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Modeling emerging contaminants breakthrough in packed bed adsorption columns by UV absorbance and fluorescing components of dissolved organic matter

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ABSTRACT

This study investigated, using rapid small-scale column testing, the breakthrough of dissolved organic matter (DOM) and eleven emerging organic contaminants (EOCs) during granular activated carbon (GAC) filtration of different water qualities, including wastewater, surface water and synthetic water (riverine organic matter dissolved in deionized water). Fluorescing organic matter was

20 better adsorbed than UV absorbance at 254 nm (UV₂₅₄) and dissolved organic carbon (DOC) in all
21 tested water. Furthermore, highest adsorption of DOM (in terms of DOC, UV₂₅₄ and fluorescence)
22 was observed during wastewater filtration. UV absorbing DOM had fast and similar breakthrough
23 in surface water and synthetic water, whereas fluorescence breakthrough was very rapid only in
24 synthetic water. PARAFAC modeling showed that different fluorescing components were differ-
25 ently adsorbed during GAC process. Particularly, fluorescing components with maxima intensity
26 at higher excitation wavelengths, which are corresponding to humic-like fluorescence substances,
27 were better removed than other components in all waters. As opposed to DOM, EOCs were better
28 adsorbed during synthetic water filtration, whereas the fastest EOCs breakthrough was observed
29 during filtration of wastewater, which was the water that determined the highest carbon fouling.
30 Exception was represented by long-chained perfluoroalkylated substances (i.e., PFOA, PFDA and
31 PFOS). Indeed, adsorption of these compounds resulted independent of water quality. In this study
32 was also investigated the applicability of UV₂₅₄ and fluorescing PARAFAC components to act as
33 surrogates in predicting EOCs removal by GAC in different water matrices. Empirical linear cor-
34 relation for the investigated EOCs were determined with UV₂₅₄ and fluorescing components in all
35 water qualities. However, fluorescence measurements resulted more sensitive than UV₂₅₄ to pre-
36 dict EOC breakthrough during GAC adsorption. When the data from all water qualities was com-
37 bined, good correlations between the microbial humic-like PARAFAC component and EOC re-
38 movals were still observed and they resulted independent of water quality if considering only real
39 water matrices (wastewater and surface water). On the contrary, correlations between EOC remov-
40 als and UV₂₅₄ removals were independent of water quality when combining data of surface waters
41 and synthetic water, but a different correlation model was needed to predict EOCs breakthrough
42 in wastewater.

Keywords: pharmaceutical and personal care products; PFAS; PARAFAC; fluorescence EEM; real-time monitoring; granular activated carbon.

1. Introduction

The occurrence of pharmaceuticals, steroid hormones, pesticides and personal care products, collectively termed as emerging organic contaminants (EOCs) or contaminants of emerging concern (CECs), have been consistently reported for over a decade in different water matrices, including wastewater, surface water and drinking water (Benotti and Brownawell, 2007; Dickenson et al., 2011; Focazio et al., 2008). Wastewater treatment plants (WWTPs) have been recognized as significant hotspots for the transfer of EOCs into the environment (Michael et al., 2013; Vieno et al., 2005), and with the increased focus on implementing potable water reuse schemes around the world, there is a greater possibility of these wastewater derived contaminants entering drinking water sources (Al-Rifai et al., 2007; Dickenson et al., 2011; Focazio et al., 2008). While effects of many EOCs on public health remain largely unknown, studies have shown that some of these contaminants can have drastic effects on aquatic organisms at concentrations typical for wastewater discharges (Bevans et al., 1979). Other studies have demonstrated that a combination of EOCs can have synergistic effects on some organisms (Carlsson et al., 2006; Daughton and Ternes, 2009).

Advanced treatment technologies have been implemented in water reuse systems and drinking water treatment plants as effective means to attenuate EOCs (Roccaro, 2018; Wert et al., 2009; Wols et al., 2013). Advanced oxidation processes (AOPs) like ozone and UV with addition of hydrogen peroxide, or high pressure membrane filtration have proven to remove many EOCs from

water (Kim et al., 2007; Wert et al., 2009; Wols et al., 2013), but with some drawbacks. For example, studies have shown that AOPs produce transformation products of generally unknown toxicity (Jia et al., 2015; Rizzo, 2011), whereas membrane processes generate concentrated brine streams and entail relevant treatment costs (Roccaro et al., 2013). In contrast, adsorption processes like granular activated carbon (GAC) are economically sustainable, do not result in transformation products and are capable of removing a wide range of EOCs (Kim et al., 2007; Roccaro et al., 2013; Snyder et al., 2007).

The analysis of EOCs at trace levels in water is laborious, time-consuming and expensive. In addition, it requires sophisticated analytical equipment and highly trained technicians. Hence, the use of surrogate parameters that can accurately predict the removal of EOCs in a simple, fast, and cost-effective manner is highly desirable. Spectroscopic parameters like UV absorbance and fluorescence have been shown to be useful monitoring tools for both conventional and emerging water contaminants in different natural and engineered water systems (Carstea et al., 2016; Korshin et al., 2018; Sgroi et al., 2018, 2017a, 2017b). Particularly, extensive recent research in this area has shown the possibility to accurately predict EOCs removal during various advanced treatments (e.g., ozonation, UV/H₂O₂, adsorption) by surrogate parameters based on spectroscopic measurements (Chys et al., 2018, 2017; Gerrity et al., 2012; Korshin et al., 2018; Merel et al., 2015; H. W. Yu et al., 2015; Zietzschmann et al., 2016a).

Studies focused on adsorption processes have discussed the performance of UV absorbance at 254 nm (UV₂₅₄) and total fluorescence (Φ_{tot}) indicators to predict EOCs removal by activated carbons in both powdered activated carbon (PAC) processes (Altmann et al., 2016; Zietzschmann et al., 2014a; Ziska et al., 2016) and granular activated carbon (GAC) filter (Anumol et al., 2015). The

developed models provided excellent predictions of EOCs removal in different secondary or tertiary wastewater effluents and these models resulted independent of the wastewater quality (Altmann et al., 2016; Anumol et al., 2015; Zietzschmann et al., 2016a; Ziska et al., 2016).

During adsorption processes, the most crucial factor impacting EOCs removal is the competition caused by the presence of organic matter (OM) in water. OM is different in concentration and composition between different waters (e.g., surface water and wastewater), and aspect of OM character such as molecular weight distribution, degree of hydrophobicity, and charge distribution affect its adsorbability as well as the extent to which it decreases micro-pollutant adsorption through direct competition and pore blockage, collectively termed fouling (Shimabuku et al., 2017; Velten et al., 2011; Zietzschmann et al., 2014b). A recent study observed significant differences between EOCs breakthrough curves in drinking water and wastewater effluent and these differences were attributed to the concentrations of the low molecular weight (LMW) acid and neutral organics of the waters (Zietzschmann et al., 2016b). Presenting the relative EOC concentrations over the specific throughput of the LMW organics, the EOC breakthrough curves in drinking water and WWTP effluent superimposed each other (Zietzschmann et al., 2016b). In a further study, the adsorption of organic micro-pollutants onto PAC was compared between regionally different waters within two groups, namely five drinking waters and seven wastewater effluents. Correlations between EOC removals and UV_{254} removals were independent of the water quality within the respective group, but different regression parameters were obtained for drinking waters and wastewaters (Zietzschmann et al., 2016a). To date, similar studies have not been accomplished using fluorescence measurements and during GAC filtration.

Fluorescence spectroscopy is a rapid, cost-effective, reagentless technique that requires little or no sample preparation prior to analysis. The acquisition of 3-dimensional excitation-emission matrices (EEMs) provides a ‘map’ of contributions of different component classes comprising dissolved organic matter (DOM) (Carstea et al., 2016; Henderson et al., 2009). EEM of natural waters and wastewater tend to have distinct features with maxima located at characteristic combinations of excitation and emission wavelengths. Thus, an important advantage of fluorescence versus UV–vis absorbance is the potential for discriminating between different sources of chromophoric DOM that absorb at similar wavelengths. A further advantage of fluorescence is that sensitivity is typically 10–1000x that of UV absorption spectroscopy (Carstea et al., 2016; Henderson et al., 2009; Korshin et al., 2018).

EEMs offer varied possibilities of data interpretation, from simple peak-picking and Fluorescence Regional Integration to the more complex Parallel Factor Analysis (PARAFAC) and Self-Organizing Maps (Carstea et al., 2016; Chen et al., 2003; Murphy et al., 2013). Among these methods, PARAFAC is becoming the most popular in the research community due to its ability to mathematically decompose the complex fluorescence spectra into a finite number of potentially overlapping independent components characterized by their distinct spectroscopic features. Such deconvolution helps discriminate and ascertain contributions of different DOM types and sources, and provides an useful tool for DOM characterization in water (Murphy et al., 2013, 2011).

Accordingly, objectives of this study were: (i) to explore breakthrough curves of different DOM components identified by PARAFAC analysis in different water matrices, including wastewater and surface water during GAC filtration; (ii) to evaluate and compare the ability of different spectroscopic indexes based on fluorescence and UV absorbance measurements to predict EOCs breakthrough using surface water and wastewater. In this study, GAC processes have been simulated

using rapid small scale column testing (RSSCT), which are bench scale tools able to accurately predict GAC performance in a short period of time (Anumol et al., 2015; Crittenden et al., 1991). In addition, two different surface waters have been utilized, a real surface water and a synthetic surface water obtained dissolving concentrate riverine organic matter in deionized (DI) water. In this latter case, no salts were added in water, and thus, the impact of ionic strength in the adsorption process is missing.

2. Materials and methods

2.1. Materials and tested waters

All purchased solvents, standards, and reagents were of high purity. The details concerning these materials are reported in the Supplementary material section (Text S1).

Waters tested in this study included a non-chlorinated secondary wastewater effluents from the city of Tucson (Arizona, USA), a surface water collected from the Central Arizona Project (CAP), which is a diversion canal that convey water from the Colorado River to Central and Southern Arizona, and a synthetic water obtained dissolving Suwannee River Natural Organic Matter (NOM) (International Humic Substances Society, St. Paul, MN, USA) in DI water. All water were filtered using a 0.45 μm cartridge filter (GE Healthcare, USA) prior to testing. Water quality parameters after filtration are provided in Table 1.

2.2. Selection of EOCs

Eleven EOCs including pharmaceutical, personal care products, and perfluorinated compounds (Table 2) were selected based on their octanol-water partition coefficients ($\log K_{ow}$), charge, occurrence in water, and availability of authenticated standards. Compounds were selected in order

to have in water micropollutants with very different adsorption characteristics. To account for ionic effects on the log K_{ow} , a pH corrected log D_{ow} term was calculated for the pH of each water (Martínez-Hernández et al., 2014). In surface water and synthetic water, compounds were spiked using a highly concentrated stock (100-250 $\mu\text{g/mL}$) in 50:50 (v/v) HPLC-water:methanol solution. In wastewater, EOCs were present at naturally occurring concentration. Due to the small amount of spiked compounds solution (100 μL), the change in dissolved organic carbon (DOC) was negligible. Relevant chemical properties and concentrations of EOCs (after spiking) in water are reported in Table 2. In surface water spiked compounds were summed to naturally occurring concentrations.

2.3. Analytical methods

All EOCs were analyzed using an automated liquid chromatography online SPE system coupled to an Agilent 6460 triple-quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA). The method required only 1.5 ml of sample thus allowing minimal sample collection during the experiment. Resulting reporting limits ranged from 1 to 20 ng/L. Further details of the analytical method are available in previously published literature (Anumol and Snyder, 2015) and are also briefly described in Supplementary material section (Text S2; Table S1 – S2). For dissolved organic carbon (DOC) analysis, samples were filtered through 0.45 mm hydrophilic polypropylene filter (GHP Membrane Acrodisc, Pall Life Sciences) and acidified to pH < 3 with hydrochloric acid. A Shimadzu TOC-L_{CSH} (Kyoto, Japan) total carbon analyzer was used for quantification.

Ultraviolet light absorbance was analyzed using Varian Cary 50 UV/Vis spectrophotometer. Fluorescence data were collected using Varian Cary Eclipse fluorescence spectrophotometer with the scanning range from excitation wavelength 200 nm to 450 nm at an interval of 5 nm and emission

wavelength from 250 nm to 580 nm at the interval of 1 nm. Excitation and emission slit widths were both set at 5 nm. The Raman scatter effect was minimized by subtracting EEMs of pure DI water from the sample EEMs; any negative intensity values produced by this subtraction were converted to zero values. Then, the emission intensity data were normalized to the Raman peak area of an emission wavelengths scan of DI water samples collected at the interval of 1 nm and related to an excitation wavelength of 350 nm to produce fluorescence intensities in Raman unit (RU) (Murphy et al., 2010). All the EEMs were subjected to inner filter effect correction according to the methodology proposed by MacDonald et al. (MacDonald et al., 1997). Non-trilinear data related to the Rayleigh scattering were eliminated and interpolated from either side of the scatter band following the tutorial published by Murphy et al. (Murphy et al., 2013). Regional integration was conducted according to previously published literature (Chen et al., 2003; Sgroi et al., 2016) to calculate the total fluorescence intensities for each sample.

The point of zero charge (p_{zc}), defined as the pH at which the number of negatively and positively charged sites on the surface of the carbon are equal (net charge on surface = 0) was experimentally determined by calculating the slurry pH (Redding et al., 2009).

2.4. PARAFAC modeling

PARAFAC analysis was carried out using the drEEM toolbox (Murphy et al., 2013). PARAFAC modeling was performed independently for each tested water to avoid that source diversity undermined the accuracy of the model (H. Yu et al., 2015). Fluorescence data set of wastewater included 74 EEMs, data set of surface water and synthetic water included 25 EEMs each. Non-negative constraints were applied for excitation and emission loadings. In order to examine the soundness of the PARAFAC modeling and to identify the number of fluorescence components, a series of

criteria was applied to each EEM dataset: (1) the examination of the core consistency, (2) the evaluation of the shape of the spectral loading, (3) the leverage analysis regarding the influence of a specific sample or certain excitation and emission wavelengths, (4) the residuals analysis and (5) the split half analysis. No outlying samples emerged during the PARAFAC modeling but it was needed to exclude part of the EEMs with excitation wavelength < 250 nm that exerted disproportionate leverage on the model and impeded a correct model validation. A PARAFAC model with 4 components was validated for the wastewater; a PARAFAC model with 2 components was validated for the surface water, whereas a PARAFAC model with 3 components was validated for the synthetic water. The fluorescence intensity at the maximum for each PARAFAC component was used as fluorescing index to monitor breakthrough curves during GAC adsorption.

2.5. RSSCT procedure

All RSSCTs were designed according to the constant diffusivity (CD) model based on previous studies (Anumol et al., 2015; Redding et al., 2009). All the RSSCTs were performed using the same GAC (NORIT DARCO 12x40) with a simulated full-scale empty bed contact time (EBCT) corresponding to 5.2 min. General characteristics of the used carbon are reported in Table S3. Before the experiment, fresh carbon was crushed with a mortar and pestle and sieved using the U.S standard sieves. The fraction between mesh size #100 and #140 ($d_p = 0.125$ mm) was collected. The carbon was washed thoroughly with ultrapure water and stored in a sterile environment until use. The crushed carbon slurry was placed in a 10 mm inner diameter glass column with polypropylene caps and fittings (Kimble Chase, New Jersey). Care was taken in selecting the column so that the aspect ratio was >10 to avoid wall effects and channeling (Knappe et al., 1997). The flowrate of the water was adjusted using a peristaltic pump to achieve the desired EBCT. Once the experiment was started, GAC effluent samples were collected periodically for EOCs, DOC, UV

and fluorescence analysis while influent control samples were collected daily to determine if there was any degradation of EOCs in the feed water. Details of the RSSCT design with comparison to a full-scale system operating with the same EBCT are presented in Table S4.

3. Results and discussion

3.1. GAC adsorption of organic matter

DOM concentration in water is typically measured by bulk parameters such as DOC, UV absorbance and fluorescence. Particularly, this latter method is growing in popularity to characterize DOM, as it is simple and provides a large amount of information. As previously discussed, PARAFAC analysis is a useful tool for EEMs interpretation. Indeed, this method enables the deconvolution of complex EEMs into independent components that represent groups of similarly behaving fluorophores (Murphy et al., 2011; Sgroi et al., 2017b). In this study, the three developed PARAFAC models identified a total number of five independently varying fluorescing components. Within these five components, four fluorescing components were identified in wastewater, two components in surface water and three components in synthetic water. Figure 1 shows the spectral fingerprint of the identified fluorescing components, denoted henceforth as C1–C5. Wavelengths corresponding to the positions of the excitation and emission maxima are reported in Table S5 – S7, whereas the excitation and emission loadings are shown in Figure S1 – S3. Based on the position of the excitation and emission peaks ($\lambda_{\text{ex}}/\lambda_{\text{em}}$), components C1 ($\lambda_{\text{ex}}/\lambda_{\text{em}} = <250/355\text{-}400$ and $285\text{-}305/355\text{-}400$), C2 ($\lambda_{\text{ex}}/\lambda_{\text{em}} = <250\text{-}265/470\text{-}495$ and $365\text{-}395/470\text{-}495$), C4 ($\lambda_{\text{ex}}/\lambda_{\text{em}} = <250/435$ and $345/435$), and C5 ($\lambda_{\text{ex}}/\lambda_{\text{em}} = <250\text{-}250/450$ and $325/450$) were identified as humic and fulvic-like fluorescence (Ishii and Boyer, 2012; Murphy et al., 2011; Sgroi et al., 2017b; H. Yu et al., 2015). Specifically, component C1 represents the contribution of a microbial humic-like

fluorescence, whereas component C2 that of a terrestrial humic-like component. These two components have been previously observed in both surface water and wastewater (Murphy et al., 2011; Sgroi et al., 2017b; H. Yu et al., 2015). In this study, component C1 was common to all the investigated waters, component C2 was found in wastewater and synthetic water. Component C4 corresponds to a group of humic-like fluorescing species found in prior studies in high nutrient and wastewater impacted environments (Murphy et al., 2011; Sgroi et al., 2017b; H. Yu et al., 2015; Yu et al., 2010). In this study, component C4 was found only in wastewater. Component C5 is commonly abundant in DOM dominated by terrestrial precursor material and it is generally absent from wastewater (He and Hur, 2015; Ishii and Boyer, 2012). Accordingly, in this study component C5 was detected only in surface and synthetic waters. Component 4 and 5 have both two fluorescence peaks situated at similar wavelength positions. However, component C4 shows its maxima intensity at an excitation wavelength of 435 nm, whereas component C5 has its maxima intensity at excitation wavelengths < 250 nm. Finally, protein and tryptophan-like fluorescing compounds, observed in prior studies as typical fluorescence component of wastewater matrices, are associated with component C3 ($\lambda_{ex}/\lambda_{em} = 275/330$) (Murphy et al., 2011; Sgroi et al., 2017a; H. Yu et al., 2015).

The Fluorescence EEMs provide a qualitative estimate of treatment process efficacy and are shown in Figure 2. As seen for all waters, initially there is a decolorizing effect in the EEMs as the GAC is effective in removing fluorescent organic matter in all regions of the EEM compared to the influent to the column. However, this decolorizing effect was very evident in wastewater and in a less extent in surface water. In the synthetic water the decolorizing effect was limited. With time, the active sites on the GAC are exhausted and gradually increased breakthrough of fluorescent matter is seen in the three waters. The amount of breakthrough varies based on water quality and

bed volume when the carbon and EBCT are constant. These observations suggest that DOM was removed in a different way from the three waters. It can be better observed in Figure 3, which shows the breakthrough curves of the identified PARAFAC components. In wastewater, breakthrough of components C1, C2, C4 was negligible at bed volumes (BVs) < 5 , except component C3 that when the experiment started showed immediately a breakthrough of 16%. Surface water had an immediate breakthrough of around 20% for component C1 and C5, whereas organic matter in synthetic water was scarcely adsorbed and components C1, C2 and C5 showed an immediate breakthrough higher than 50%. It is interesting to observe that PARAFAC components with maxima fluorescence intensity at higher excitation wavelengths, which are corresponding to humic-like fluorescence substances, were better removed than other components in all waters. Component C4 was the component most adsorbed during the GAC process, followed by the microbial humic-like component C1 (Figure 3).

Various DOM characteristics affect its adsorption in GAC filters and these include aromaticity, degree of hydrophobicity, molecular size, charge distribution and ability to form hydrogen bonds with the GAC surface (Shimabuku et al., 2017; Velten et al., 2011; Zietzschmann et al., 2015, 2014b). Particularly, recent studies showed that DOM adsorbability decreases when aromaticity increase (Shimabuku et al., 2017). Accordingly, in this study component C3, which is typical of aromatic protein and tryptophan-like substances, was the less adsorbed fluorescing component of wastewater (Figure 3). In addition, it was shown that fluorescence components differ also for molecular size (Wu et al., 2003), and that small sized DOM contains better adsorbable compounds, which largely affects micro-pollutants fouling (Zietzschmann et al., 2014b). Furthermore, the charge of DOM and ionic strength of waters may have had a significant role in the adsorption process, particularly determining the low adsorbability of DOM of synthetic water. The pH_{Zc} for

the Norit DARCO 12 x 40 was found to be 6.4, which meant that at pH of tested waters, its surface was negatively charged in surface water (pH 8.4) and wastewater (pH 7.5), and slightly negatively charged in synthetic water (pH 6.7). Because of the presence of carboxylic acid and phenolic groups in the DOM structure, DOM carries a negative charge at these pH values (Perdue and Lytle, 1983). In these circumstances, surface-DOM electrostatic interaction should oppose adsorption, because both DOM and carbon surface are negatively charged. However, it has been demonstrated that if salts are present in water the ionic strength of water can increase adsorption and salts effectively screen electrostatic repulsion (Bjelopavlic et al., 1999). In synthetic water the absence of salts along with effects related to manipulation of Suwannee River NOM during extraction and concentration processes may have reduced the adsorption capability of this DOM. However, more research is needed to understand this phenomenon.

The rate of breakthrough of the different bulk parameters of water considered in this study was in the order: $\text{DOC} > \text{UV}_{254} > \text{fluorescence indexes } (\text{O}_{\text{tot}} \text{ and PARAFAC components})$. It is in agreement with previous studies, where it has been hypothesized fluorescence DOM to be lower in molecular weight than UV-absorbing DOM or DOC measured compounds to explain its preferential adsorption (Anumol et al., 2015; Shimabuku et al., 2017; Velten et al., 2011). In Figure 4 is reported a comparison for breakthrough curves of DOC, UV_{254} , O_{tot} and PARAFAC components in the three tested waters. Wastewater showed the slowest breakthrough for all these parameters except component C1, which was better adsorbed in surface water. On the other hand, the fastest breakthrough for all the bulk parameters was always observed in synthetic water. The breakthrough of UV_{254} was very fast and very similar in surface water and synthetic water, suggesting that typical UV-absorbing DOM of surface water is scarcely adsorbed and probably non-affected by ionic strength of water and/or other electrostatic interactions. On the contrary, fluorescence DOM was

309 better adsorbed in surface water than in synthetic water. $\emptyset_{\text{tot}}$ had a similar breakthrough in surface
310 water and wastewater. However, differences can be observed in the adsorption process if consid-
311 ering specific fluorescing PARAFAC components. For example, the adsorption rate of component
312 C1 was similar in surface water and wastewater until 60% breakthrough. Then, C1 breakthrough
313 was faster in wastewater, probably due to the higher carbon fouling of this water. Thus, these data
314 show that DOM adsorption in GAC filter is a very complex process, which is strongly influenced
315 by DOM composition and charge distribution. In addition, different bulk parameters of water, such
316 as DOC, UV absorbance and various fluorescence components, are measurements of different
317 components of DOM, which are differently adsorbed in GAC processes.

318 **3.2. Breakthrough curves of EOCs**

319 The breakthrough curves of four representative EOCs in GAC reactors are shown in Figure 5. The
320 complete set of breakthrough profiles for the eleven investigated EOCs in all water qualities are
321 shown in Figure S4. The fastest breakthrough (i.e., the lowest adsorption) for all the compounds
322 was always observed in wastewater. On the contrary, the slowest breakthrough and highest ad-
323 sorption of EOCs was observed in synthetic water. Thus, adsorption dynamics of EOCs were op-
324 posed to those of DOM. Indeed, in waters where a higher DOM adsorption and carbon fouling was
325 observed, EOCs have always shown lower adsorbability. These evidences suggest that competition
326 effect with DOM was the main reason of differences in EOCs adsorption observed between the
327 tested water qualities. Only exception was represented by the perfluoroalkylated substances (PFAS),
328 which had a similar breakthrough in all water qualities and seemed to not be influenced by the rate
329 of DOM adsorption and carbon fouling. PFOA, PFDA and PFOS are long-chained PFAS that due
330 to the presence of a long hydrophobic chain are able to form molecular aggregates which can be
331 retained on the active surface (McCleaf et al., 2017; Zaggia et al., 2016). Thus, adsorption of these

compounds seems to be mainly related to hydrophobic interaction, and the number of available active sites on activated carbon does not represent the main limiting factor. This rationale may explain the similar breakthrough curves observed for long-chained PFAS in waters with different content and quality of DOM. However, authors encourage further research on this topic.

By an accurate analysis of breakthrough curves in Figure 5 and Figure S4, it can be observed that, excluding PFAS compounds, breakthrough curves of EOCs in wastewater and surface water almost overlapped each other during the initial phase of the GAC process, later breakthrough was faster in wastewater due to the higher carbon fouling. Breakthrough curves for these two waters overlapped until ~20% of breakthrough for carbamazepine, trimethoprim and primidone, until ~40% for gemfibrozil and until ~60% for sulfamethoxazole. This trend was also observed for the breakthrough of PARAFAC component C1, as discussed previously. On the other hand, breakthrough of EOCs in surface water was faster than in synthetic water during the initial phase of the GAC process, whereas EOCs breakthrough curves tended to have similar values after 40% – 80% breakthrough. Exceptions was ibuprofen, which had a very similar breakthrough in these two waters, and sulfamethoxazole, where overlap of breakthrough curves was not observed. Finally, overlap of EOCs breakthrough curves was not observed when comparing GAC filtration of wastewater and synthetic water.

3.3. Development of correlation models

In this study, a regression analysis was carried to establish relationships between spectroscopic indexes and EOCs removal during GAC filtration of wastewater, surface water and synthetic water. Data was plotted as % breakthrough of surrogate parameter (x-axis) vs. % breakthrough of

EOC (y-axis). Only samples with breakthroughs between 5 and 95% were chosen for the correlation models. This was done because the primary goal of this study is to develop a model which can be used for tracking the breakthrough of EOCs, and to prevent clustering of data points at the high and low end which would skew the R^2 . The regression data for an individual water quality indicate very good linear correlation when comparing UV_{254} , Φ_{tot} and PARAFAC fluorescing components breakthrough with EOCs breakthrough. This suggests that all these spectroscopic indexes can be used as surrogates to estimate EOCs breakthrough in a GAC process for a particular water quality. The regression parameters of the elaborated regression models for each water quality and surrogate parameter are reported in Table S8 – S14. DOC breakthrough, on the other hand, did not correlate well with EOCs breakthrough (Table S15) as observed in our previous study (Anumol et al., 2015). Thus, DOC was not considered for further elaborations. It is noteworthy to observe that the slopes of the lines relating to breakthrough of EOCs and surrogate parameters were much greater for UV_{254} compared to fluorescence indexes (Table S8 – S14) indicating more EOCs removal per unit % change in UV_{254} , which showed a very limited range of % breakthrough variation, particularly during surface waters filtration (>80 – 100%) (Figure 6). It points to the potential greater sensitivity of fluorescence compared to UV_{254} when looking at small changes in removal. Hence, fluorescence could be used as a better surrogate to predict EOC attenuation in a GAC process compared to UV_{254} .

In Figure 6 and Figure S5 – S9 the data-points from all waters were combined to try to find a unique empirical prediction model of EOCs breakthrough valuable for all water qualities and for a particular carbon and EBCT. Plots of combined data were accomplished for all the developed spectroscopic indexes. However, particular attention was given to spectroscopic parameters that were concurrently available for all the investigated water qualities (i.e., UV_{254} , Φ_{tot} and PARAFAC

component C1). From the plots in Figure 6 and Figure S9, it is possible to observe that Φ_{tot} data-points from different waters were not well aligned, and, thus, this parameter does not seem effective to predict EOCs breakthrough regardless of water quality. However, as reported in our previous study (Anumol et al., 2015), this parameter is useful to predict EOCs removal during adsorption process by an unique empirical correlation model when using different wastewater effluents. Correlations between EOC removals and UV_{254} removals were independent of the water quality when considering only surface waters, but a different correlation model was needed to predict EOCs breakthrough in wastewater (Figure 6 and Figure S8). This result is in agreement with recent observation in PAC processes (Zietzschmann et al., 2016a). On the other hand, data related to the microbial humic-like fluorescence PARAFAC component C1 were perfectly aligned when using real water matrices, including wastewater and surface water. Hence, PARAFAC component C1 seem to be the surrogate parameter effective to predict EOCs breakthrough independently of water qualities (Figure 6 and Figure S5). However, a different correlation model was needed to predict EOCs removal from the synthetic water using this fluorescing component. This exception has to be ascribed to the unnatural fast breakthrough of DOM observed during GAC filtration of this water. Regression parameters for correlation model developed using combined data for the PARAFAC component C1 and UV_{254} absorbance are reported in Table 3. Correlation models of combined data with the highest R^2 have been obtained for the PARAFAC component C1. Excluding primidone ($R^2 = 0.777$), R^2 values were always > 0.85 . Combined data of surface and synthetic water have produced linear correlation for the UV_{254} parameter with $R^2 > 0.7$. Exception was sulfamethoxazole. Indeed, for this contaminant, correlation with UV_{254} data had a low R^2 (0.302).

4. Conclusions

This study investigated the adsorption of DOM during GAC filtration from different water qualities (i.e., wastewater, surface water and synthetic water) through the use of different bulk parameters of water, including DOC, UV₂₅₄ and PARAFAC fluorescing components. Hence, the ability of these parameters to predict EOCs breakthrough using different waters was evaluated. Based on the results of the study, the following conclusions can be obtained:

- The different bulk parameters of water DOC, UV absorbance and fluorescence are measurements of different components of DOM, which are differently adsorbed during GAC processes. Particularly, the order of adsorption rate was fluorescence > UV₂₅₄ > DOC in all tested waters;
- Different fluorescing PARAFAC components were differently adsorbed during GAC filtration. PARAFAC components with maxima fluorescence intensity at higher excitation wavelengths, which are corresponding to humic-like fluorescence substances, were better removed than other components in all waters;
- EOCs were better adsorbed when filtering synthetic water, whereas the fastest breakthrough of EOCs was observed during wastewater filtration. These experimental differences can be ascribed to the different rate of DOM adsorption and carbon fouling that took place during the filtration of different waters;
- Correlation models were developed to monitor breakthrough of EOCs during GAC filtration using fluorescence indexes and UV₂₅₄. Particularly, fluorescence indexes resulted more sensitive surrogate than UV₂₅₄ to predict EOC breakthrough during GAC adsorption;
- The need of different correlation models to predict EOCs breakthrough in different water qualities was related to the surrogate parameter used for the prediction (i.e., UV absorbance

or fluorescence) and its adsorption during GAC processes. Particularly, correlations between EOC removals and the microbial humic-like PARAFAC component C1 removals were independent of water quality when considering real water matrices (i.e., surface water and wastewater). On the contrary, two different correlation models were needed to predict EOCs breakthrough in surface waters and wastewater when using UV₂₅₄ as surrogate.

Supplementary data

Text S1 – S2, Table S1 – S15 and Figures S1 – S9. This material is available free of charge.

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Tables

Table 1. Water qualities parameters of tested waters.

Water Matrix	DOC (mg/L)	UV ₂₅₄ (cm ⁻¹)	SUVA (L/m/mg)	Ø _{tot} (RU)	pH
Synthetic water	4.3	0.096	2.3	1130	6.7
Surface water	5.4	0.184	3.4	858	8.4
Wastewater	7.0	0.162	2.3	10822	7.5

Table 2. Relevant chemical properties and concentration (ng/L) of EOCs in the three water qualities.

Compound	pK _a	Log D _{ow} (pH:6.7)	Log D _{ow} (pH:7.5)	Log D _{ow} (pH:8.4)	Charge	Synthetic water	Surface water	Wastewater
Atrazine	14.48	2.2	2.2	2.2	Neu	165	360	A
Carbamazepine	15.96	2.77	2.77	2.77	Neu	157	194	370
Gemfibrozil	4.42	2.13	1.44	0.99	Neg	195	226	214
Ibuprofen	4.85	2	1.25	0.61	Neg	78	295	A
Primidone	11.5	1.12	1.12	1.12	Neu	A	284	349
Perfluorodecanoic acid (PFDA)	-	2.98	2.98	2.98	Neg	282	238	A
Perfluorooctanoic acid (PFOA)	-	1.58	1.58	1.58	Neg	138	269	174
Perfluorooctane sulfonate (PFOS)	-	3.05	3.05	3.05	Neg	153	246	556
Sucralose	11.91	-0.47	-0.47	-0.47	Neu	210	961	A
Sulfamethoxazole	6.16	0.29	-0.03	-0.14	Neu/Neg	130	214	1294
Trimethoprim	7.16	0.74	1.13	1.26	Pos/Neu	A	362	100

A = compound non available; Neg = negative; Pos = positive; Neu = neutral. Chemical properties determined using ChemAxon software.

Table 3. Summary of regression parameters for UV₂₅₄ absorbance and PARAFAC component C1 models for combined datasets.

Compound	C1 model (surface water and wastewater)				UV ₂₅₄ model (surface water and synthetic water)			
	Slope	y-intercept	R ²	n	Slope	y-intercept	R ²	n
Atrazine	A	A	A	A	6.25	-578	0.742	27
Carbamazepine	1.470	-69.00	0.931	31	6.23	-577	0.719	27
Gemfibrozil	1.345	-41.47	0.959	32	6.09	-541	0.786	30
Ibuprofen	A	A	A	A	5.46	-473	0.854	31
PFDA	A	A	A	A	3.15	-238	0.749	33
PFOA	1.11	2.63	0.861	28	4.87	-392	0.924	26
PFOS	1.06	-8.89	0.852	24	4.95	-416	0.904	29
Primidone	1.27	-33.30	0.777	25	A	A	A	A
Sucralose	A	A	A	A	5.91	-509	0.713	27
Sulfamethoxazole	1.78	-47.40	0.966	20	3.99	-332	0.302	26
Trimethoprim	1.58	-88.20	0.912	29	A	A	A	A

A = correlation model non available; n = number of data points

Figure 1. Spectral fingerprints of the identified fluorescing components in the three water qualities.

Figure 2. EEMs at different bed volumes (BV) for the investigated water qualities.

Figure 3. Breakthrough curves for PARAFAC components C1-C5 in the tested water qualities.

Figure 4. Breakthrough curves for DOC, UV₂₅₄, total fluorescence (Ø_{tot}) and PARAFAC components C1, C2 and C5 in all tested waters.

Figure 5. Examples of breakthrough curves for EOCs in tested water qualities.

Figure 6. Correlations between PARAFAC component C1, UV₂₅₄ absorbance and total fluorescence (Φ_{tot}) breakthrough and EOCs breakthrough.

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