activated carbon adsorbers. Part II. Model parameterization and verification. Environ. Sci. Technol. 40, 6812–6817. https://doi.org/10.1021/es060603w

Smith, E.H., Tseng, S., Weber Jr., W.J., 1987. Modeling the adsorption of target compounds by GAC in the presence of background dissolved organic matter. Environ. Prog. 6, 18–25. https://doi.org/10.1002/ep.670060119

Speth, T.F., Miltner, R.J., 1989. Effect of preloading on the scale-up of GAC microcolumns. J. Am. Water Work. Assoc. 81, 141–148.

Villadsen, J. V., Stewart, W.E., 1967. Solution of Boundary Value Problems by Orthogonal collocation. Chem. Eng. Sci. 22, 1483–1501. https://doi.org/10.1016/0009-2509(96)81831-8

Vulliet, E., Cren-Olivé, C., 2011. Screening of pharmaceuticals and hormones at the regional scale, in surface and groundwaters intended to human consumption. Environ. Pollut. 159, 2929–2934. https://doi.org/10.1016/j.envpol.2011.04.033

649 Vulliet, E., Cren-Olivé, C., Grenier-Loustalot, M.-F., 2011. Occurrence of pharmaceuticals
650 and hormones in drinking water treated from surface waters. Environ. Chem. Lett. 9,
651 103–114. https://doi.org/10.1007/s10311-009-0253-7

652 Wakao, N., Funazkri, T., 1978. Effect of fluid dispersion coefficients on particle-to-fluid mass
653 transfer coefficients in packed beds. Chem. Eng. Sci. 33, 1375–1384.
654 https://doi.org/10.1016/0009-2509(78)85120-3

655 Wilson, E.J., Geankoplis, C.J., 1966. Liquid mass transfer at very low reynolds numbers in
656 packed beds. Ind. Eng. Chem. Fundam. 5, 9–14. https://doi.org/10.1021/i160017a002

657 Yu, Z., Peldszus, S., Huck, P.M., 2009. Adsorption of selected pharmaceuticals and an
658 endocrine disrupting compound by granular activated carbon. 1. Adsorption capacity and
659 kinetics. Environ. Sci. Technol. 43, 1467–1473. https://doi.org/10.1021/es801961y

660 Zhang, Q., Crittenden, J., Hristovski, K., Hand, D., Westerhoff, P., 2009. User-oriented batch
661 reactor solutions to the homogeneous surface diffusion model for different activated
662 carbon dosages. Water Res. 43, 1859–1866. https://doi.org/10.1016/j.watres.2009.01.028

663 Zietzschmann, F., Worch, E., Altmann, J., Ruhl, A.S., Sperlich, A., Meinel, F., Jekel, M.,
664 2014. Impact of EfOM size on competition in activated carbon adsorption of organic
665 micro-pollutants from treated wastewater. Water Res. 65, 297–306.
666 https://doi.org/10.1016/j.watres.2014.07.043

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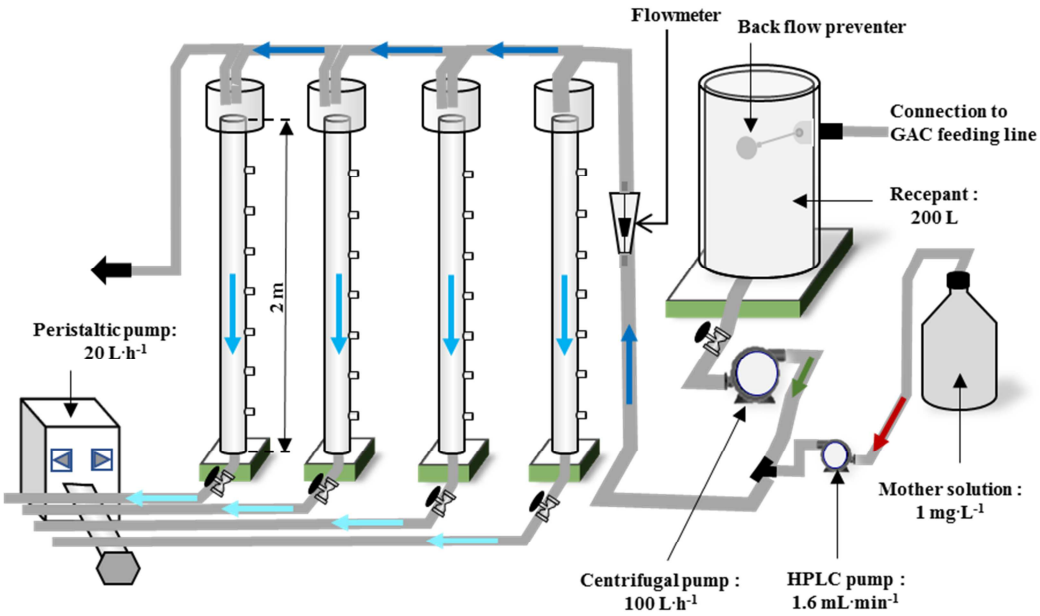

Figure 1: Schematic description of the full-scale pilot installation

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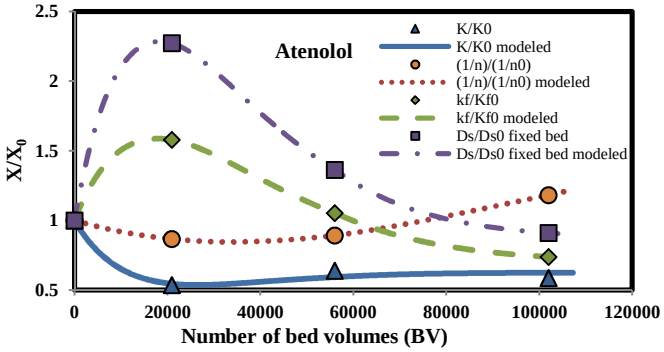

Figure 10: Example of fitted timely correlations for the various equilibrium and kinetic parameters of fixed bed HDSM model compared to the experimental data.

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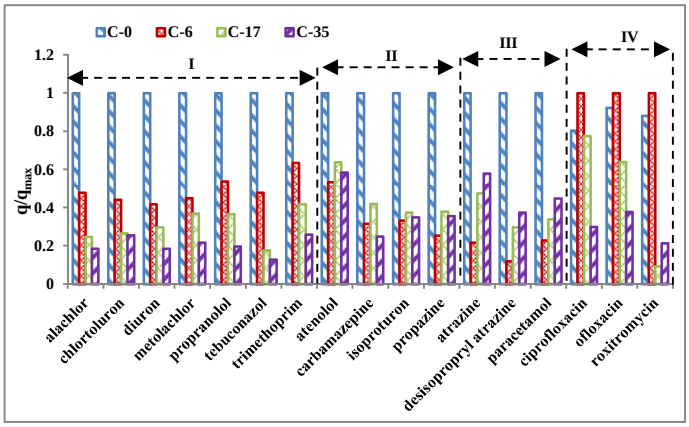

Figure 2: Relative adsorption capacities of micropollutants (q value compared to maximum q value of the four GACs) with various aged GACs (C-0, C-6, C-17 and C-35 represent respectively the virgin GAC and the aged GACs being in service for 6, 17 and 35 months). Four different groups of behaviors, labeled I to IV, are identified.

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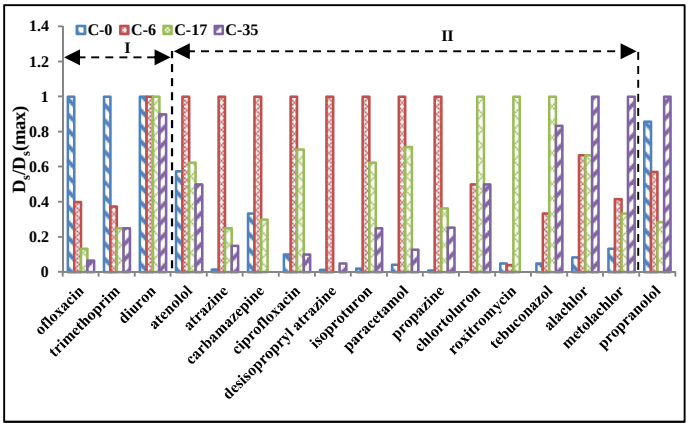

Figure 3: Relative surface diffusivities of micropollutants (D_s value compared to maximum D_s value of the four GACs) with various aged GACs (C-0, C-6, C-17 and C-35 represent respectively the virgin GAC and the aged GACs being in service for 6, 17 and 35 months). Two different groups of behaviors with exception of propranolol, labeled I to II, are identified.

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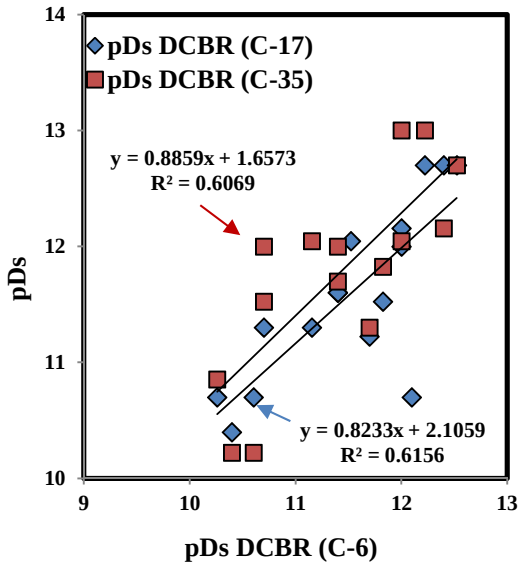

Figure 4: Correlation analysis of the pD_s values for DCBR setup among the aged GACs

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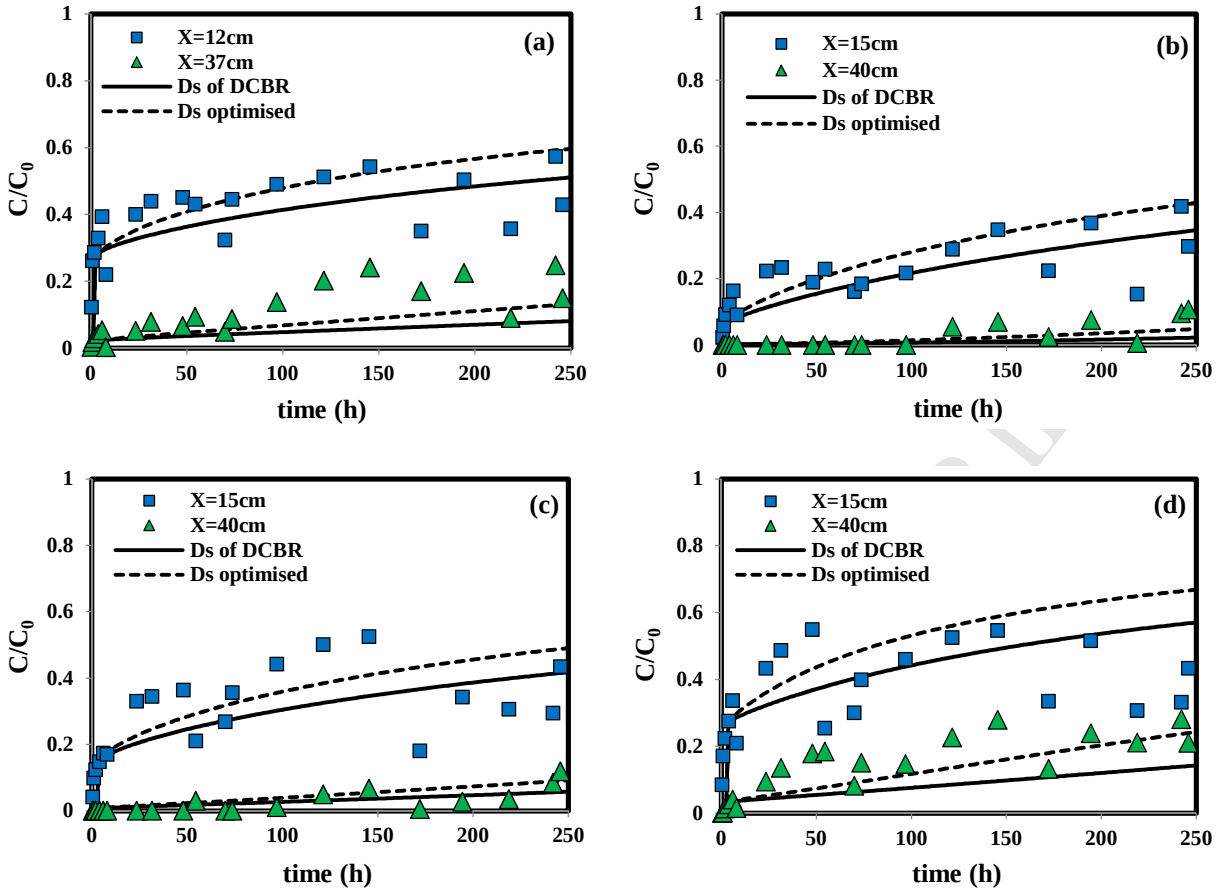

Figure 5: Breakthrough curves of atenolol with 4 GACs at the two depths: (a) C-0; (b) C-6; (c) C-17 and (d) C-35. Continued black line is HSDM modeling curve with D_s value obtained in DCBR setup, discontinued black line is HSDM modeling curve with optimized D_s value.

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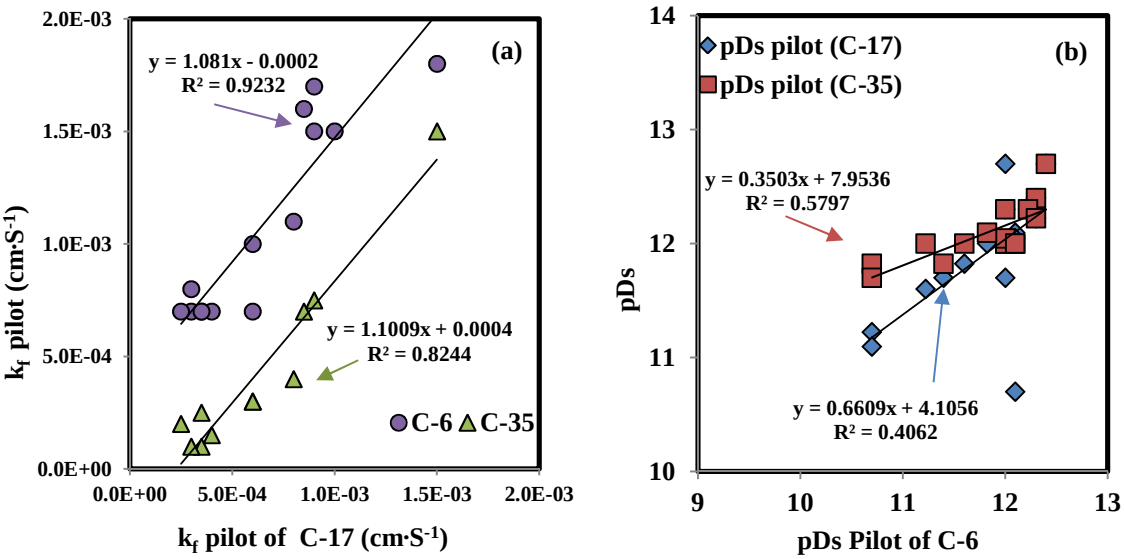

Figure 6: (a) Correlation among the fitted k_f values for full-scale pilot of virgin and aged GAC for the various compounds (k_f values have been discarded when the Biot number exceeded 100); (b) Correlation analysis of the pD_s values for full-scale pilot of aged GACs

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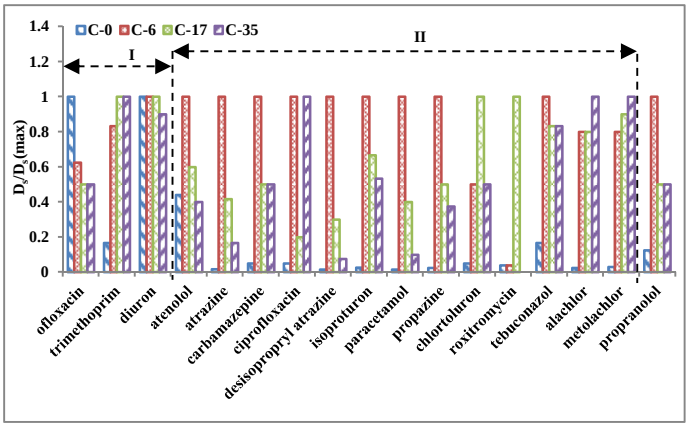

Figure 7: Time evolution of relative D_s values obtained from the fixed bed experiments. Group I and II are those defined in **Figure 3**.

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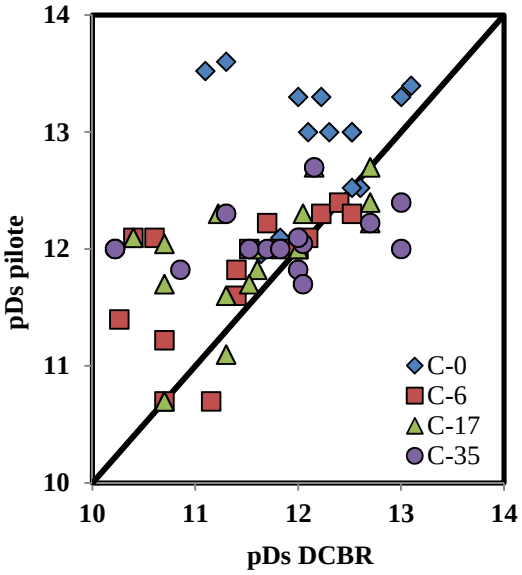

Figure 8: Cross correlation of pD_s values between the fixed bed and the batch kinetics tests of the 4 different GACs

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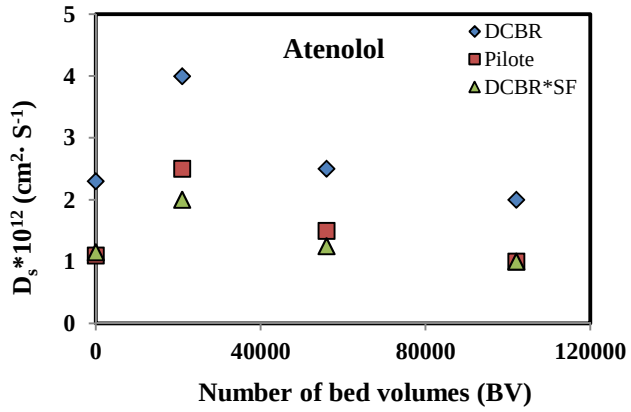

Figure 9: Example of application of scaling factor (SF)

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Highlights:

- Adsorption capacities of the GAC reduced seriously after the 6 months of use
- D_s reached maximum after several months of use followed by a decrease
- An SF was required to predict the adsorption behaviors of the fixed bed
- A new pseudo-first order function was employed to model the impact of GAC aging on the adsorption parameters

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