Micro-pollutant removal from wastewater treatment plant effluent by activated carbon

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Chapter 1

Introduction

1.1. Pharmaceutically active compounds (PhACs)

1.1.1. PhAC occurrence in the treated wastewater

In the last decades, micro-pollutants such as pharmaceutically active compounds (PhACs) have raised great concerns due to their potential risks to the aquatic environment and to human health. PhACs mostly consist of the over-the-counter, prescription drugs and chemicals (Hedgespeth et al., 2012). There are hundreds of tons of PhACs that are dispensed and consumed worldwide, still, their consumption is consistently increasing due to population expansion, the inverting age structure and the discovery of new drugs (Jelić et al., 2012). Via the human (and other organism) ingestion and excretion process, a considerable proportion of the parent compounds are discharged, in either their un-metabolized or metabolized form, into the sewerage system and are further transported to the wastewater treatment plants (WWTPs) (Jelić et al., 2012). However, the conventional WWTPs are typically not designed to eliminate these emerging micro-pollutants, thus, many of them are able to pass the treatment processes and end up into the receiving aquatic environment (Luo et al., 2014). Overall, the effectiveness of micro-pollutant removal in a WWTP is spatially and temporally variable, and is largely dependent on the operational conditions, technologies used and the associated microbial community composition (Radjenović et al., 2009; Hedgespeth et al., 2012).

The occurrence of PhACs in the WWTP secondary effluents have been extensively and comprehensively assessed in the past few years, highlighting the substances most frequently detected and with higher concentrations (Verlicchi et al., 2012). According to the review of Verlicchi et al. (2012) focusing on 118 PhACs, it was found that compounds with the highest average mass loads discharged through secondary effluents pertained to: hydrochlorothiazide (an antihypertensive), atenolol (a beta-blocker), and several analgesics/anti-inflammatories (e.g. naproxen, ibuprofen, diclofenac and ketoprofen). Whereas the highest risks were derived from the antibiotics (e.g. sulfamethoxazole), psychiatric drugs (e.g. carbamazepine) and the analgesics/anti-inflammatories. The results of an EU-wide survey on emerging polar micro-pollutants in 90 European WWTP effluents demonstrated that, PhACs such as tramadol, trimethoprim, caffeine and carbamazepine were among the most frequently detected compounds with a frequency higher than 90%, and carbamazepine had a median concentration higher than 0.5 μg/L. In addition, compounds like carbamazepine, gemfibrozil, caffeine, ibuprofen, sulfamethoxazole, ketoprofen exhibited maximum detected concentrations higher than 1 μg/L (Loos et al., 2013). Moreover, a summary of Luo et al. (2014) covering WWTP effluents of US, Europe (an EU-wide including Greece, Sweden, Spain, Switzerland and the western Balkan Region), UK and Asia (Korea, China), revealed that, the concentration of most micro-pollutants ranged from 0.001 to 1 μg/L;

while PhACs (e.g. atenolol, caffeine, ibuprofen, naproxen) were detected in concentrations generally higher than 1 μg/L.

1.1.2. Indicator compounds

Due to the regional PhAC usage/treatment patterns and the increasing number of detected PhACs, the concept of compound indicators was proposed to assess the impact of PhACs in wastewater effluents on the receiving water bodies (Dickenson et al., 2011), or to evaluate the performance of a certain treatment process (Jekel et al., 2015). According to Dickenson et al. (2011), three categories of indicator compounds were identified based on their investigation of four North American WWTP effluents: the recalcitrant indicators (e.g. meprobamete and carbamazepine), photolabile indicators (e.g. diclofenac and sulfamethoxazole) and biotransformed indicators (e.g. ibuprofen and gemfibrozil). Furthermore, acesulfame (not a PhAC but an artificial sweetener) was emphasized as a promising indicator due to its poor removal in most conventional WWTPs (Loos et al., 2013; Jekel et al., 2015). In Switzerland, benzotriazole (a corrosion inhibitor), carbamazepine, diclofenac, mecoprop (a biocide) and sulfamethoxazole have been suggested as indicators for conventional and advanced wastewater treatments using ozone or activated carbon. More specifically, sulfamethoxazole was considered as a moderately adsorbable, well oxidizable indicator, while benzotriazole as a well adsorbable, moderately oxidizable indicator (Jekel et al., 2015).

1.1.3. Relevant legislation

Legislation is gradually initiated to protect the aquatic environment and the related organisms. Directive 2008/105/EC has published a list of Priority Substances for surface water and their associated Environmental Quality Standards (EQSs); while no PhACs were included. Thereafter, other commissions, e.g. Oslo and Paris Commission (OSPAR) and Global Water Research Coalition have launched a high priority level for PhACs such as carbamazepine, sulfamethoxazole, diclofenac, ibuprofen, naproxen, bezafibrate, atenolol etc (GWRC, 2008; Verlicchi et al., 2012). Switzerland (the Ecotoxicity Centre of EAWAG) has also proposed the Environmental Quality Criteria (EQC) for micro-pollutants (including PhACs, steroidal estogens, pesticides, industrial chemicals and complexing agents) in terms of their maximum allowable concentrations and their annual average concentrations in surface waters (R. Kase, 2011). Nowadays, Directive 2013/39/EU has emended the previous 2008/105/EC and included diclofenac, 17-α- and 17-β-estradiols on the first watch list (EC, 2013; Mailler et al., 2015).

1.1.4. The techniques to reduce PhAC discharge into the aquatic environment

Additional tertiary treatment in WWTPs is highly advocated to reduce PhAC release from the secondary effluent into the surface water. Technologies such as ozonation, activated carbon adsorption and ‘dense membrane’ filtration were regarded as potentially effective approaches (Christian Abegglen, 2009). Considering the efficiency, costs and energy requirements (Joss et al., 2008; Margot et al., 2013), ozonation and activated carbon adsorption are more acceptable in a full-scale application, as the dense membrane e.g. reverse osmosis and nanofiltration can lead to problems of the concentrate discharge. However, ozonation would inevitably induce by-product formation, which can possibly contaminate the produced water, and activated carbon is thus more preferable in this respect.

1.2. Micro-pollutant adsorption on activated carbon

1.2.1. Adsorption competition with the background organic matter

Activated carbon is generally known for its adsorption ability towards a broad spectrum of micro-pollutants (Snyder et al., 2007; Rossner et al., 2009), due to the well-developed porosity, large surface area and the high degree of surface reactivity (Dias et al., 2007). According to the International Union of Pure and Applied Chemistry (IUPAC), the pores of an activated carbon can be classified into: macropores (with diameter ≥ 50 nm), mesopores (with diameter between 2-50 nm), secondary micropores (with diameter between 0.8-2 nm) and primary micropores (with diameter ≤ 0.8 nm). The adsorption characteristics can be varied depending on the source material and the activation process during manufacturing of the activated carbon (Zietzschmann et al., 2014a).

Activated carbon is commonly applied as a powdered slurry feed (i.e. the powdered activated carbon, PAC), or in a granular form (i.e. the granular activated carbon, GAC) in a packed bed filter (Snyder et al., 2007). With respect to the tertiary treatment in a WWTP, PAC can be easily integrated into the existing facilities, for instance, PAC can be directly dosed on top of the tertiary filter together with a coagulant to facilitate its retention in the filter (Altmann et al., 2014a); or it can firstly be contacted with the secondary effluent in a contact reactor before being separated by a final membrane installation (Margot et al., 2013). In addition, a stand-alone reactor with fluidized PAC bed can be employed as the tertiary treatment step (Mailler et al., 2015). GAC is usually used either as a separate full bed adsorber (Grover et al., 2011), or as a replacement of the anthracite on the upper layer of a tertiary anthracite-sand dual media filter (Meinel et al., 2015).

However, the micro-pollutant adsorption onto activated carbon is significantly deteriorated by the background organic matter (BOM) which is ubiquitously present in the aquatic environment. In this thesis, BOM originating from the biologically treated wastewater (i.e. the secondary effluent) was mainly studied, which can also be termed as effluent organic matter (EfOM). Generally, EfOM consists of the natural organic matter (NOM) with a drinking water origin, and the soluble microbial products (SMPs) released from the bacterial metabolism during the biological treatment (Michael-Kordatou et al., 2015). Due to a much higher organic carbon concentration of EfOM, a substantial decrease (up to one-thousandth) in the micro-pollutant adsorption capacity has been observed in the background of WWTP effluent compared to the pure water (Snyder et al., 2007). The competitive adsorption induced by BOM can be explained by two mechanisms basically: (1) direct competition with small organic molecules for the same adsorption sites, e.g. the high energy adsorption sites in the micropores of the activated carbon; (2) pore blocking by the large organic molecules that hinder the entrance of micro-pollutants into the appropriate adsorption sites.

The competitive adsorption depends on a variety of factors, such as the activated carbon particle size, pore size distribution, surface area/pore volume and surface chemistry (hydrophobicity, charge, acidity/basicity etc.); as well as the organic carbon content and the molecular composition of the BOM. Moreover, the specific physicochemical properties of the target micro-pollutant determine its adsorption potential (or the resistance against the adsorption competition) on the employed activated carbon and in the specific water matrix.

In normal PAC application, where a contact reactor with a relatively short contact time is used, site competition is regarded as the most important competing mechanism (Matsui et al., 2003). Whereas, preloading by the previously adsorbed organic matter is a typical phenomenon during the GAC fixed bed filtration, especially when the GAC filter is operated over a long period of time (Knappe et al., 1999).

In the following sections, influential factors of the adsorption competition are identified and are briefly discussed.

1.2.2. Characteristics of activated carbon

Particle size

Particle size appears to be the most apparent difference between the activated carbons, while its influence on the adsorption competition was scarcely reported. Even, for a simplicity of experiment, GAC is usually pulverized or grinded to determine batch adsorption isotherms or rapid small-scale column tests (RSSCT). A general concern arises in such cases since the adsorption characteristics of the small-sized GAC might not represent that of the original GAC (Jekel et al., 2013).

The batch isotherm is typically conducted to obtain the micro-pollutant adsorption capacity of an activated carbon under equilibrium condition. It was hypothesized that the adsorption capacity is not affected by a change in the GAC size, as the internal surface, which determines the micro-pollutant adsorption capacity, remains the same (Jekel et al., 2013). However, controversial results were obtained in this respect. Nowotny et al. (2007) found that the micro-pollutant adsorption capacity of GAC (in deionized water) increased with decreasing particle size, due to an increase in pore volume. Whereas Matsui et al. (2009) claimed that it was the large molecular BOM rather than the low molecular micro-pollutants whose adsorption capacity were influenced by the carbon particle size. The adsorption competition did not intensify even when the organic matter uptake increased by milling normal PAC into the superfine PAC (Matsui et al., 2012).

In the RSSCT employing GAC, the results turned out to quite different from that observed for PAC. For instance, during a co-loading of three GACs with different particle sizes (but a same carbon origin) by micro-pollutants and BOM, the BOM breakthrough curve overlapped while the micro-pollutant adsorption deteriorated as GAC particle size increased (Corwin and Summers, 2010). The authors explained that the pore blockage occurring in the larger GAC resulted in more surface area behind the blockage unavailable for adsorption than in the smaller GAC, leading to more hindered adsorption kinetics and a reduced adsorption capacity of the micro-pollutant (Corwin and Summers, 2010). Furthermore, a recent study found that the capacity of GAC which is widely used in the fixed bed was not fully explored before regeneration, and a significant capacity can be recovered by pulverising the spent GAC (Meinel et al., 2015). The authors attributed the lower utilisation efficiency of GAC (*versus* pulverized GAC) to the pore blockage effects and the kinetically unfavourable conditions during the GAC filtration process (Meinel et al., 2015).

Pore structure

It is acknowledged that size exclusion plays an important role in the activated carbon adsorption process. From an energy point of view, pollutants are prone to adsorb in the pores that closely fit their molecule size, as the multiple contact points can create an optimal high-energy adsorption site (Moore et al., 2001; Zhang et al., 2011). The optimal region for micro-pollutant adsorption varies depending on the molecular dimensions of the target compound, but mostly constrains to the micropores of activated carbon. Whereas, numerous studies identified that the molecular diameter of the BOM was within 0.84-2.1 nm (Li et al., 2003b; Yoon et al., 2005), and that a significant portion of the BOM cannot access the pores with a width less than 1.25 nm (Wigton and Kilduff, 2004). As such, 1 nm is usually chosen as a cut-off value for developing strategies to minimize the impact of BOM on micro-pollutant adsorption (Karanfil et al., 2006). Specifically, (1) for small molecular micro-pollutants, activated carbon with an uniform and small pore size distribution is expected to act as a molecular sieve, which is able to mitigate the competition as long as the BOM does not completely block the pore entrance; (2) for larger molecular micro-pollutants, activated carbon with a broader pore size distribution and more pore volume is favoured as it can obtain both micro-pollutants and the BOM.

In addition to the molecular size of micro-pollutants and BOM, the selection criteria of activated carbon is also dependent on the competition mechanism in the particular application. For instance, a broader pore size distribution including secondary micropores and small mesopores of activated carbon is important to alleviate the direct site completion (Pelekani and Snoeyink, 1999; Pelekani and Snoeyink, 2000, 2001), and is thus preferred in the application of a PAC batch reactor. Still, a wider micropore size distribution with extended pore widths to approximately twice the kinetic diameter of the target micro-pollutant was recommended for a less occurrence of pore blockage (Quinlivan et al., 2005). However, during GAC fixed bed filtration (e.g. for monochloramine attenuation in the natural water), an increase in the carbon surface area with pore diameter larger than 2 nm was found to intensify the BOM impact (Fairey et al., 2006).

Recently, the concept of predicting micro-pollutant removal in an organic matter background by using descriptors of activated carbon pore structure was proposed (Ruhl et al., 2014b; Zietzschmann et al., 2014a). Instead of the pore size distribution which requires a time-consuming and expensive measurement (i.e. the nitrogen gas adsorption/desorption isotherm analysis), other parameters, e.g. the BET specific surface area, iodine number and nitrobenzene number were considered (the latter two were based on the standardized testing methods) (Zietzschmann et al., 2014a). However, the findings reflected that the BET specific surface area and iodine number were not effective predicators, while nitrobenzene number could only predict the removal of benzotriazole which exhibits a similar structure as nitrobenzene.

Surface chemistry

Activated carbon surface chemistry is linked to the presence of its surface functional groups. The oxygen-containing functional groups (carboxylic, phenolic, carbonyl groups, etc.) can render an acidic character to the carbon surface, while the functional groups such as chromene- and pyrone- types usually offer a basic character (Li et al., 2002; Rivera-Utrilla et al., 2011). It is a consensus that such basic character is primarily derived from a delocalization of the π electrons on the carbon basal plane and is associated with a removal of the oxygen element from the carbon manufacturing material (Li et al., 2002; Yin et al., 2007). Previous studies confirmed that the oxygen-containing functional groups can promote water adsorption on the activated carbon, which interferes with the adsorption of both hydrophobic and hydrophilic micro-pollutants by blocking the entrance to their optimal adsorption sites (Li et al., 2002; Karanfil and Dastgheib, 2004; Quinlivan et al., 2005). Quinlivan et al. (2005) suggested that a hydrophobic activated carbon with the sum of oxygen and nitrogen content less than 2-3 mmol/g can be adopted for an efficient micro-pollutant removal from the aqueous solution. In contrast, the surface chemistry characteristics e.g. acidity/basicity and charge, were found not to be decisive for BOM uptake during the GAC filtration, and thus imposing negligible influence on adsorption competition as compared to the pore structure characteristics (Fairey et al., 2006).

1.2.3. Characteristics of BOM

In previous studies, the BOM (e.g. EfOM and NOM) have been analysed via fractionation on basis of their molecular size, hydrophobicity and charge. The relevant techniques include: size exclusion chromatography (SEC), membranes with varying molecular weight cut-offs (MWCO) (Matilainen et al., 2011), Amberlite XAD resins and anionic exchange resins (Kim and Dempsey, 2012). The investigation of adsorption competition between micro-pollutants and BOM can be facilitated by virtue of these fractionation methods.

Molecular compositions

In order to determine which fraction of BOM is most responsible for adsorption competition, ultrafiltration membranes with a series of MWCO values (i.e. 500 Da, 3000Da, 10,000 Da and 30,000 Da) were employed to fractionate the BOM by size (Newcombe et al., 1997a). Earlier studies reported that organic fractions with a molecular weight (MW) less than 500 Da were the major contributors to site competition with target compounds (2-methylisoborneol), while the other fractions exerted no impact on either adsorption capacity or adsorption kinetics of these compounds in a simultaneous adsorption scenario (Newcombe et al., 2002a; Newcombe et al., 2002b). By examining the adsorption kinetics (i.e. the diffusion coefficients) of atrazine on PAC preloaded by two different water sources, Li et al. (2003b) concluded that the disparity in organic matter MW distribution of the two water sources (200-700 Da) was the main pore blockage contributor. However, it should be noted that the data provided by different researchers were based on their specific measurements and instrumentations.

During the last 20 years, a combination of liquid chromatography (using SEC as a column) and on-line organic carbon detection (OCD) has been developed, which offers information on the component identification as well as the respective content of organic matter (Matilainen et al., 2011). Overall, the SEC separates the bulk dissolved organic matter

(DOC) into hydrophobic and hydrophilic fractions, the latter can be further divided into: biopolymers, humic substances, building blocks and low molecular weight acids and neutrals according to their respective retention times in the applied SEC column (Huber et al., 2011b). By using the LC-OCD technique, organic matter removal characteristics on activated carbon were elucidated. Investigations of the long-term performance of drinking water GAC filters showed that, the adsorbability of individual DOC fractions generally increased with a decrease in molecular size; however, the most loaded was the humic substances fraction, due to their predominance in the influent water (Velten et al., 2011; Gibert et al., 2013).

In order to analyse the competitive impacts of different fractions of EfOM on micro-pollutant adsorption, the bulk EfOM was separated by a nanofiltration (NF) membrane (Zietzschmann et al., 2014b). The LC-OCD results showed that the NF retentate contained mainly large molecular humic substances and building blocks; while the NF permeate contained mostly small organic acids and neutrals. Micro-pollutant adsorption experiments demonstrated that the NF permeate was most competitive (comparing with the NF feed and the NF retentate) due to direct site competition with the target compounds (Zietzschmann et al., 2014b). However, simultaneous adsorption of target micro-pollutants and BOM using PAC batch systems were conducted in this study, which could not well explain the adsorption competition during GAC dynamic filtration where BOM preloading becomes the main issue (Knappe et al., 1999).

Hydrophobicity

It is accepted that hydrophobic organic matter is characterized by aromatic, phenolic structures and conjugated double bonds, while hydrophilic organic matter contains a higher proportion of aliphatic carbon and nitrogenous compounds, such as carbohydrates, proteins, sugars and amino acids (Matilainen et al., 2011). The SUVA index, which is defined by UV absorbance at 254 nm divided by the corresponding DOC, is used as a general measure of the hydrophobicity of bulk organic matter in water samples. The bulk organic matter can also be fractionated using a series of functional resins, such as a neutral XAD-8 (and/or XAD-4) resin, a strong cation exchange resin and a strong anion exchange resin, under the respective appropriate pH conditions (Michael-Kordatou et al., 2015). Ultimately, six categories can be obtained: humic substances (equivalent to hydrophobic acids), hydrophobic bases, hydrophobic neutrals, hydrophilic acids, hydrophilic bases, and hydrophilic neutrals. An previous study revealed that, hydrophilic acids and humic substances were the two dominant organic fractions in the investigated Japanese WWTP effluents (Imai et al., 2002).

By preloading different activated carbons with hydrophobic and hydrophilic fractions (with different SUVA values) of a natural water, Karanfil et al. (2006) found that the competitive effects were mostly dependent on BOM loading and molecular configuration, but not necessarily related to the BOM hydrophobicity (measured via XAD-8/XAD-4 resins). However, de Ridder et al. (2011) preloaded GAC by a surface water and a WWTP effluent with the same DOC concentration but different hydrophobicity (determined by LC-OCD); the results demonstrated that the WWTP effluent-preloaded GAC provided less pharmaceutical adsorption, due to a more severe competition between the pharmaceuticals and the more hydrophobic organic matter associated with WWTP effluent.

Adsorption of micro-pollutants and BOM occurs simultaneously due to the non-selective nature of activated carbon adsorption process. Therefore, even though the micro-pollutants and BOM adsorb to different extents, an increase in removal of BOM is usually accompanied by an increase in the micro-pollutant removal (Altmann et al., 2015b). As UV_{254} is easy to measure, and represents the aromaticity of the BOM, which is relevant to activated carbon adsorption (Hu et al., 2014b), it was proposed as a surrogate parameter for estimation of the micro-pollutant removal from WWTP secondary effluent (Zietzschmann et al., 2014a). Zietzschmann et al. (2014a) found that the removal of a majority of the investigated micro-pollutants can be deduced from UV_{254} removal (except for compounds as sulfamethoxazole and benzotriazole), and that the average PAC doses required to remove the investigated micro-pollutants by 80% correlated with the PAC doses to reduce UV_{254} by 50%. Furthermore, Anumol et al. (2015) extended the surrogate to a total fluorescence parameter, and conducted RSSCTs (using a GAC) in different WWTP effluents. The total fluorescence performed even better for micro-pollutant breakthrough predictions than UV_{254}, especially for compounds with higher hydrophobicity (Anumol et al., 2015).

However, it was realized that predicting the removal of micro-pollutants would be difficult without considering the effect of BOM (Anumol et al., 2015), i.e. the adsorption competition. Therefore, this surrogate method needs to be further validated on different activated carbons and in different types of WWTP effluents.

1.3. Objectives and research questions

Activated carbon is the among the most promising techniques for micro-pollutant removal from the WWTP effluent. However, the ubiquitously occurring organic matter compromises the micro-pollutant adsorption efficiency, the extent to which depends on parameters associated with the specific activated carbon, the water matrix (as was discussed in Section 1.2), and also the micro-pollutant itself. Besides, the approach how activated carbon is applied can determine its utilization efficiency. Although numerous studies have attempted to elucidate the mechanisms of adsorption competition, there seems very few successful strategies that have been proposed in practice to reduce adsorption competition.

The objectives of this thesis, therefore, are to further clarify the adsorption competition between micro-pollutants and the BOM originated mainly from WWTP secondary effluents, and to provide practical solutions to maximize activated carbon adsorption ability towards target micro-pollutants such as PhACs from the WWTP secondary effluents.

To realize these objectives, the following research questions are raised:

(1) What type of activated carbon is less subjected to adsorption competition?

(2) Which fraction of BOM contributes most to the adsorption competition?

(3) How are the physicochemical properties of target micro-pollutants related to the adsorption competition?

(4) Can recycling the secondary effluent-used PAC into the activated sludge tank offer an additional micro-pollutant adsorption?

(5) What strategy of dosing PAC, directly or continuously, to the WWTP tertiary filter enables a later micro-pollutant breakthrough?

1.4. Thesis outline

In response to the research questions, this thesis is unfolded as the following chapters, and the relationships between these chapters are illustrated in Figure 1.1. Where, chapter 2 and chapter 3 were designed to clarify the adsorption competition mechanisms by analysis of the BOM, while chapter 4 offers insights into the influence of activated carbon properties on micro-pollutant adsorption, and a suitable activated carbon type for micro-pollutant removal from wastewater is suggested. Based on chapter 4, chapter 5 and chapter 6 were executed to address the questions of 'where' and 'how' to integrate the activated carbon into the wastewater treatment processes. Besides, the adsorption competition mechanisms obtained in the former two chapters were verified in chapter 5. The detailed contents in each chapter are as follows:

Chapter 2 aims at differentiating the site competition and pore blocking effects from different organic fractions separated by an anionic exchange resin, which was supposed to be capable of removing most of the charged BOM. The batch and dynamic adsorption experiments were performed respectively. Firstly, simultaneous adsorption of target micro-pollutants and BOM were carried out in the batch experiment, the extent to which site competition can be alleviated by an anionic exchange pre-treatment was explained and the site competition contributor was identified. Subsequently, the RSSCTs were performed to examine the predominance of site competition and/or pore blocking effects in the dynamic filtration process.

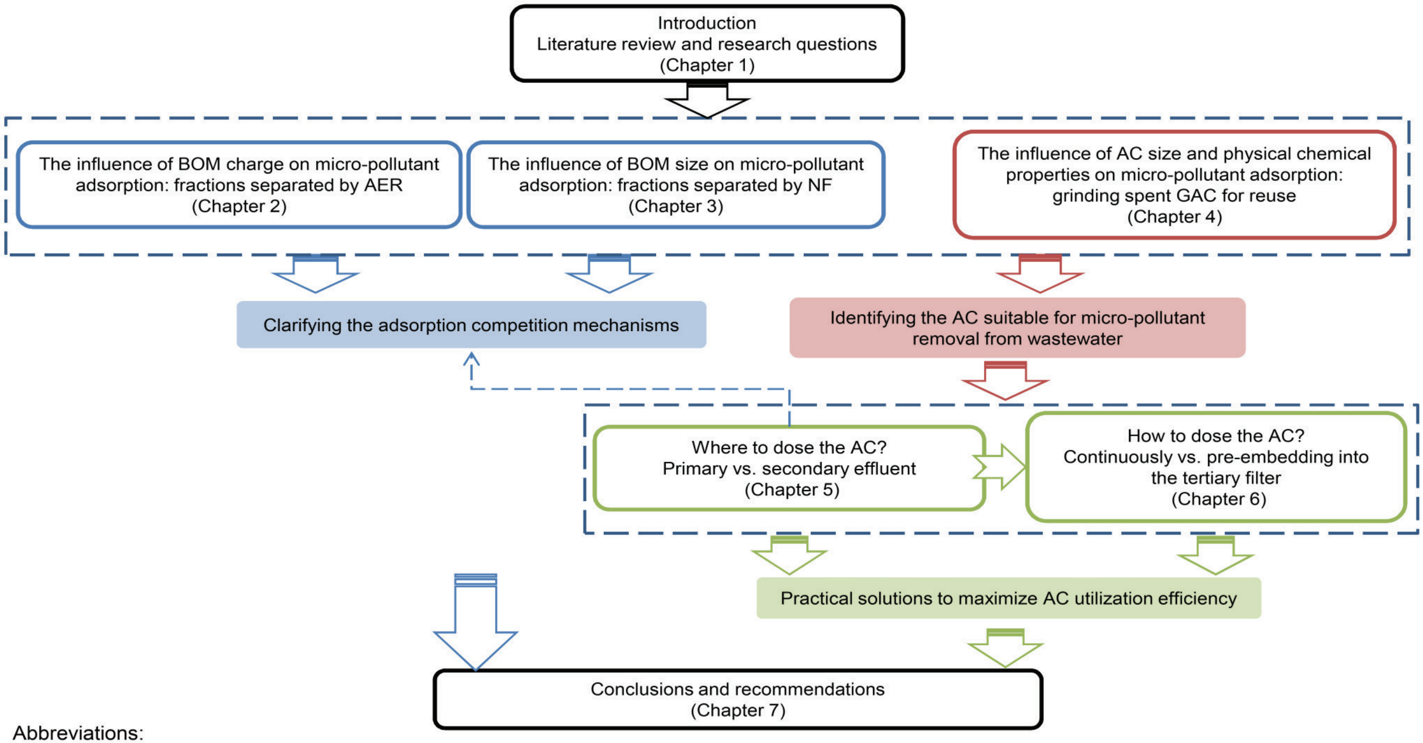
During the dynamic filtration of a GAC filter, the mass transfer zone of BOM usually moves faster than that of the target micro-pollutants, resulting in a preloading of the GAC before it contacts with the target compounds. The impact of preloading on the subsequent micro-pollutant adsorption was investigated in chapter 3. Specifically, two GACs were preloaded in a batch system using different organic fractions separated by a nanofiltration (NF) membrane, with its molecular weight cut-off approximating that of the carbon micropores. The preloading of differently sized organic fractions (i.e. the NF rejected and non-rejected fractions) was hypothesized to play different roles in the subsequent micro-pollutant adsorption. A subset of PhACs with varying physicochemical properties was chosen, which allowed to determine the responses of different PhACs to the preloading effect.

After preloading, the GAC characteristics were altered in terms of the pore structures and the surface chemistry. Chapter 4 describes the change of carbon characteristics after being preloaded by different types of organic matter (i.e. derived from surface water and groundwater, respectively), during full-scale operation of GAC filters for drinking water purification. The influences of the carbon pore structure/surface chemistry change on micro-pollutant adsorption were examined in pure water. In addition, these preloaded GACs were grinded for reuse in WWTP secondary effluent, adsorption competition was assessed to determine the potential for reusing the exhausted drinking water GACs into the wastewater treatment.

Considering the application of activated carbon for an advanced wastewater treatment, the grinded GAC (or PAC) presents its advantage over GAC for an easy implementation and faster adsorption kinetics for the micro-pollutants. However, questions regarding where and how to dose PAC still remain to be answered. In chapter 5, the suitability of dosing PAC for PhAC elimination in the primary and secondary effluents were compared. Batch PhAC adsorption experiments and molecular composition analysis of the two waters were executed. Moreover, the used PAC for PhAC adsorption in secondary effluent was tested for its recycling potential into the prior activated sludge tank for additional PhAC adsorption.

Based on the results from chapter 5, PAC was preferably dosed in the secondary effluent. To make a use of the existing WWTP tertiary filter, a new approach was proposed in chapter 6 to integrate PAC into the tertiary filter, as a simple and efficient way for micro-pollutant removal from the secondary effluent. Specifically, continuous dosing PAC with the filter influent and pre-embedding of PAC inside the filter bed were compared. The better dosing approach was selected based on the breakthrough behaviour of the investigated micro-pollutants. In addition, the influence of PAC distribution profiles in the filter bed on micro-pollutant breakthrough was examined.

Chapter 7 presents the general conclusions and recommendations.



Abbreviations:

BOM: background organic matter
AC: activated carbon
GAC: granular activated carbon

Figure 1.1. *Schematic demonstration of the relationship between chapters in this thesis.*

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Chapter 2

Adsorption competition effects from organic fractions separated by anionic exchange resin

To efficiently remove micro-pollutants from surface water and groundwater by activated carbon adsorption, the concurrent natural organic matter (NOM) was removed by anionic exchange resin (AER) to reduce the adsorption competition. The studied AER showed a great affinity to the NOM fractions 'humic substances' and 'building blocks' measured by liquid chromatography with organic carbon detection. The overlapping adsorption isotherms of the target compounds (atrazine and caffeine) in the presence of raw water and AER-treated water reflected an irrelevance of AER-removed NOM to site competition. Instead, it was likely the hydrophobic low molecular organics, refractory to AER treatment, competed with the target compounds. Microporous carbon, which contains higher amounts of small and secondary micropores, tended to have less site competition, and a lower dosage was required to achieve e. g. 90% removal of the target compounds. During fixed adsorber filtration, however, AER pre-treatment slightly prolonged the breakthrough of most of the investigated micro-pollutants. This could be attributed to less pore blockage due to the lower contents of 'humic substances' and 'building blocks' in the background water.

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2.1. Introduction

Activated carbon adsorption is regarded as the best available technology for micro-pollutant removal in water by the United States Environmental Protection Agency (Karanfil and Kilduff, 1999). However, adsorption competition from the ubiquitously co-present natural organic matter (NOM) hampers the adsorption efficiency of micro-pollutants by activated carbon (Yu, 2007). As compared to the specific target micro-pollutant, NOM is a heterogeneous mixture of humic substances, hydrophilic acids, proteins, lipids, carbohydrates etc, with varying molecular characteristics. Normally, NOM influences micro-pollutant adsorption via two pathways: direct site competition and pore entrance blockage (Carter and Weber Jr, 1994; Li et al., 2003a; Li et al., 2003b). It is accepted that the molecular weight (MW) of background NOM exerts a stronger impact on adsorption competition than charge and polarity (Newcombe et al., 1997b; Kilduff et al., 1998; Newcombe et al., 2002b). As a result, the pore size distribution of activated carbon in relation to the MW of NOM and the target micro-pollutants plays an important role in determining the competitive behaviour (Newcombe et al., 2002a). In general, site competition occurs between micro-pollutants and the small NOM molecules in pore regions accessible to both of them, whereas pore blockage predominates when the activated carbon pores are preloaded with NOM which hinders the transport of micro-pollutants to reach the optimal adsorption sites (Pelekani and Snoeyink, 1999).

In the application of powdered activated carbon (PAC) for batch adsorption, the mechanism for micro-pollutant adsorption competition is mainly the direct site competition (Matsui et al., 2003), because the competing NOM adsorbs simultaneously with the micro-pollutants onto the PAC, and it does not hinder their internal diffusion along the PAC pores (Li et al., 2003b; Matsui et al., 2003). In GAC fixed bed filtration, site competition and pore blockage take place concurrently, due to the preloading by previously adsorbed NOM. As a result, both adsorption capacity and kinetics of the target micro-pollutant are adversely affected (Yu, 2007). In light of these mechanisms, batch adsorption and dynamic adsorber filtration of the target micro-pollutant could be compared to gain insights into the site competition and pore blockage by the background NOM.

Although numerous efforts have been made to understand the competitive mechanisms, only a limited number of successful strategies have been proposed to mitigate the competitive adsorption. For example, despite being a widely applied pre-treatment method, coagulation and flocculation showed a poor removal efficiency towards small MW NOM, having hardly any influence on reducing competition during PAC adsorption (Zoschke et al., 2011). Further, nanofiltration (NF) membrane, with a molecular weight cutoff of 200 Da, was adopted as a pre-treatment for granular activated carbon (GAC) removing pharmaceuticals from surface water, which resulted in less pore blockage and a prolonged

GAC filtration lifetime (Heijman and Hopman, 1999; Verliefde et al., 2007). However, disposal of the NF concentrate and the high investment costs of NF are two major drawbacks. As an alternative, anionic exchange resin (AER) is being highlighted recently as a NOM remover (Tan and Kilduff, 2007; Cornelissen et al., 2008). AER is generally found to have a preference for charged NOM components (Bolto et al., 2002); and also for high specific ultraviolet adsorption substances, mainly consisting of aromatic hydrophobic NOM (humic and fulvic acids) (Humbert et al., 2005). Although problems, e.g. brine production, are accompanied with AER regeneration, the easy implementation and the ability to remove NOM over a wide range of MWs offer AER advantages over the other treatment methods such as NF.

In this study, we hypothesized that AER removes NOM fractions that potentially cause site competition or pore blockage during activated carbon adsorption. Strong-based AER was used and target micro-pollutant adsorption in the presence of AER-treated water was compared with that in non-treated raw water. Batch adsorption and small-scale column tests were carried out to examine the adsorption competition behaviour, with the emphasis on site competition and pore blockage, respectively. In addition, activated carbons with various pore structures were selected to evaluate their uptake of micro-pollutants from the raw water and the AER-treated water.

2.2. Methods and materials

2.2.1. Anionic exchange resin and activated carbons

NOM removal was realized by a commercial strong base gel type AER (Lewatit VP OC 1071, Bayer, UK). Three pulverized coal-based GACs (PGACs): HD4000 (Norit, The Netherlands), UC830 (Siemens, USA) and F-400 (Chemviron, Belgium) were used with a particle size of around 0.1 mm, obtained after mechanical milling and sieving. The pore size distribution and surface area of the PGACs were determined by the nitrogen gas adsorption/desorption isotherm technique (ASAP 2010, Micromeritics, USA). As shown in Figure 2.1 and Table S2.1 in the supporting information, F-400 and UC830 are typically microporous, while HD4000 contains widely distributed pores including micropores (with diameters < 2 nm) and mesopores (with diameters between 2 and 50 nm). In the rapid small-scale column test (RSSCT), the strong-based AER was used as well to treat the influent water. F-400 with a particle size of 0.1 mm was adopted for the RSSCT.

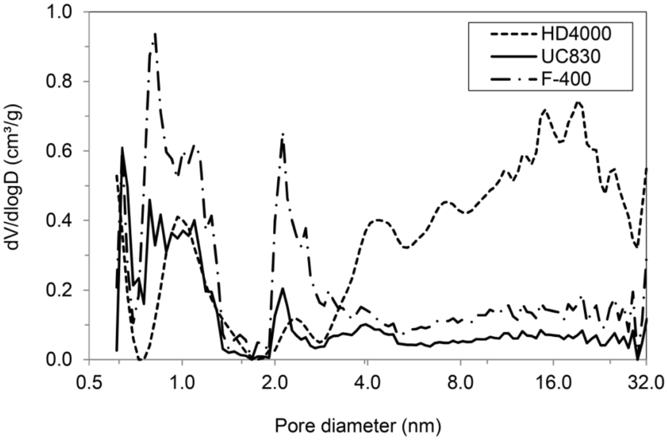

Figure 2.1. *Pore size distribution of HD4000, UC830 and F-400.*

2.2.2. Background water matrices

Two different raw waters and the respective AER-treated raw waters were collected for batch micro-pollutant adsorption experiments. The raw waters were sampled from a local 'Schie' canal (Delft, The Netherlands, Schie RW) after passing a 1 μm cartridge filter, and a groundwater of 'Sint Jansklooster' after rapid sand filtration (Sint Jansklooster, The Netherlands, Sint RW), respectively. The AER-treated Schie RW and AER-treated Sint RW were produced under their respective optimal conditions at a mixing speed of about 300 rpm (as described in Section 2.3.1), and denoted as Schie TW and Sint TW, respectively. Besides, demineralized water (DW) was included as a non-organic reference, which was obtained from the tap water after an ultrafiltration-reverse osmosis-ion exchange system in the Waterlab of TU Delft (Delft, The Netherlands). The measured dissolved organic carbon (DOC) concentration of this DW was constantly below 0.1 mg/L. In the RSSCT experiment, Sint RW and two AER-treated Sint RW were used as influents. For comparison, AER-treated Sint RW with different DOC removal percentages were produced, i.e. 16% at lower AER dose (Sint AER TW-1) and 63% at higher AER dose (Sint AER TW-2), respectively.

2.2.3. Micro-pollutants and batch/column tests

Atrazine and caffeine with a neutral charge (at a normal drinking water pH value) but different polarities and molecular structures were selected for the batch adsorption experiments. Adsorption isotherms in the presence of the aforementioned water matrices were conducted using the bottle-point method (Yu et al., 2008); where each compound was spiked to reach an initial concentration of 5 μg/L, and carbon dosages varied from 1 to 20 mg/L. After 7 days' adsorption at a mixing speed of around 180 rpm at room temperature (25±1 ºC), equilibrium was reached and samples were extracted by 0.45 μm syringe filters (Whatman, UK) for analysis by enzyme-linked immunoassay kits (Abraxis LLC, Warminster PA, USA).

The columns used in the RSSCT experiment were 0.5 cm in diameter and 14.6 cm in length, each column was packed with 1.15 g of F-400 to reach a density of 0.4 g/mL. The filtration flow rate was controlled at 1.0 L/h with an empty bed contact time (EBCT) of 10.4 seconds. In the RSSCT, a cocktail of pesticide micro-pollutants including pirimicarb, metribuzin, atrazine, bentazon, MCPA (2-methyl-4-chlorophenoxyacetic acid), DNOC (2-methyl-4,6-dinitrophenol) and MCPP (2-(2-Methyl-4-chlorophenoxy) propionic acid) was spiked into the Sint RW, Sint AER TW-1 and Sint AER TW-2 with a level of 2 μg/L for each compound. The physicochemical properties of these compounds are listed in Table 2.1.

Table 2.1. *Physicochemical characteristics of the studied micro-pollutants.*

	Compound	MW (Da)	pK_a [a]	Charge [b] (pH=7)	Log D [b] (pH=7)
batch isotherm test	Atrazine	216	1.64	Neutral	2.63
	Caffeine	194	10.4	Neutral	- 0.13
RSSCT	Pirimicarb	238	4.54	Neutral	1.56
	Bentazone	240	3.30	Neutral	0.8
	MCPA	201	3.07	Negative	-1.43
	DNOC	198	4.31	Negative	0.37
	MCPP	214	3.10	Positive	0.49

[a]: Obtained from PubChem (http://pubchem.ncbi.nlm.nih.gov).

[b]: Obtained from calculated value ChemAxon (http://www.chemspider.com).

2.2.4. Analytical methods

The DOC concentration was determined by a TOC analyser (TOC-VCPH, Shimadzu, Japan); ultraviolet absorbance UV_{254} was measured by a UV-vis spectrophotometer (Thermo Scientific, Germany) after passing the water samples through 0.45 μm syringe filters. Liquid chromatography coupled with organic carbon detection (LC-OCD) was executed for NOM MW distribution (MWD) analysis (Waterlaboratorium in Haarlem, The Netherlands). According to LC-OCD chromatography, five organic fractions can be differentiated (Huber et al., 2011b), namely 'biopolymers' (nitrogen-containing material such as proteins or amino sugars with MW >> 20 kDa), ‘humic substances’ (the most prevalent NOM species with MW ~1 kDa), ‘building blocks’ (a humic substances-like material identified as the breakdown products of ‘humic substances’ with MW between 300 to 500 Da), ‘low molecular weight acid’ (anions at the neutral pH with MW < 350 Da) and ‘low molecular weight neutrals’ (weakly charged non-hydrophobic compounds with MW < 350 Da). Still, there is a calculated fraction that retained on the chromatography column, which is hydrophobic and expressed as ‘hydrophobic organic carbon’ (Cornelissen et al., 2008).

For the enzyme-linked immunoassay analysis, a calibration curve was established each time using the standards provided by the manufacturer, and samples were measured in triplicate under constant temperature without sunlight. Microplate reading (Infinite M200, TECAN, Switzerland) was employed to record the final absorbance data under an UV wavelength of 450 nm. Sample concentration was determined by interpolating the detected absorbance data against the standard curve constructed in each run. The detection limits ranged from 0.04 to 5 μg/L for atrazine and from 0.15 to 5 μg/L for caffeine.

RSSCT effluent samples were pre-condensed prior to the analysis by HPLC with an UV detector (Perkin-Elmer, The Netherlands). A 2 mL poly-laboratory reversed phase PLRP-S column (Agilent, The Netherlands) with adsorbent particle size of 15-25 μm, pore size of 300 Å was used for the sample pre-concentration, which was connected directly to the HPLC system. The analytical column (200*4.6 mm) in the HPLC was packed by Chrompack microsphere C18 with a particle size of 3 μm. The HPLC was operated in a gradient elution mode with mobile phases of ultrapure water, analytical pure acetonitrile and 1 g/L KH_2PO_4. The detailed eluent gradient program is provided in Table S2.2. The detection limit for each compound was 0.02 μg/L.

2.2.5. Modelling

A simplified equivalent background compound (SEBC) model was used to describe the isotherm data of atrazine and caffeine in Schie RW and Schie TW on each PGAC. This model is originated from the ideal adsorbed solution theory and is based on the following assumptions: (1) only one fraction of NOM, the equivalent background compound (EBC), competes with the target compound (Najm et al., 1991); (2) adsorption of EBC is greater than that of the target compound; (3) Freundlich exponent of EBC and the target compound are comparable (Knappe et al., 1998). The SEBC model was theoretically justified and experimentally validated by Qi et al. (2007) and Zoschke et al. (2011), and it describes that the relative removal of the target micro-pollutant in an organic matrix is highly dependent on the adsorbent dosage, but not the micro-pollutant’s initial concentration. The SEBC model can be expressed as (Worch, 2010):

$$\frac{C_{0,1}}{C_1} = \frac{1}{A} D^{1/n_1} + 1 \tag{1}$$

with

$$A = C_{0,2}^{1/n_1 - 1} \left(\frac{n_1}{n_2 K_1}\right)^{1/n_1} \tag{2}$$

The Freundlich equation is:

$$q_1 = K C_1^n \tag{3}$$

Where $C_{0,1}$ and $C_{0,2}$ are the initial concentrations of the target compound and EBC; C_1 and q_1 are the equilibrium liquid and solid concentrations of the target compound, respectively; D is the carbon dosage, K (equals to K_1), n (equals to n_1) and n_2 are the Freundlich parameters for target compound and EBC adsorption in the organic-free water, while A is a summary of the parameters of target compound and EBC (Zoschke et al., 2011). The logarithmic form of Equation (1) can be used to find the parameters A and n_1 from the experimentally determined curve by linear regression. Once they are known, the adsorbent dose required for a given micro-pollutant removal objective can be calculated (Worch, 2010).

2.3. Results and discussion

2.3.1. NOM removal by AER

NOM removal in response to the AER dose is depicted in Figure 2.2. For both Schie RW and Sint RW, the removal efficiency increased with an increase in the AER dose from 2 to 10 ml/L. However, a further increase in AER dose to 12 ml/L did not improve the NOM removal: t-test results demonstrate no statistically significant difference between 10 and 12ml/L AER in terms of DOC removal (p-value = 0.87 > 0.05 for Schie RW, p-value = 0.94 > 0.05 for Sint RW) and UV_{254} removal (p-value = 0.92 > 0.05 for Schie RW, p-value = 0.89 > 0.05 for Sint RW). Regarding the NOM removal kinetics, for both types of raw water, 10 and 12 ml/L AER showed a substantial DOC (UV_{254}) decrease in the first 45 min followed by a plateau afterwards. According to these observations, 10 ml/L AER can be considered as a sufficient dose for NOM treatment in both Schie RW and Sint RW at a contact time of e.g. 1 h, which is slightly longer than the ‘cut-off’ 45 min to ensure the equilibrium. Comparing Schie RW and Schie TW by 10 ml/L AER after 1 hour’s reaction, DOC decreased with a percentage of 69% and UV_{254} decreased with 86%, respectively. For Sint RW, DOC and UV_{254} reductions were up to 80% and 91%, respectively. The better NOM removal was associated with the groundwater (Sint RW), which is in accordance with a previous study (Cornelissen et al., 2010), and is likely due to the higher portion of negatively charged organic components in the groundwater that could be effectively exchanged by the AER. Moreover, the better removal of UV_{254} versus DOC in both raw waters indicates that, AER had a preference towards the aromatic compounds of the NOM (Kaewsuk and Seo, 2011; Graf et al., 2014).

The MWDs of the raw waters and the AER-treated waters are presented to elucidate the extent to which different organic fractions were eliminated by AER. In Figure 2.3, it can be observed that AER exhibited little ability towards the high MW ‘biopolymers’ in Schie RW. Even a slight increase in ‘biopolymers’ was noticed in Schie TW, probably because of the leaching of polymeric material from the AER backbones during the attrition in the batch tests. However, AER substantially reduced ‘humic substances’ in Schie RW and Sint RW with 88% and 92% removal, respectively; followed by ‘building blocks’ in Schie RW and Sint RW with 74% and 82% removal, respectively. The removal of these two organic fractions accounted for 89% and 92% of the total DOC reduction in Schie RW and Sint RW. The selectivity of AER towards humic substances-like components can be ascribed to the ionic interactions between NOM acidic components and the anionic resin (Cornelissen et al., 2008). With respect to the low molecular weight fractions, AER was able to eliminate 55% and 65% of the ‘low molecular weight acids’ from Schie RW and Sint RW, respectively; whereas the ‘low molecular weight neutrals’ in both raw waters remained almost unchanged. Because of its weakly charged character, ‘low molecular weight neutrals’ are less likely to interact with AER through anion exchange. For the ‘hydrophobic organic carbon’ fraction, no clear removal trend was found (107 μg/L in Schie RW as compared to 214 μg/L in Schie TW; while 194 μg/L in Sint RW *versus* 163 μg/L in Sint TW). This might be due to the low concentration of ‘hydrophobic organic carbon’ in the water samples, which easily generates inaccuracy in the LC-OCD calculation method.

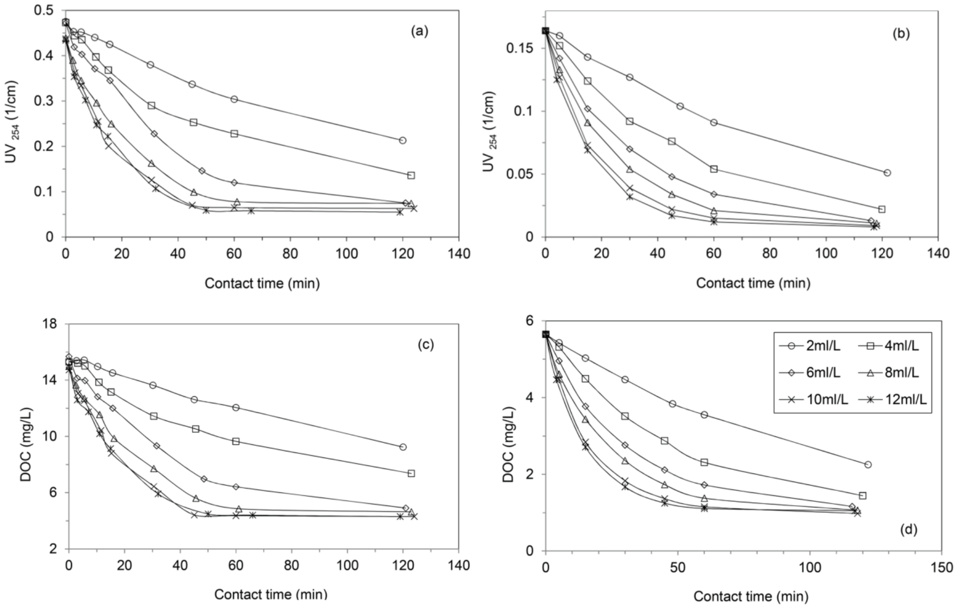

Figure 2.2. *NOM removal in Schie RW and Sint RW as a function of the contact time and AER dose: UV_{254} removal in Schie RW (a), UV_{254} removal in Sint RW (b), DOC removal in Schie RW (c) and DOC removal in Sint RW (d).*

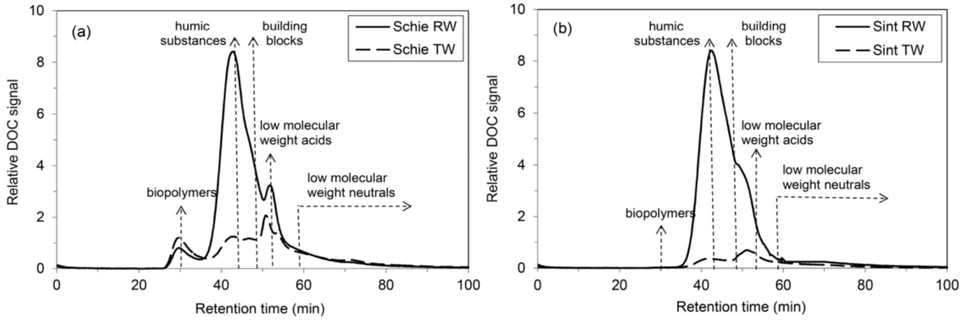

Figure 2.3. *LC-OCD chromatography of Schie RW and Schie TW (a), Sint RW and Sint TW (b).*

2.3.2. Batch adsorption tests

The adsorption isotherms of atrazine and caffeine by different PGACs in Schie RW and Schie TW are presented in Figure 2.4(a) and Figure 2.4(c). For comparison, the adsorption isotherms in DW were given as well, the best-fit Freundlich parameters were listed in Table S2.3. Apparently, in both organic backgrounds, the adsorption capacity of atrazine and caffeine decreased considerably compared to that in DW. This is largely resulted from the competing NOM molecules which occupy the same adsorption sites during simultaneous adsorption in the batch tests (Li et al., 2003b). It is also noted that, although Schie RW and Schie TW exhibited different MW characteristics and DOC loads on the individual PGAC (data not shown), their influence on the target compound adsorption were not obvious, as can be concluded from the overlapping adsorption isotherms of both compounds in Schie RW and Schie TW. This phenomenon also holds true for the atrazine adsorption isotherms of F-400 in Sint RW and Sint TW (Figure 2.5). Nonetheless, a significantly better atrazine adsorption was achieved in Sint RW (and Sint TW) than in Schie RW (and Schie TW).

The obtained observations indicate that: (1) NOM measured as a lumped DOC was not an appropriate representative of the competing NOM (Hepplewhite et al., 2004; Matsui et al., 2012; Matsui et al., 2013); (2) the AER-treated water had no advantage over the raw water on mitigating adsorption competition. It is the ‘low molecular weight neutrals’ which were not removed by AER could have an effect on the competition. However, by definition, this fraction is characterized by the non-hydrophobic organic matter (e.g. alcohols, aldehyde, ketone, sugars and amino acids) (Cornelissen et al., 2008); that does not result in hydrophobic interactions with the activated carbon surface, and is thus less competitive. In this sense, the low MW ‘hydrophobic organic carbon’ might be the most responsible NOM fraction for competing with the target micro-pollutants (Newcombe et al., 2002b; Zoschke et al., 2011; Matsui et al., 2013), while the AER-removed, larger-MW fraction, i.e. ‘humic substances’ and ‘building blocks’, appeared to be less adsorbable and irrelevant for direct competition (Zoschke et al., 2011). Additionally, the larger MW organics (e.g. with MW > 2 kDa) tended to adsorb onto the outer surface of the activated carbon particles, and only the smaller ones can penetrate into the interior pores and compete with the target micro-pollutants (Matsui et al., 2013).

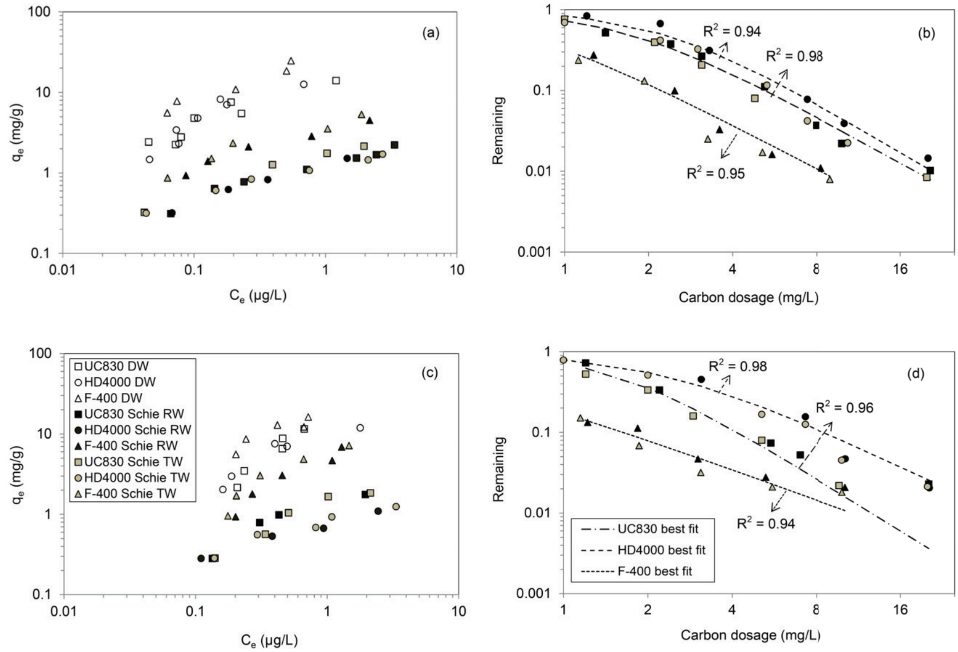

Figure 2.4. *Atrazine (a) and caffeine (c) isotherms of UC830, HD4000 and F-400 in DW, Schie RW and Schie TW, respectively; SEBC best-fitting of the percent removal of atrazine (b) and caffeine (d) in Schie RW, Schie TW as a function of the PGAC dosage.*

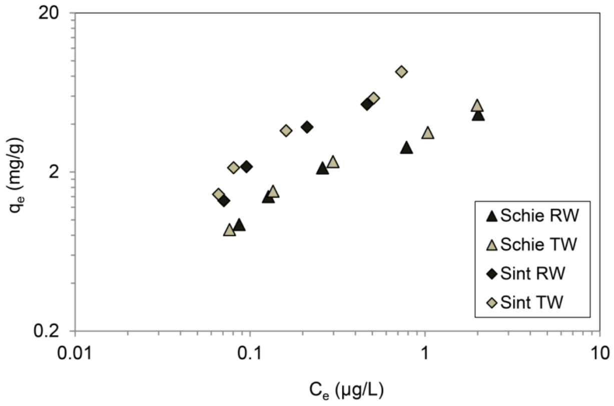

Figure 2.5. *Atrazine adsorption isotherms of F-400 in Schie RW, Schie TW and Sint RW, Sint TW.*

2.3.3. Evaluation of activated carbon during simultaneous adsorption

As can be seen in Figure 2.4(a) and Figure 2.4(c), different PGACs displayed different extents of micro-pollutant adsorption in the organic matrices. This may depend on the load of competing NOM on the individual PGAC. To better describe the competitive adsorption, and gain more insights into the performance of the activated carbons (e.g. the dosage needed for a given treatment objective of the micro-pollutants), the SEBC model was applied to simulate the experimental data of section 2.3.2.

Figure 2.4(b) and Figure 2.4(d) summarize the adsorption isotherms for the percent removal of atrazine and caffeine in Schie RW and Schie TW as a function of the PGAC dosage (the best-fit parameters are listed in Table S2.3). It clearly shows that for each compound, the experimental data in Schie RW and Schie TW collapsed on a single fitting-curve, confirming the same competing effects derived from these two waters. The performances of PGACs on the uptake of atrazine and caffeine in organic matrices are in the order of: F-400 > UC830 ≥ HD4000, this holds particularly true at the lower PGAC dosages. According to the best-fit results, the predicted dosage for e.g. 90% atrazine removal in Schie RW (and Schie TW) is 6.5 mg/L HD4000, 5.2 mg/L UC830 and 2.2 mg/L F-400, respectively; while it is 8.5 mg/L HD4000, 4.2 mg/L UC830 and 1.6 mg/L F-400 for caffeine. These results demonstrate that the microporous F-400, which contains both high amounts of small (< 1 nm) and secondary (1-2 nm) micropores, would be more effective to mitigate the site competition, thus enabling a lower dosage for the required micro-pollutant removal during simultaneous adsorption of NOM and micro-pollutants. On the other hand, the poorest removal efficacy associated with HD4000 proved that mesopores did not play an important role in the site competition.

Figure S2.1(a) in the supporting information indicates that atrazine uptake by HD4000 and UC830 in Schie RW (and Schie TW) were not significantly different, the 95% confidence intervals of the SEBC fitting for atrazine removal by UC830 merges completely into the range of that for atrazine removal by HD4000. Whereas for caffeine, UC830 performed much better than HD4000. Given that caffeine has a lower MW and a relatively planar structure, it might be able to penetrate into the small micropores, which are more present in UC830 than in HD4000. In contrast, atrazine adsorption competition mainly occurs in the secondary micropores (Pelekani and Snoeyink, 1999), the comparable volume of which in UC830 and HD4000 resulted in a comparable atrazine uptake from Schie RW (and Schie TW). However, aside from the textural properties of activated carbon and the molecular structure of target compounds, other factors, such as the oxygen content of the activated carbons in relation to the functional groups of the target compounds can also influence the adsorption behaviours (Apul et al., 2013b). The apparent contradiction between a similar caffeine uptake by HD4000 and UC830 in DW and the different caffeine uptake by HD4000 and UC830 in Schie

RW (and Schie TW) implies that the interaction mechanisms between micro-pollutants and activated carbon changed in the presence of background NOM.

2.3.4. Rapid small scale column test

Unlike the batch test for atrazine adsorption on F-400, a slight improvement of the atrazine adsorption breakthrough was observed after the AER pre-treatment of the influent Sint RW (Figure 2.6). It is also clear that the more background DOC was removed, the better the atrazine was adsorbed. Compared to the site-competing low molecular organic fractions, the larger MW ‘humic substances’ and ‘building blocks’ are expected to be more responsible for pore blockage. During the fixed bed filtration, the less adsorbable ‘humic substances’ and ‘building blocks’ molecules were transferred faster through the column than the low MW micro-pollutants, thus preloading the pores of the activated carbons near the column outlet before they could make contact with the target micro-pollutants (Li et al., 2003b). The continuous preloading would induce pore blockage, leading to lower atrazine adsorption kinetics and a lower adsorption capacity during a constant EBCT operation.

Examination of the atrazine isotherms of F-400 in DW (Figure 2.4(a)) and in Sint RW (Figure 2.5) reflects that, site competition caused almost 80% reduction in the adsorption capacity (at atrazine equilibrium concentration of 0.1 µg/L). In comparison to the slight improvement after 63% background DOC removal in Sint RW (21.4% increase in passed bed volume at an effluent concentration of 0.1 µg/L), pore blockage appeared to be not decisive in the decreased atrazine uptake.

In addition to atrazine, other spiked compounds with varying physicochemical properties were evaluated as well. Their adsorption breakthrough in terms of the passed bed volumes at an effluent concentration of 0.1 µg/L (equals to 5% breakthrough of the initial concentration) are presented in Figure 2.7. Analogously, slightly increased bed volumes after AER pre-treatment were obtained for the studied micro-pollutants (with the exception of metribuzin). Among those, bentazon received the most appreciable improvement after 63% DOC removal in Sint RW. Due to its relatively large MW, bentazon might be more susceptible than other compounds to the pore blockage effect. Overall, this observation suggests that with a preceding AER step, the service time of a GAC adsorber for uptake of a wide range of micro-pollutants might be possibly prolonged, which is beneficial for decreasing the GAC regeneration costs. However, to what extents this benefit can be offered in a long-term requires more investigation.

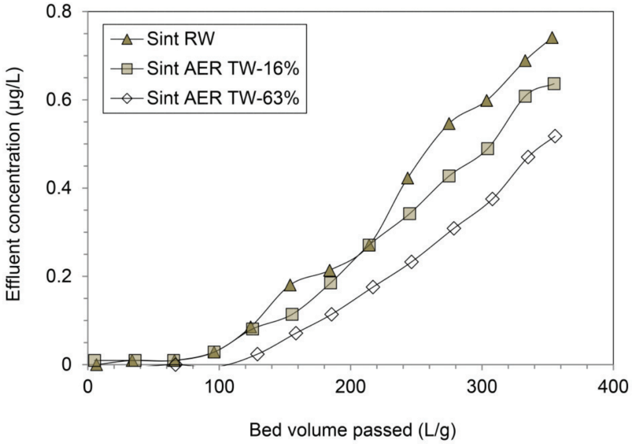

Figure 2.6. *Atrazine adsorption breakthrough on F-400 in Sint RW and the AER-treated Sint RW.*

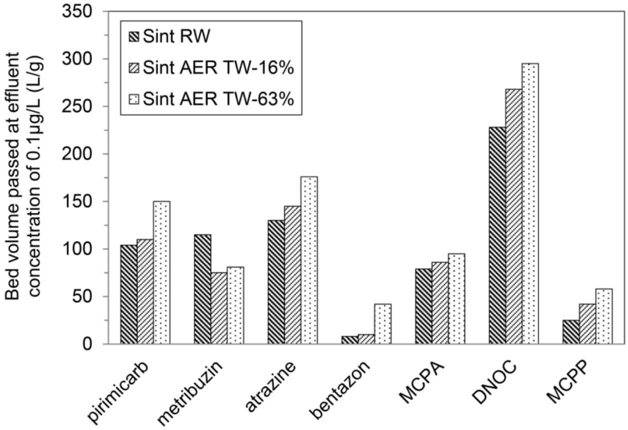

Figure 2.7. *Bed volumes passed at 5% breakthrough for different micro-pollutant adsorption on F-400 in Sint RW and the AER-treated Sint RW.*

2.4. Conclusion

To mitigate NOM competition with the target micro-pollutant adsorption on activated carbons, AER pre-treatment was exercised for NOM removal. Batch adsorption results showed no influence of the AER pre-treatment on mitigating site competition between surface water/groundwater NOM and the studied micro-pollutants (atrazine and caffeine). It was probably the hydrophobic low molecular weight organics fraction, which was refractory to AER treatment, that served as the main competitor. The most microporous F-400 outperformed the less microporous UC830 and the mesoporous HD4000 for a less occurrence of site competition in the simultaneous adsorption. In the continuous filtration RSSCT experiment, AER pre-treatment resulted in less pore blockage, which was caused by the relatively larger 'humic substances' and 'building blocks' molecules in the influent.

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Supporting information

Chapter 2

Adsorption competition effects from organic fractions separated by anionic exchange resin

Table S2.1. *Textural properties of the activated carbons.*

	Specific surface area (m^2/g)				Specific pore volume (cm^3/g)			
Carbon	S_{BET}	S_{micro}		S_{meso}	V_{total}	V_{micro}		V_{meso}
		< 1 nm	1-2 nm			< 1 nm	1-2 nm	
HD4000	801.4	513.10	70.03	218.3	0.68	0.15	0.04	0.49
UC830	851.8	727.14	65.29	59.4	0.36	0.24	0.03	0.09
F-400	1091.6	808.3	117.7	165.6	0.53	0.26	0.07	0.20

Table S2.2. *Eluent gradient program in HPLC analysis.*

Step	Time (min)	Flow (ml/min)	A: ultrapure water (%)	B: acetonitrile (%)	C: 1 g/L KH_2PO_4 (%)	Comments
0	0.2	1.0	90	10	0	Standby
1	2	1.0	90	10	0	Switch on
2	32	1.0	35	65	0	Linear gradient elution
3	6	1.0	0	100	0	
4	2	1.0	100	0	0	
5	4	1.0	0	0	100	
6	9	1.0	90	10	0	Back to start

Table S2.3. *The best-fit parameters for Freundlich isotherms in DW and SEBC model in Schie RW (Schie TW).*

PGAC	Atrazine					
	Freundlich parameters in DW			S_{EBC} parameters in Schie RW (Schie TW)		
	K (mg/g)(L/μg)^n	n	R^2	A	n_1	R^2
UC830	14.0	0.54	0.90	2.70	0.52	0.98
HD4000	20.2	0.56	0.87	5.17	0.49	0.94
F-400	30.5	0.58	0.96	0.47	0.55	0.95

PGAC	Caffeine					
	Freundlich parameters in DW			S_{EBC} parameters in Schie RW (Schie TW)		
	K (mg/g)(L/μg)^n	n	R^2	A	n_1	R^2
UC830	12.1	0.51	0.95	2.46	0.46	0.96
HD4000	12.8	0.68	0.88	3.94	0.60	0.98
F-400	20.3	0.76	0.86	0.21	0.79	0.94

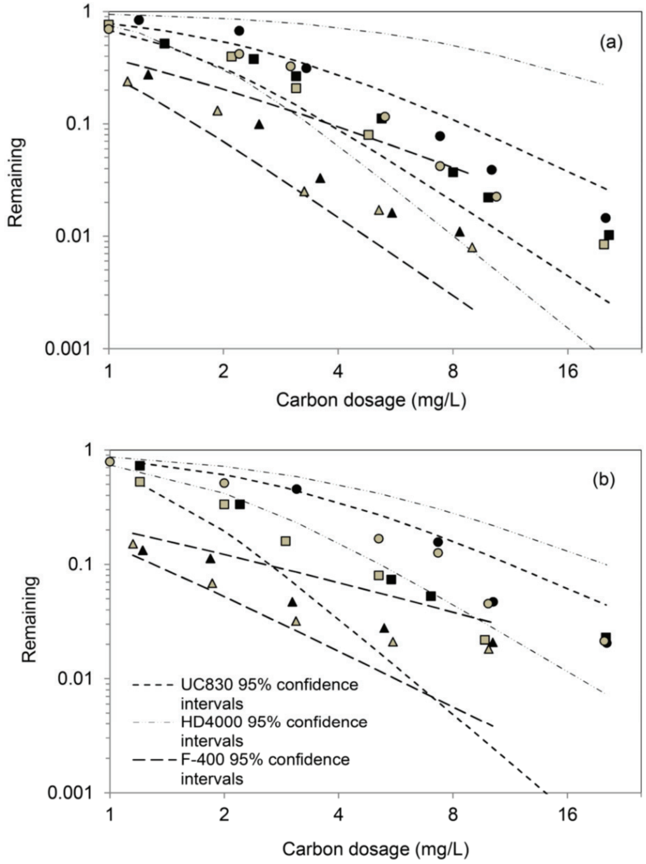

Figure S2.1. *The upper and lower 95% confidence intervals of SEBC-fitting of the percent removal of atrazine (a) and caffeine (b) in Schie RW (and Schie TW) as a function of PGAC dosage.*

Chapter 3

Preloading effects from organic fractions separated by nanofiltration membrane

In this study, the preloading effects of different fractions of wastewater effluent organic matter (EfOM) on the subsequent granular activated carbon (GAC) adsorption of trace-level pharmaceutically active compounds (PhACs) were investigated. A nanofiltration (NF) membrane was employed to differentiate the studied EfOM by size, and two GACs with distinct pore structures were chosen for comparison. The results showed that preloading the EfOM substantially decreased the PhAC uptake of GACs; however, comparable PhAC adsorption capacity was achieved on GACs preloaded by feed EfOM and the NF-permeating EfOM. These indicate that: (1) the NF-rejected, bigger molecules with an expectation to block the PhAC adsorption pores exerted no impact on the adsorbability of PhACs; (2) the permeate with smaller molecules contributed mainly to the decrease in PhAC uptake, mostly due to site competition. Of the two examined GACs, the wide pore size distributed GAC was found to be more susceptible to EfOM preloading than the microporous GAC. Furthermore, among the fourteen investigated PhACs, the negatively charged hydrophilic PhACs were generally subjected to a greater EfOM preloading impact.

This chapter has been submitted to Chemosphere as:

Jingyi Hu, Ran Shang, Bas Heijman, Luuk Rietveld. (2016) Influence of activated carbon preloading by EfOM fractions from treated wastewater on adsorption of pharmaceutically active compounds. Accepted.

3.1. Introduction

Pharmaceutically active compounds (PhACs) can enter the urban sewage system via various pathways, e.g. human excretion, improper discharge, or leaching from the urban area during rainfall (Margot et al., 2013). Some PhACs have been shown to persist through the conventional wastewater treatment processes, rendering the wastewater treatment plant (WWTP) effluents main source of PhAC inputs into the aquatic environment (Zhang and Zhou, 2008; Yang et al., 2011). Nowadays, environmental quality standards have been increasingly raised for emerging micro-pollutants in the freshwaters (C. Götz, 2010; R. Kase, 2011; EC, 2013), particularly for the PhACs (e.g. diclofenac), which might be considered in the future for modification of the existing European or national regulations (Mailler et al., 2015). In this context, additional treatment of the WWTP effluents will be required if these new regulatory limits are coming into force (Jekel et al., 2015). Several treatment approaches have been attempted to update the conventional WWTPs for an effective micro-pollutant removal in both pilot and large scale investigations, e.g. activated carbon adsorption (Boehler et al., 2012; Margot et al., 2013; Mailler et al., 2015), advanced oxidation (Reungoat et al., 2012; Margot et al., 2013), and dense membrane filtration (Christian Abegglen, 2009). These technologies are typically originated from the drinking water treatment processes, amongst, the granular activated carbon (GAC) filtration has been recognized as a suitable advanced treatment for micro-pollutant control (Grover et al., 2011; Corwin and Summers, 2012), due to the little release of harmful by-products as compared to ozonation, and no extra concentrate solutions to be disposed as compared to i.e. nanofiltration, Still, GAC might be more sustainable than the powdered activated carbon (PAC), as it can be regenerated rather than discharged once the adsorption saturation occurs.

A crucial factor impacting micro-pollutant adsorption by GAC from a complex background water (e.g. the WWTP effluent) is the depletion of pollutant (e.g. PhAC) adsorption sites, due to the competition with other co-present adsorbates via either site competition or pore blocking. In a fixed-bed GAC adsorber, the mass transfer zone of organic matter usually moves ahead of the mass transfer zone of a micro-pollutant. As a consequence, the target compound has to adsorb on GAC grains that have already been loaded with organic matter (Li et al., 2003b; Karanfil et al., 2006). This preloading effect greatly impairs GAC uptake of the target micro-pollutants. Previous study identified that the direct site competition is more substantial than the pore restriction for PAC adsorption of micro-pollutants in a WWTP effluent (Zietzschmann et al., 2014b). However, a distinguish between the applications of PAC and GAC has to be aware of, that PAC is typically utilized in batch reactor where simultaneous adsorption of micro-pollutants and EfOM occurs mostly, in contrast to the EfOM preloading encountered usually in the GAC adsorber. Since GAC has a particle size over one to three magnitude of PAC, it is therefore more apt to surfer from the organic matter preloading (fouling) than PAC (Corwin and Summers, 2010). Investigation of the GAC-associated competition behaviour induced by different EfOM fractions is then necessary, in order to explore the maximum GAC usage towards the target micro-pollutants.

In addition, the properties of GAC, especially the pore structure (i.e. the pores have a width larger than 0.8 nm where most organic matter adsorbs (Yu et al., 2009a)), is important for dictating the degree to which organic matter influences PhAC adsorption (Karanfil et al., 2006). GAC with micropores exclusively accessible for PhACs is postulated to have a good performance because a low amount of organic matter would enter the pores to compete; while it is prone to suffering from pore blocking. On the other hand, GAC with pores of a wide size range that can admit both organic matter and PhACs can resist the pore blocking, while it could induce serious site competition. As such, the dominant adsorption competition mechanism needs to be identified, in order to select an appropriate type of GAC for PhAC removal under the preloading condition.

In this study, we examined the EfOM preloading effects on PhAC adsorption by two GACs with different pore structures. A nanofiltration membrane with a molecular weight cutoff approximating 800 Da was chosen to separate the EfOM by size, the permeate produced was then in the same size range of most of the micro-pollutants (e.g. between 100-1000 g/mol (Zietzschmann et al., 2014b)). Particularly, a large collection of PhACs at µg/L level was studied, which makes it possible to determine the responses of different PhACs to GAC preloading in an environmentally-relevant manner. The primary objectives of this study were to: (1) examine the preloading effects of different EfOM size fractions on the adsorptive performance of GAC towards PhACs; (2) identify an appropriate type of GAC which is less prone to the preloading effects; (3) clarify the mechanisms by which preloading exerts an impact on the adsorption behaviour of different PhACs.

3.2. Materials and methods

3.2.1. Materials

Fourteen PhACs (Sigma Aldrich, The Netherlands) were selected in this study to cover a diverse range of physicochemical properties (Table 3.1). To prevent co-solvent effect and a possibly enhanced biological growth in the subsequent experiments, tap water (City of Delft, The Netherlands), instead of methanol, was used to prepare the cocktail PhAC stock solution (2 mg/L per PhAC) (Verliefde et al., 2008). Two commercially available coal-based GACs: HD4000 (Hydrodarco 4000, Norit Inc., The Netherlands) and UC830 (UltraCarb 830, Siemens Inc., USA), were used as adsorbents. In order to promote the adsorption process, both GACs were gently grinded and sieved to obtain a comparatively identical grain size around 0.3 mm. It has to be noted that although the pore blockage effect is particle size dependent (Corwin and Summers, 2010), the applied GAC size in this study is still far more than that of PAC and can represent a relatively smaller GAC size (i.e. ≥ 0.297 mm according to the definition of AWWA B604). The obtained GACs were thoroughly washed with demineralized water to discard impurities and the fine particles. A commercial spiral wound NF membrane (NP010, Microdyn Nadir GmbH, Germany) was employed as a means to separate the WWTP effluent by size. The NF membrane has a Na_2SO_4 retention rate between 25-55% and an approximate molecular weight cut-off of 800 Da, according to the manufacturer.

Table 3.1. *Physicochemical characteristics of PhACs.*

Compounds	Molecular weight (g/mol)	Molecular dimension x (Å) [a]	Molecular dimension y (Å) [a]	Molecular dimension z (Å) [a]	Log D [b] (pH=7.4)	Charge
Sulfadiazine	250.3	6.086	5.998	6.834	-1.01	-1
Sulfamethoxazole	253.3	6.155	4.449	7.149	-0.68	-1
Ketoprofen	254.3	7.181	4.496	10.315	-0.33	-1
Ibuprofen	206.3	4.658	3.627	10.540	0.58	-1
Gemfibrozil	250.3	6.938	4.243	12.145	1.35	-1
Diclofenac	296.1	6.316	5.227	6.848	1.57	-1
Hydrochlorothiazide	297.7	8.353	6.230	11.350	-0.18	0
Caffeine	194.2	6.502	1.805	7.041	0.11	0
Acetaminophen	151.2	4.645	1.799	8.270	0.54	0
Carbamazepine	236.3	6.790	2.932	9.065	2.23	0
Phenytoin	252.3	4.841	4.764	9.406	2.47	0
Metoprolol	267.4	6.396	3.786	14.137	-0.01	+1
Trimethoprim	290.3	6.296	4.614	11.509	0.91	+1
Roxithromycin	837.0	10.669	9.043	17.614	2.24	+1

[a]: Molecular structure was obtained firstly by Chemsketch (Freeware version), and then optimized by Hyperchem release (software 7.5).

[b]: Obtained from ACD/I-Lab web software (https://ilab.acdlabs.com/iLab2),

3.2.2. Water samples

The secondary effluent was collected as the supernatant from the secondary clarifier of a domestic WWTP (Leiden Noord, The Netherlands), which adopts a conventional mechanical/activated sludge treatment process. Upon the water sample's arrival in the lab, suspended solids (and bacteria) were removed by a 1 µm wound polypropylene filtering medium (Syntech Fibres Ltd, US). The filtered water was denoted as feed water (FW), a portion of the FW was further treated by the NF membrane operated as follows: 5 bar as the feed pressure, 0.012 m/s as the crossflow velocity and 6 $L/(m^2 \cdot h)$ as the permeate flux, the recovery rate was maintained around 10%. The produced permeate was referred to as PW and stored together with the FW at 4 °C, which were used within 48 hours to avoid any biological degradation. Demineralized water as a non-organic reference was obtained by passing tap water through an ion exchange- reverse osmosis combined system (WATERLAB of Delft University of Technology). The dissolved organic carbon (DOC) concentration of this demineralized water is constantly lower than 0.1 mg/L. The phosphate buffer (0.2 M K_2HPO_4 and 0.2 M NaH_2PO_4) was emended in the demineralized water to maintain a constant pH value (pH=7.4) in the solution for adsorption isotherm tests.

3.2.3. Activated carbon preloading and PhAC adsorption

In the preloading experiment, a relatively high organic matter concentration to activated carbon dose ratio (500 mg DOC/g GAC) was adopted according to a previous study (Karanfil et al., 2006). Specifically, the pre-calculated amounts (23 mL, 46 mL, 92 mL, 185 mL, 460 mL and 920 mL) of FW (with ~13 mg/L DOC concentration) were brought into contact with the fresh GACs with corresponding dose of 0.6 mg, 1.2 mg, 2.4 mg, 4.8 mg, 12 mg and 24 mg in 6 × 2 L Duran glass bottles for a period of 7 days; while for PW (with ~8 mg/L DOC concentration), the pre-calculated amounts were 37 mL, 75 mL, 150 mL, 300 mL, 750 mL and 1500 mL, which were then in contact with the fresh GACs having the same dose series as in the FW preloading experiment. This preloading approach allowed a theoretically identical preloading extent of organic carbon on the GAC granules while different weights of these GAC granules per bottle for the following PhAC isotherm tests. An orbital incubator (Innova 44, Eppendorf, USA) was used to shake these bottles continuously under 22 °C at 150 rpm in the dark. Thereafter, the supernatant was drained and the buffered demineralized water was introduced into each bottle; meanwhile, predetermined amount of the cocktail PhAC stock solution was spiked to reach an initial concentration of 5 µg/L per PhAC in a final working volume of 250 mL. These bottles were agitated for an additional 7 days in the same conditions as above to determine the adsorption isotherms on the preloaded GACs. Previous study confirmed that 3 days was sufficient for both micro-pollutant adsorption (e.g. galaxolide with initial concentration of 1.38 µg/L in de-ionized water) and organic matter adsorption (i.e. DOC equals to 10 mg/L) onto a GAC (i.e. GAC1240) with particle size of 1.25-1.6 mm (Nowotny et al., 2007). It is then assured that the applied 7 days can guarantee the PhAC adsorption equilibrium, especially considering a much smaller GAC particle size in the present study. Additionally, PhAC and the DOC (in FW and PW) adsorption isotherms of the fresh GACs were determined respectively in the same conditions as that of the preloaded GACs. In each adsorption isotherm test, a blank bottle with the same spiked PhAC concentrations without GAC dosing was placed simultaneously to check any loss of PhACs, and served as the initial PhAC concentrations for the isotherm.

3.2.4. Analytical methods

Surface area and pore size distribution of the two GACs were characterized by N_2 adsorption and desorption isotherms using a gas adsorption analyser (ASAP2010, Micromeritics, USA). Surface chemistry in terms of the point of zero charge (pHpzc), oxygen surface density (including the amounts released as CO and CO_2, respectively), enthalpy of immersion in water and the ash content were determined according to the protocols as mentioned in previous studies (Yang et al., 2004; De Ridder et al., 2012b; de Ridder et al., 2013). Water qualities in terms of DOC and UV absorbance at 254 nm were determined by a TOC analyzer (TOC-VCPH, Shimadzu Co., Japan) and an UV-vis spectrophotometer (Thermo Scientific, Germany), respectively. pH was detected using a multimeter (Multi 340i, WTW, Germany). The molecular weight distribution of organic matter in the FW and PW was analysed by the Liquid Chromatography with Organic Carbon Detection (LC-OCD) technique (Het Waterlaboratorium in Haarlem, The Netherlands).

At the end of the isotherm tests, 50 mL sample was obtained from each bottle by filtrating through a 0.45 μm nylon syringe filter (Polycap AS, Whatman, UK), which was then concentrated with the hydrophile-lipophile solid phase extraction cartridges (Oasis HLB, Waters, USA). 5 mL analytical grade methanol (≥ 99.9%, Sigma Aldrich) and 5 mL demineralized water were used in series to condition the cartridges before loading with the PhAC samples. The protocol of PhAC elution, extraction and reconstitution was based on (Bertelkamp et al., 2014) and the detailed HPLC-MS/MS procedure was described in (Reungoat et al., 2012). The PhAC concentration was quantified by an internal calibration established for each run. Quality control standards were injected during the run to ensure a less than 10% variation in the signal intensity. The sample recovery was determined by spiking the PhAC stock solution to 1 μg/L per PhAC in the given water matrix before the extraction and after reconstitution in duplicate.

3.2.5. Data analysis

The Freundlich model was used to simulate the isotherm data, based on the finding that it described the 'sub-saturation' behaviour of the heterogeneous adsorption isotherms well, e.g. for PhACs adsorption in an ultrapure water (Yu et al., 2008). The expression is:

$$q_e = K_f C_e^n$$

Where q_e is the adsorption amount of the individual PhAC on GAC (mg/g), C_e is the equilibrium concentration of PhAC (μg/L); K_f is a measure of the adsorption capacity ((μg/g)·(μg/L)$^{-n}$) and n is an indicator of the adsorption site energy distribution. The best-fit Freundlich parameters were obtained via non-linear least squares regression between the experimental data and the simulated data.

To evaluate the similarity between two investigated sets of data (e.g. the PhAC adsorbability on the FW preloaded GAC and PW preloaded GAC), a two way ANOVA analysis was performed. The significance level was set at 0.05, and the probability (p) value < 0.05 indicates a statistically significant difference, while the p-value > 0.05 indicates no statistically significant difference between the two sets of data.

3.3. Results and discussion

3.3.1. WWTP effluent water quality and NF treatment

DOC and UV_{254} in the FW were reduced up to 37% and 49% by NF, respectively (Table 3.2), and the aromatic index (specific ultraviolet absorbance, SUVA) was slightly reduced, which rendered the PW less aromatic and less hydrophobic than the FW. Molecular weight distribution was regarded as an important characteristic determining organic matter adsorption on activated carbon (Newcombe et al., 1997a; Pelekani and Snoeyink, 2000). Figure 3.1 shows the LC-OCD chromatography of the FW and PW, as well as their differences. It is clear that the macromolecules (i.e. 'biopolymers') in the FW were completely rejected by NF, followed by the intermediate molecules 'humic substances' with 42% removal and their fragments 'building blocks' with 44% removal, whereas the 'low molecular weight acids' and 'low molecular weight neutrals' having similar MW with the PhACs were only reduced by 11.5% and 1.8%, respectively (Table S3.1 in the supporting information).

The background PhAC concentrations in the FW ranged from less than 0.02 μg/L for sulfadiazine, caffeine, acetaminophen and phenytoin to above 2 μg/L for metoprolol and carbamazepine (Table S3.2). Specially, the employed NF showed appreciable rejections towards i.e. diclofenac and carbamazepine, probably due to their adsorption onto the membrane surface or the inner membrane structures, based on their higher log D values and the fact that membrane adsorption dominated during the initial non-equilibrium phrase (e.g. less than 4 days' continuous operation of the membrane set-up) (Verliefde et al., 2009).

Table 3.2. *Water quality parameters of the FW and PW.*

Water samples	DOC (mg/L)	UV_{254} (cm^{-1})	SUVA (L/mg·m)	Conductivity (ms/cm)	pH
FW	12.76 ± 0.85	0.371 ± 0.002	2.91	3.197	7.8
PW	8.03 ± 0.48	0.189 ± 0.001	2.35	2.871	7.6

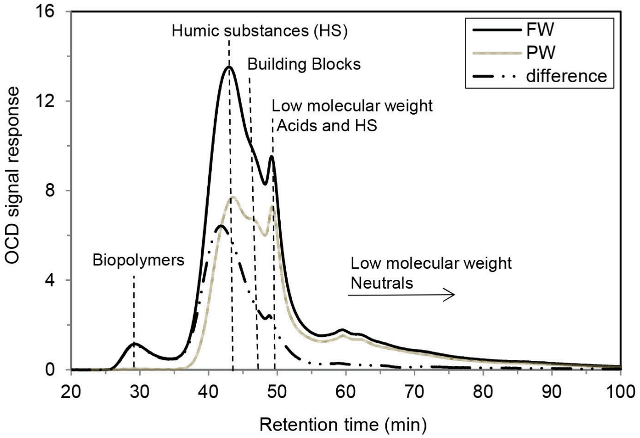

Figure 3.1. *LC-OCD chromatography of the molecular weight distribution of feed water (FW) and the NF permeate water (PW).*

3.3.2. GAC characteristics and adsorption of EfOM

The main characteristics of HD4000 and UC830 are presented in Table 3.3. Both GACs have a similar specific surface area S_{BET}, while HD4000 has a much higher total pore volume V_{total} than UC830. Specifically, HD4000 provides a substantially higher volume of mesopores (> 2 nm) and a slightly higher volume of secondary micropores (in the vicinity of 2 nm), whereas UC830 shows only a higher volume of primary micropores (< 1 nm) (Hu et al., 2014a). With regard to the surface chemical properties, a higher surface oxygen density and a higher ΔH_{imm} reveals a more acidic and polar character for HD4000 than UC830 (De Ridder et al., 2012b). Moreover, the pH_{pzc} values indicate a positive charge present on both fresh GACs in the studied water matrices (i.e. demineralized water, FW and PW with pH values of 7.4, 7.8 and 7.6, respectively).

Table 3.3. *Textural and chemical properties of the studied activated carbons.*

Textural property								
Carbon	Specific surface area (m^2/g)				Specific pore volume (cm^3/g)			
	S_{BET}	S_{micro}		S_{meso}	V_{total}	V_{micro}		V_{meso}
		< 1 nm	1-2 nm			< 1nm	1-2 nm	
HD4000	729	513.10	70.03	146	0.766	0.15	0.04	0.58
UC830	819	727.14	65.29	26.6	0.399	0.24	0.03	0.13

Chemical property						
Carbon	pH_{pzc}	ΔH_{imm} in water (mJ/m^2) [a]	O surface density (μmol/m^2) [a]	CO (μmol/g) [a]	CO_2 (μmol/g) [a]	Ash (wt/%) [a]
HD4000	8.0	40.3	1.87	723	226	23
UC830	8.8	26.6	0.57	387	66	1

[a]: Data sources in (De Ridder et al., 2012b).

Figure 3.2 depicts the DOC adsorption isotherms of both GACs in FW and PW. Obviously, HD4000 exhibited a higher DOC adsorption capacity than UC830. Despite its surface acidity which was thought to be not favourable for organic matter adsorption (Karanfil et al., 1999; Karanfil et al., 2006), the higher degree of mesoporosity and secondary microporosity in HD4000 was able to compensate for this effect and adosrb organic matter across a broad molecular weight distribution spectrum (Cheng et al., 2005; Karanfil et al., 2006). Moreover, for both GACs, PW was found to have a higher adsorption potential than FW: a higher solid phase DOC concentration was achieved in the PW than the FW at an equal equilibrium liquid DOC concentration (Figure 3.2). This was in accordance with a previous finding, in that nanofiltration of wastewater effluent increased the adsorption affinity of the DOC remaining in the permeate (Ernst et al., 2000). It can be attributed to the higher percentage of low molecular weight organics in PW, which are more adsorbable than the bigger organic molecules present mainly in FW (Zietzschmann et al., 2014b).

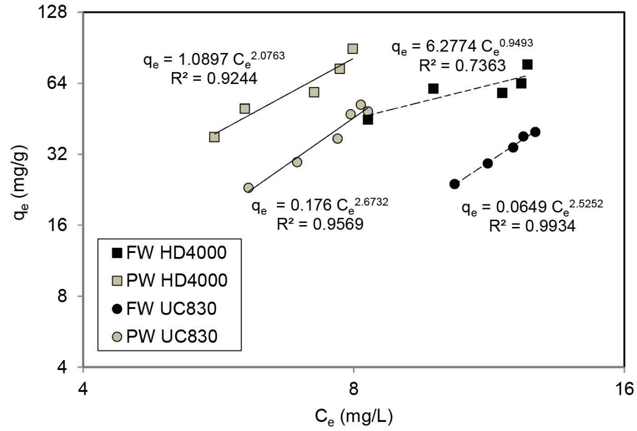

Figure 3.2. *DOC adsorption isotherms of HD4000 and UC830 in FW and PW, respectively.*

3.3.3. Adsorption of PhACs on preloaded GACs

The fourteen PhACs in this study were classified into three groups based on their dominant species in the buffered demineralized water (pH = 7.4): negatively charged, neutral and positively charged. PhAC adsorption capacity of HD4000 and UC830 were presented in both their fresh and preloaded conditions (Table 3.4), and were expressed by Freundlich K_f, i.e. the PhAC loading q_e at the equilibrium concentration of 1 µg/L, which fell in the isotherm range for all PhACs and can represent an environmentally-relevant PhAC concentration. Table 3.4 reveals that K_f decreased substantially on the preloaded GACs as compared to the fresh GACs, regardless of the type of PhAC. It is also found that the influence of NF-rejected EfOM on PhAC adsorption was marginal in the case of HD4000: the difference of K_f between the FW-preloaded HD4000 and the PW-preloaded HD4000 was not statistically significant (p = 0.69, t = 2.07). In the case of UC830, except for the neutral PhACs (explanation is given in Section 3.3.5), the charged PhACs exhibited also comparable K_f on FW-preloaded UC830 and PW-preloaded UC830 (p = 0.45, t = 2.18).

The aforementioned results demonstrate the importance of NF-permeating EfOM for interfering with PhAC adsorption on both GACs. It was anticipated that the big EfOM molecules retained on NF is more likely to block the GAC pores, and therefore reducing the adsorption sites for PhACs. However, since GAC consists of a network of interconnected pores (De Ridder et al., 2012a), it seems that alternative diffusion routes would still be available for the target PhACs if there was not a complete blockage within the GAC pore framework. On the contrary, the NF-permeating EfOM is composed more of small molecules (e.g. the ‘low molecular weight acids’ and ‘low molecular weight neutrals’), which are comparable to PhACs in size and exhibit also higher adsorption potential to GACs (Section 3.3.2); these factors therefore enable them to compete directly with the target PhACs for adsorption sites on GACs.

In addition to the adsorpiton capciaty K_f, another Freundlich parameter n is also examined. The t-test results demonstrate a stastically singnificant differnece of the n values between fresh HD4000 and preloaded HD4000 ($p=3.5\times10^{-5}$, t=2.06 for fresh HD4000 and FW preloaded HD4000 and $p=3.6\times10^{-5}$, t=2.06 for fresh HD4000 and PW preloaded HD4000); whereas a stastically insignificant difference exists between FW preloaded HD4000 and PW preloaded HD4000 (p=0.74, t=2.06). The increased n values for PhAC adsorption on the preloaded HD4000 revealed a more homogeneous surface due to the loss of high-energy adsorption sites by EfOM preloading (Zhang et al., 2011). However, the n values between fresh UC830 and preloaded UC830 appreared to be insignificantly different according to the t-test results: p=0.05. t=2.07 for fresh UC830 and FW-preloaded UC830, p=0.08, t=2.06 for fresh UC830 and PW preloaded UC830, and p=0.80, t=2.06 for FW preloaded UC830 and PW preloaded UC830. These indicate that surface heterogeneity of the microporous UC830 was not substantially impacted by EfOM preloading. An explanation might be that the batch EfOM preloading of GACs in this study resembled more an early preloading stage (e.g. during the practical GAC filter operation), that adsorpiton of the low molecular weight EfOM prodominated in particular on the microporous UC830, which reduced only the PhAC adsorption capacity but not the overall site energy distribution (Carter et al., 1992; Yu et al., 2009a).

Table 3.4. *The best-fit Freundlich isotherm parameters of PhACs adsorption on fresh GACs and preloaded GACs.*

Compound	Preloaded EfOM fractions	HD4000				UC830			
		K_f [a]	Rel. K_f red. [b]	n	R^2	K_f [a]	Rel. K_f red. [b]	n	R^2
Sulfadiazine	Non	441.6		0.344	0.889	238.9		0.442	0.931
	FW	72.64	83.55	0.600	0.992	93.02	61.06	0.698	0.882
	PW	70.30	84.08	0.601	0.947	95.66	59.96	0.674	0.925
Sulfamethoxazole	Non	517.4		0.453	0.888	260.2		0.473	0.882
	FW	91.78	82.26	0.756	0.931	86.28	66.85	0.578	0.932
	PW	83.11	83.94	0.731	0.910	69.02	73.48	0.55	0.885
Ketoprofen	Non	578.3		0.487	0.913	277.9		0.426	0.895
	FW	129.8	77.54	0.586	0.969	89.26	67.88	0.475	0.940
	PW	178.9	69.06	0.671	0.876	84.66	69.54	0.457	0.956
Ibuprofen	Non	562.1		0.459	0.811	238.6		0.446	0.887
	FW	86.58	84.60	0.774	0.908	79.07	66.86	0.584	0.946
	PW	61.30	89.09	0.491	0.919	57.05	76.09	0.525	0.972
Gemfibrozil	Non	517.5		0.399	0.935	278.2		0.466	0.911
	FW	162.3	68.63	0.620	0.994	90.89	67.33	0.564	0.902
	PW	164.0	68.30	0.563	0.921	87.32	68.61	0.529	0.975
Diclofenac	Non	422.6		0.403	0.895	195.9		0.609	0.909
	FW	129.3	69.39	0.608	0.976	75.74	61.35	0.743	0.903
	PW	161.1	61.86	0.675	0.934	68.73	64.93	0.797	0.992
Hydrochlorothiazide	Non	536.3		0.607	0.980	308.8		0.664	0.885
	FW	70.78	86.80	0.718	0.998	88.49	71.34	0.675	0.942
	PW	90.30	83.16	0.611	0.953	116.2	62.36	0.679	0.976
Caffeine	Non	553.3		0.346	0.933	345.5		0.499	0.919
	FW	71.55	87.07	0.428	0.847	98.91	71.37	0.513	0.959
	PW	76.13	86.24	0.486	0.935	150.1	56.55	0.488	0.969
Acetaminophen	Non	506.2		0.363	0.961	353.2		0.523	0.912
	FW	118.9	76.51	0.773	0.979	140.2	60.29	0.524	0.963
	PW	112.4	77.80	0.666	0.945	97.74	72.33	0.505	0.998
Carbamazepine	Non	458.0		0.274	0.927	241.7		0.490	0.935
	FW	129.5	71.72	0.640	0.983	123.7	48.83	0.626	0.934
	PW	147.2	67.85	0.687	0.968	88.31	63.47	0.630	0.998
Phenytoin	Non	484.8		0.484	0.883	217.8		0.426	0.981
	FW	95.65	80.27	0.708	0.918	99.39	54.36	0.760	0.936
	PW	99.35	79.51	0.758	0.969	67.44	69.04	0.679	0.970
Metoprolol	Non	392.3		0.209	0.746	234.0		0.321	0.906
	FW	136.2	65.28	0.443	0.918	108.4	53.68	0.358	0.938
	PW	124.0	68.38	0.465	0.894	117.0	49.98	0.384	0.994
Trimethoprim	Non	442.3		0.447	0.885	259.7		0.408	0.906
	FW	188.4	57.40	0.547	0.985	123.7	52.35	0.371	0.879
	PW	182.0	58.85	0.579	0.920	122.3	52.89	0.360	0.963
Roxithromycin	Non	386.6		0.489	0.967	183.4		0.438	0.935
	FW	211.2	45.37	0.742	0.958	82.92	54.81	0.397	0.979
	PW	243.1	37.11	0.768	0.925	83.35	54.57	0.427	0.831

[a]: Equals to the PhAC loading q_e (µg/g) at the PhAC equilibrium concentration of 1µg/L.

[b]: Relative K_f reduction, described by the reduced K_f on preloaded GAC in relation to the original K_f on fresh GAC, expressed in the units of %.

3.3.4. Comparison of two GACs under preloading

The EfOM adsorbed onto UC830 during preloading was 26.84 mg/g for FW and 21.93 mg/g for PW, respectively; this differs considerably from that of HD4000 with 61.13 mg/g and 48.75 mg/g for FW and PW, respectively. For a direct comparison, the extent preloaded EfOM affected the adsorption of each PhAC was described quantitatively by the reduced K_f on the preloaded GACs in relation to the original K_f on the fresh GACs, which was then referred to as the relative K_f reduction. Figure 3.3 summarizes the relative K_f reduction of the fourteen PhACs on the preloaded GACs. Clearly, the reduction was more pronounced on the preloaded HD4000 than the preloaded UC830, reflecting a higher susceptibility of HD4000 to EfOM preloading. This can apparently be attributed to the higher EfOM loading and essentially, to the higher volume of pores with width larger than 0.8 nm in HD4000; such that organic molecules with varying size can easily access and cause a severe adsorption site occupation for PhACs (Yu et al., 2009b). It is also noted that the fresh HD4000 exhibited a generally higher PhAC adsorption capacity than fresh UC830 (Table 3.4), and was presumably able to adsorb an accordingly higher amount of the direct competing EfOM. The preloading of these EfOM therefore largely impaired the subsequent PhAC adsorption. However, it has to be pointed out that although a microporosity of activated carbon tended to lessen the EfOM preloading effect, it does not necessarily represent an absolutely higher micro-pollutant adsorption capacity on the preloaded activated carbon, as was evident from the lower K_f of PhACs on preloaded UC830 than the preloaded HD4000.

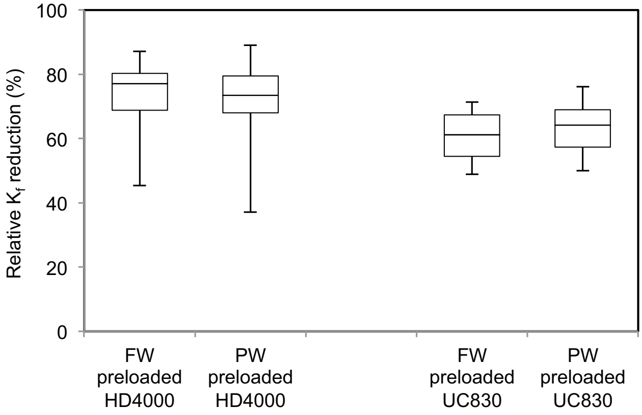

Figure 3.3. *PhAC adsorption reduction on preloaded HD4000 and preloaded UC830 as compared to fresh HD4000 and fresh UC830, respectively. The box plots show the minimum, first quartile, median, third quartile, and the maximum of the K_f reduction values among the fourteen PhACs.*

3.3.5. The impact of preloading on PhAC adsorption

PhAC adsorption reduction on preloaded HD4000

Figure 3.4 shows the relative K_f reductions of PhACs in different charge groups. It can be seen that the negative and neutral PhACs had a generally comparable K_f reduction, which was generally higher than that of the positive PhACs. Previous studies identified that a significant negative charge can be obtained on the activated carbon surface after adsorbing even a small amount of organic matter (Morris and Newcombe, 1993; Fairey et al., 2006), hence, the electrostatic attraction tended to mitigate the adsorption reduction of positive PhACs. Moreover, within each charge group, the K_f reduction roughly decreased with an increase in log D values of the PhACs, indicating that the hydrophilic PhACs were more affected by EfOM preloading of HD4000. This observation coincides with the finding that hydrophobic compounds bearing stronger competitive potential were subjected to less capacity loss on the preloaded GACs (Yu, 2007). As HD4000 has an intrinsically polar character (Section 3.3.2), competing the polar adsorption sites (e.g. H bond-donor and -accepter) of HD4000 between EfOM and the hydrophilic PhACs might possibly be involved. The specific chemical property of HD4000 thus determined a severity of the adsorption competition for hydrophilic PhACs.

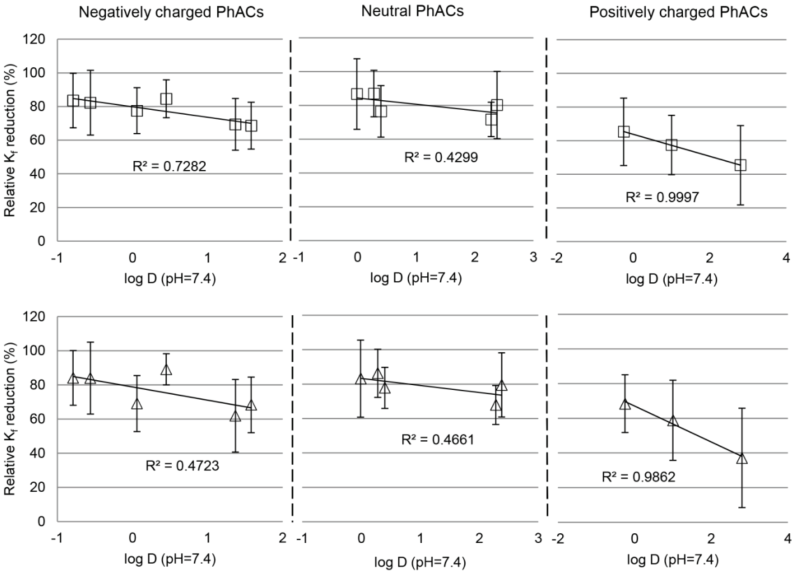

Figure 3.4. *The relative K_f reduction of PhACs by FW preloading (rectangle) and PW preloading (triangle) of HD4000 as a function of PhAC log D values. The lines represent the least square linear regression for each data set.*

PhAC adsorption reduction on preloaded UC830

Similar to HD4000, the positively charged PhACs were less affected by preloading as compared to the negatively charged PhACs (Figure 3.5), reaffirming the prevalence of electrostatic interaction in PhAC adsorption on the EfOM preloaded GACs. However, a roughly constant K_f reduction was found for different negatively charged PhACs and different positively charged PhACs as compared to the neutral PhACs, suggesting that the adsorption of charged PhACs was independent of their log D values. It seems that the i.e. polar or hydrophobic interaction between PhACs and the preloaded UC830 surface were possibly compensated by the electrostatic interaction effect.

In contrast to HD4000, varying K_f reduction patterns were observed for the neutral PhACs: caffeine received a higher uptake on PW preloaded UC830 than FW preloaded UC830 while acetaminophen, phenytoin and carbamazepine showing higher log D values had an opposite trend (Figure 3.5). It was shown in Table 3.1 that caffeine and acetaminophen both exhibit the similarly small (planar) molecular structure and a neutral charge, while their difference lies largely in their hydrophobicity (i.e. log D value). Caffeine with a lower log D appeared to suffer site competition even from the weakly adsorbable, bigger molecular EfOM which was retained by the NF membrane (Zietzschmann et al., 2014b), provided that pore blocking was not responsible for its K_f reduction. On the contrary, acetaminophen (and the other neutral PhACs) with higher log D values benefited from the NF-rejected EfOM. Since neutral PhACs are not likely to be affected by electrostatic interaction, this positive effect derived from the NF-rejected EfOM could be ascribed to the association (partitioning) between the hydrophobic PhACs and the pre-adsorbed organic macromolecules (i.e. ‘biopolymers’ which was contained exclusively in the NF-rejected EfOM) (Kimura et al., 2009). As is observed from Figure 3.5, K_f reduction of the neutral PhACs roughly decreased as a function of their log D values on the FW preloaded UC830 (R^2=0.8116), while no such tendency was found for PW preloaded UC830. Nonetheless, this association between PhACs and the macromolecules present in FW was insignificant in the case of HD4000. Due to the larger availability of mesopores with width > e.g. 4 nm (Gibert et al., 2013) in HD4000, the macromolecules were supposed to adsorb sparsely as opposed to e.g. accumulate in the microporous UC830, which led to a little association effect in HD4000.

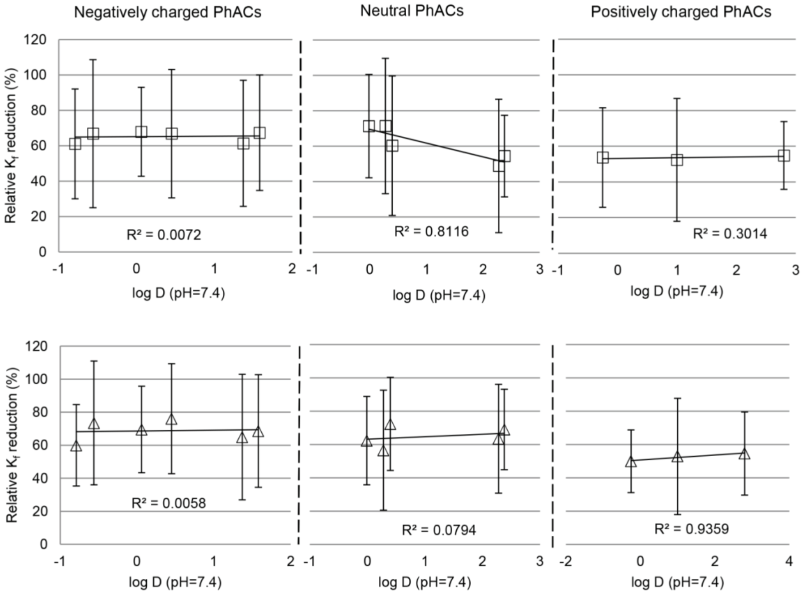

Figure 3.5. *The relative K_f reduction of PhACs by FW preloading (rectangle) and PW preloading (triangle) of UC830 as a function of PhAC log D values. The lines represent the least square linear regression for each data set.*

3.4. Conclusion

Different EfOM size fractions were preloaded onto GACs to investigate their influences on the subsequent PhAC adsorption. Significant adsorption reduction was found for each PhAC on the preloaded GACs in comparison to the fresh GACs. The wide pore size distributed GAC (HD4000) had an overall serious PhAC adsorption reduction *versus* the microporous UC830 after being preloaded by EfOM. This can be explained by the higher organic loading and principally a more accessible pore structure of HD4000. For most PhACs, a similar adsorbability on GAC preloaded by FW and PW was found, indicating the irrelevance of NF-rejected EfOM for interfering equilibrium adsorption with the PhACs. Moreover, as compared to the negatively charged and neutral PhACs, positively charged PhACs were generally subject to a less preloading impact due to electrostatic attraction with the negatively charged surface of preloaded GACs (especially for UC830). It was also observed that on the preloaded GACs, hydrophilic PhACs were subjected to a higher preloading impact than hydrophobic PhACs within the same charge group.

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Supporting information

Chapter 3

Preloading effects from organic fractions separated by nanofiltration membrane

Table S3.1. *LC-OCD chromatography results of FW and PW.*

Parameters	FW	% TOC	PW	% TOC	Molecular weight (g/mol)
TOC (ppb-C)	10,404	100	7,150	100	
HOC (hydrophobic) (ppb-C)	360	3.46	400	5.59	
Biopolymer (ppb-C)	388	3.73	13	0.18	>>20,000
Humic substances (HS) (ppb-C)	6,327	60.81	3,665	51.26	~1,000
with SUVA (L/mg·m)	4.62		4.22		
with mol. weight (g/mol)	627		544		
Building blocks (ppb-C)	1,485	14.27	831	11.62	300-500
Low molecular acids and HS (ppb-C)	2,170	20.86	1,920	26.85	<350
Low molecular neutrals (ppb-C)	326	3.13	320	4.47	<350

Table S3.2. *PhACs present in FW and PW as their ambient concentrations and the NF rejection efficiency.*

Compound	Concentration in FW (µg/L)	Concentration in PW (µg/L)	NF rejection (%)
Sulfamethoxazole	0.29	0.26	10.3
Ketoprofen	0.03	0.03	0
Ibuprofen	0.07	0.07	0
Diclofenac	0.43	0.03	93
Gemfibrozil	0.02	0.02	0
Sulfadiazine	NA	NA	NA
Caffeine	NA	NA	NA
Acetaminophen	NA	NA	NA
Phenytoin	NA	NA	NA
Carbamazepine	2.04	0.72	64.7
Metoprolol	2.3	1.84	20
Trimethoprim	0.07	0.08	-14.3

NA: not applicable, below the detection of measurement limitation 0.02 µg/L.

Chapter 4

Reuse of spent granular activated carbon for organic micro-pollutant removal from treated wastewater

Spent granular activated carbons (sGACs) for surface water and groundwater treatments were reused via pulverizing as low-cost adsorbents for micro-pollutant adsorption from a wastewater secondary effluent. The changes of physicochemical characteristics of the spent carbons (in relation to the respective fresh carbons) were determined and were correlated to the molecular properties of the influents (surface water and groundwater, respectively). Pore size distribution analysis showed that the carbon pore volume decreased over a wider size range due to preloading by surface water, which contains a broader molecular weight distribution of organic matter in contrast to the groundwater. There was still considerable capacity available on the pulverized sGACs for micro-pollutant (atrazine) adsorption in the demineralized water (and also the secondary effluent), and this was particularly the case for the groundwater spent GAC. However, as compared to the fresh counterparts, the decreased surface area and the induced surface acidic groups on the pulverized sGACs contributed both to the lower uptake and more impeded adsorption kinetic of atrazine in the demineralized water. Nonetheless, the pulverized sGACs (i.e. preloaded by the surface water) were less susceptible to adsorption competition in the secondary effluent than the fresh ones, due to its negatively charged surface which can repulse the accessibility of the co-present organic matter. This suggests the reusability of the drinking water spent GACs for micro-pollutant adsorption from the treated wastewater.

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4.1. Introduction

The occurrence of emerging organic micro-pollutants in the aquatic environment has received widespread concerns and has undergone much research over the last few decades (Daughton and Ternes, 1999; Heberer, 2002; Fatta-Kassinos et al., 2011). Traditional wastewater treatment plants are typically not designed to remove micro-pollutants and, consequently, most of these contaminants are present in the treated wastewater (e.g. the secondary effluent) and subsequently enter the receiving aquatic ecosystem (Fent et al., 2006). In practice, wastewater tertiary treatment includes a sand filter that aims at removing suspended solids, phosphate and ammonia; its efficiency for micro-pollutant removal may not be significant. To this end, the addition of powdered activated carbon (PAC) before the sand filter has been proposed as an approach to enhance micro-pollutant elimination (Joss et al., 2008; Boehler et al., 2012; Margot et al., 2013). However, PAC particles retained on top of the sand filter are being frequently flushed out by backwashing and discharged into the sewage system, much of which might not have reached the maximum adsorption capacity. This would be an economic issue since a large quantity of the commercially fresh PAC is required.

In this study, cheaper PACs were obtained by pulverizing the spent granular activated carbons (sGACs) from drinking water companies. These PACs could potentially be recycled as replacements of the fresh PACs for the aforementioned purpose. The hypotheses lie in:

(1) The decreased ability of sGACs to remove organic pollutants (e.g. the dissolved organic carbon, DOC), is not indicative of their capacity to remove the micro-pollutants with comparatively lower concentrations and smaller molecules (Drikas et al., 2009). Therefore, sGACs can continue to be used rather than regenerated;

(2) The reduction of the carbon particle size might help to open up pores to create adsorption sites, for instance, the sGAC pores previously occupied by the influent natural organic matter (NOM) might be recovered as a consequence of mechanical pulverizing;

(3) The treated wastewater typically contains higher concentrations of micro-pollutants than drinking water does (i.e. the influent of the GAC filter). According to the classical Freundlich adsorption equation, a higher background adsorbate concentration would induce a higher adsorbate loading on the same PAC. This “double-stage” PAC usage strategy was demonstrated as capable of effectively exploiting PAC sorption capacity (Boehler et al., 2012).

In drinking water facilities, a GAC filter is continuously loaded by the influent NOM, causing “site competition” or “pore blockage” for the successive uptake of the target micro-pollutants. These two mechanisms cannot be distinguished easily. Normally, at the lower

NOM loading in a GAC filter's initial operation, site competition is more obvious and contributes mainly to the adsorption reduction of the micro-pollutants. After a long run, pore blocking predominates and leads to both reduced adsorption capacity and kinetics (Yu et al., 2009a). Concerning the pore blocking phenomena, the extent can be attributed to the physicochemical properties of the GAC applied (Newcombe et al., 1997b; Newcombe et al., 2002a), and the molecular composition (e.g. the molecular weight distribution, MWD) of the influent NOM (Yuasa et al., 1997; Li et al., 2003b; Karanfil et al., 2006). By virtue of the size exclusion chromatography technique, NOM can be fractionated into biopolymers, humic substances (HS), building blocks (BB) and the low molecular weights (LMW) based on their molecular weight (Huber et al., 2011a; Huber et al., 2011b). With respect to their adsorbability on activated carbon, biopolymers tend to be refractory due to their relatively large size; for the other NOM fractions, the adsorbability generally increases with a decrease in molecular size (Velten et al., 2011).

In view of the adsorption competition, the low molecular weight NOM with strong adsorption potential is able to migrate into the inner micropores, thus reducing the uptake of target micro-pollutants considerably (Wigton and Kilduff, 2004). By contrast, the larger molecular weight NOM which is unlikely to access the same pore region as the target micro-pollutants is capable of constricting the pore entrance, thereby reducing their adsorption kinetics (Li et al., 2003a; Li et al., 2003b). However, most of these observations were derived from the batch-scale experiments under conditions not representative of the full-scale GAC filters. By monitoring the variation of GAC porosity over one year's operation, it was concluded that the intermediate HS and the GAC super-microporosity (0.7-2nm) appear to be the best removed fraction and the most-occupied pore range (Gibert et al., 2013), respectively.

In addition to the pore occupation effect, NOM adsorbed on the activated carbon serves to alter the surface chemical characteristics as well. Due to the presence of acidic (e.g. carboxyl, phenolic) functional groups in the NOM moieties, the adsorbed NOM inevitably imparts a net negative charge to the carbon surface at ambient pH conditions (Morris and Newcombe, 1993). An increase in the carbon surface acidity was reported to reduce adsorption of both NOM and the hydrophobic organic contaminant (Karanfil and Kilduff, 1999; Karanfil et al., 1999). Additionally, preloading with the more hydrophobic NOM was found to result in a stronger adsorption reduction of the investigated pharmaceuticals, due to a higher competition on the altered carbon surface (De Ridder, Verliefde et al. 2011).

The above shows that both pore occupation and surface chemistry changed by NOM preloading can affect the adsorption of micro-pollutants. The goal of this study is to understand these physicochemical changes on sGACs saturated with different influent NOM (i.e. surface water and groundwater), and to determine the remaining adsorption capacity of the spent GACs via mechanical pulverizing. Meanwhile, atrazine has been selected as a micro-pollutant to study how the altered carbon characteristics influence its adsorption, and if the drinking water spent GACs can be reused for micro-pollutant removal from the treated wastewater.

4.2. Materials and Methods

4.2.1. Activated carbons

Two field-spent GACs were obtained from the drinking water companies (Waternet and Oasen) in the Netherlands. Waternet treats surface water by coagulation, rapid sand filtration and ozonation before the GAC filter; while Oasen extracts groundwater to feed the GAC filter having a different carbon origin. The sGACs were sampled after a full cycle of filtration (around 1 year) and just before their thermal regenerations. To ensure that the sGACs were completely saturated, they were collected from the top layer of the filters. In addition, the regenerated GACs were also collected to serve as the fresh references. Upon arrival in the lab, the GAC samples were thoroughly washed with demineralized water to remove the impurities. Afterwards, GACs were pulverized in wet form with a disk mill (HSM100, Herzog, Germany) to obtain PAC slurry. Freeze-drying was performed to dry the wet GACs and PAC slurry in order to minimize the destruction of preloaded organic substances on the spent carbons. The final carbon samples were stored in the desiccator until use. sGACs loaded by surface water and groundwater were denoted as sGAC-SW and sGAC-GW, respectively, and their pulverized forms were denoted as sPAC-SW and sPAC-GW, respectively. In the same manner, the regenerated fresh carbons were named as fGAC-SW, fGAC-GW or fPAC-SW, fPAC-GW. Nominal particle size of the GACs ranged from 0.4-0.5mm in width according to the wet sieving results. The obtained PAC particles were shown to be less than 10 µm by particle counter analysis (Model 3000, Pacific Scientific Instruments, the Netherlands).

4.2.2. Water types

Influents of the two GAC filters were sampled during carbon collection. After being treated by 0.45 µm glass fibre syringe filters (Whatman, UK), the two influents were analyzed by liquid chromatography coupled with organic carbon detection (LC-OCD) in the WDRC lab (KAUST, Thuwal, Saudi Arabia) to determine the NOM molecular weight distribution. The wastewater secondary effluent was obtained from Leiden Noord municipal wastewater treatment plant (Leiden, the Netherlands); 1 µm wound polypropylene filter medium (Syntech

Fibres Ltd, US) was used to remove the visible suspended solids and bacteria in the effluent water before being stored in the refrigerator at 4 ℃.

4.2.3. Target micro-pollutant

Atrazine was purchased as analytical standard from the Sigma-Aldrich Company (the Netherlands). A stock solution (2 mg/L) was prepared by mixing atrazine powder in demineralized water for at least three days to ensure complete dissolving. An enzyme-linked immunoassay kit (Abraxis LLC, Warminster PA, the USA) was used to quantify the concentration of atrazine. A calibration curve was established for each measurement using the standards provided by the manufacturer, and samples were measured carefully in triplicate under constant temperature without sunlight. A microplate reader (TECAN Infinite M200, Switzerland) was employed to record the final absorbance data under a 450 nm UV wavelength. Sample concentrations were determined by interpolating the detected absorbance data against the standard curve constructed in each run. The detection limitation ranged from 0.04 to 5 μg/L.

4.2.4. Characterization of the activated carbons

Nitrogen gas adsorption/desorption isotherm analyses (ASAP 2010, Micromeritics, USA) were executed at 77 K to examine the textural characteristics of all sGACs and sPAC-SW; the freeze-dried samples were used for this measurement. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method while the pore size distribution (PSD) was calculated by the Non-local Density Functional Theory. Surface chemistry in terms of the surface oxygenated functional groups was quantified by Boehm's titration method, in which two main categories, basic and acidic functional groups, were determined. The point of zero charge pH_{pzc} (the pH at which the carbon surface reaches neutral charge) was assessed by the pH drift method (Yang et al., 2004). Immersion calorimetry as an index of carbon surface hydrophobicity was measured following (De Ridder et al., 2012b).

4.2.5. Adsorption test

Adsorption isotherms were conducted with PACs in the demineralized water (DW) following a bottle-points method (Yu et al., 2008), the DOC content in the DW was less than 0.2 mg/L as measured by a total organic carbon analyzer (TOC-V_{CPH}, Shimadzu, Japan). One litre Duran glass bottles were used after a thorough washing with 0.1 N HCl, 0.1 N

NaOH, methanol, and consequently rinsed three times with DW. Atrazine stock solution (2 mg/L in DW) was spiked to attain the nominal concentration of 2 μg/L in each bottle, which can well represent an environmentally-relevant micro-pollutant concentration. The PAC dosages ranged from 0.5 to 50 mg/L; blanks with the same atrazine concentration but no PAC addition were running simultaneously to check any loss of atrazine. All the bottles were tightly sealed and stirred for one week at approximately 150 rpm in the dark and at room temperature (22±1 ℃).

For atrazine adsorption kinetic test, 10 mg/L PAC was introduced into a 2 L glass bottle with an initial and nominal atrazine concentration of 2 μg/L under stirring at 150 rpm. Samples were withdrawn at predetermined time intervals. Atrazine adsorption isotherms in the effluent water were carried out with varying carbon dosages from 1 to 75 mg/L for one week. All of the atrazine samples were extracted by filtering through 0.45 μm syringe filters to remove carbon particles, no atrazine loss was detected after this filtration.

4.2.6. Adsorption models

The Freundlich model was used to described the obtained atrazine adsorption isotherms, given that this model is valid for adsorption data over a restricted concentration range on the heterogeneous surface (Zhang et al., 2010). The model is expressed as:

$$q_e = K_f C_e^n \tag{1}$$

Where C_e (μg/L) and q_e (mg/g) are the liquid-phase and solid-phase equilibrium concentrations; K_f ((mg/g)· (μg/L$^{)-n}$) and n are the Freundlich constants.

To investigate the atrazine adsorption kinetic, pseudo-second-order kinetic model was employed, due to its good presentation of the experimental data for most of the adsorbent-adsorbate systems (Ho and McKay, 1999), the expression is:

$$\frac{t}{q_t} = \frac{1}{k_p q_{eq}^2} + \frac{t}{q_{eq}} \tag{2}$$

Where, q_t (mg/g) and q_{eq} (mg/g) are the adsorbate solid phase concentrations at time t (h) and at equilibrium; k_p (g·mg^{-1}·h^{-1}) is the pseudo-second-order adsorption rate constant.

4.3. Results and discussion

4.3.1. Characterization of activated carbons

Pore structure

Figure 4.1 shows that the pore volume of larger mesopores (8-32 nm) remained unchanged when comparing sGACs with the respective fGACs, whereas the narrow mesopores (2-4 nm) and micropores (< 2 nm) were significantly decreased. It is important to note that the primary micropores (e.g. < 0.7 nm) of sGAC-SW were diminished due to the complete pore occupation by the adsorbed NOM. On the contrary, a higher pore volume in the secondary micropore region (1.6-2 nm) was detected on sGAC-SW rather than fGAC-SW, which might be caused by a partial blockage of the narrow mesopores, thus reducing the pore size to a smaller range. In regard to sGAC-GW, however, only a slight volume reduction in the secondary micropores (0.8-1.4 nm) was observed.

After pulverizing, there was no noticeable increase in the pore volume on sPAC *versus* sGAC (Figure S4.1 in the supporting information). A similar observation was also obtained by Ando et al (2010), who found that the pulverized ‘superfine’ PAC exhibited similar hysteresis behaviour as the original normal PAC in the nitrogen adsorption/desorption isotherm, and confirmed that the structural features of the carbon internal pores are unlikely to alter by pulverizing. Based on these observations, the pore size distribution (PSD) of PACs could be regarded as the same as the measured PSD of their respective GACs.

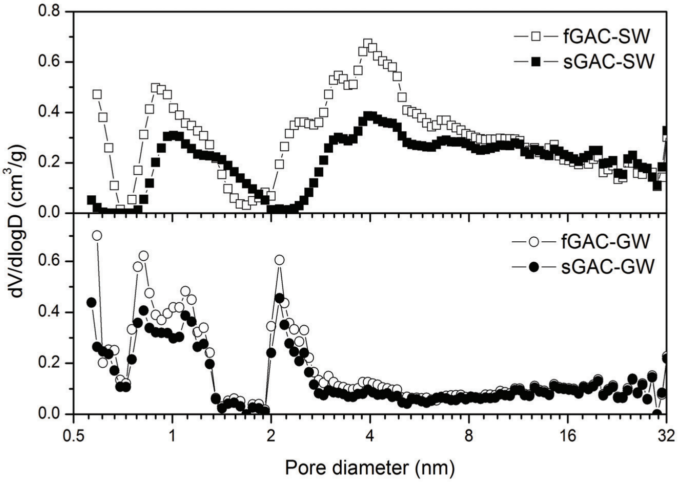

Figure 4.1. *Pore size distribution of fresh GAC (fGAC) and spent GAC (sGAC). Top: fresh and spent GAC for surface water treatment; bottom: fresh and spent GAC for groundwater treatment.*

Molecular weight distribution (MWD) of the GAC filter influents

The PSD change on the spent carbons can be ascribed to the preloaded NOM. The lower influent DOC concentration in groundwater did potentially convey less NOM loading on the sGAC-GW; however, it might not necessarily influence the pore blocking, which is more dependent on the molecular composition of the influent NOM (Newcombe et al., 1997b; Yuasa et al., 1997; Pelekani and Snoeyink, 1999; Pelekani and Snoeyink, 2000).

Table 4.1 provides the DOC concentration of each NOM fraction in surface water and groundwater, their MWD are illustrated in Figure S4.2. It can be observed that, the two influents showed a prevalence of intermediate fractions of humic substances (MW approximates 1 kDa) and building blocks (MW between 300 to 500 Da); the DOC of each fraction in groundwater was 75% lower than that in surface water. However, 'low molecular weight acids' (anions with MW < 350 Da) were present exclusively in the surface water, and the 'low molecular weight neutrals' (weakly charged components with MW < 350 Da) in groundwater was only 12% of that in the surface water.

From the adsorption free energy viewpoint, organic matter would be preferentially adsorbed in pores with a comparable size, due to a greater number of contact points between the organic molecules and the adsorbent surface (Pelekani and Snoeyink, 1999; Ebie et al., 2001). It is therefore deduced that the low molecular weight components were able to occupy the primary micropores (< 0.8 nm) or block the entrances to the primary micropores, thus leading to a more serious reduction in the primary micropores on sGAC-SW than on sGAC-GW.

On the other hand, a reduction in secondary micropores for both sGACs might be attributed to the preloading by humic substances and building blocks as common constituents in both surface water and groundwater (Gibert et al., 2013). Moreover, the observed mesopore reduction in mesoporous fGAC-SW was probably due to the accumulation of certain larger molecular weight humic substance or even biopolymers under a continuous filtration condition; which, in contrast, was less obvious in the comparatively microporous fGAC-GW.

Table 4.1. *DOC concentration of each NOM fraction in surface water and groundwater by LC-OCD.*

Parameters	Surface water	% TOC	Groundwater	% TOC	Molecular weight (g/mol)
TOC (ppb-C)	7598	100	1847	100	
HOC (hydrophobic) (ppb-C)	882	11.6	392	21.2	
Biopolymer (ppb-C)	57	0.8	6	0.3	>>20,000
Humic substances (ppb-C)	3621	47.7	922	49.9	~1,000
with SUVA (L/mg·m)	2.60		3.64		
with mol. weight (g/mol)	535		504		
Building blocks (ppb-C)	1210	15.9	297	16.1	300-500
Neutrals (ppb-C)	1803	23.7	230	12.5	< 350
Acids (ppb-C)	26	0.3	0	0	< 350

Surface chemistry

The surface chemical parameters of the studied PACs are presented in Table 4.2. Obviously, NOM loaded on both carbons imparted the negative charge to their surfaces, the pH_{pzc} values decreased 2.5 units for sPAC-SW and 1.5 units for sPAC-GW compared to their fPACs. Titration results showed a slight decrease in basicity and a dramatic increase in acidity on the carbon surface after preloading, with sPAC-SW more pronounced than sPAC-GW. Similarly, the heat of immersion results revealed a more hydrophilic carbon surface after NOM preloading, and this effect was again more conspicuous on sPAC-SW than on sPAC-GW. These distinct surface chemistry changes were most likely resulted from the higher NOM concentration in the surface water, which correspondingly led to a higher NOM loading and a more NOM-like characteristic on the surface of sPAC-SW.

Combined with the physical properties of the two sGACs (or sPACs), it is obvious that surface water is more deleterious to GAC preloading than groundwater. On one hand, the higher ‘low molecular weight’ composition in surface water yielded a serious pore reduction; on the other hand, its higher NOM concentration caused a heavier surface coverage and largely altered the carbon surface chemistry.

Table 4.2. *Pore structure and surface chemistry characteristics of the studied activated carbons.*

Samples	Pore structure characteristics			
	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
fGAC-SW	725	0.60	0.16+0.1 [a]	0.31
fGAC-GW	773	0.43	0.2+0.09	0.12
sGAC-SW	437	0.44	0.05+0.08	0.28
sGAC-GW	635	0.36	0.17+0.06	0.11

Samples	Surface chemistry characteristics			
	pH_{pzc}	Basic groups ($\mu mol/m^2$)	Acidic groups ($\mu mol/m^2$)	ΔH_{imm} in water (mJ/m^2)
fPAC-SW	9.7	11.00	16.42	53.78
fPAC-GW	9.1	13.27	14.58	43.68
sPAC-SW	7.2	9.71	44.10	71.48
sPAC-GW	7.6	13.93	31.57	48.27

[a]: The primary micropore volume plus the secondary micropore volume.

4.3.2. Atrazine adsorption in demineralized water by PACs

Adsorption isotherms

Figure 4.2(a) presents atrazine adsorption isotherms of all the studied PACs in demineralized water, the best-fit Freundlich parameters are listed in Table 4.3. It is clear that there still remained considerable adsorption capacity on the pulverized spent GACs (i.e. sPACs). The order of atrazine adsorption capacity represented by K_f was: fPAC-GW > fPAC-SW > sPAC-GW > sPAC-SW (Table 3). As compared to the fresh PACs, K_f of sPAC-GW accounted for 60.3% of its fresh counterpart fPAC-GW, while it was 13.8% for sPAC-SW as to fPAC-SW. This reduction in adsorption capacity can be related to the heavier NOM preloading in surface water spent activated carbon, as was explained in Section 4.3.1.

In order to examine the impact of carbon surface area on atrazine adsorption and differentiate it from the impact of surface chemistry, the BET surface area-normalized isotherms are illustrated. Figure 4.2(b) shows that the surface area normalization was able to suppress the adsorption differences among the PACs, with $K_{f\text{-}SA}$ of sPAC-GW and sPAC-SW constituting 73.4% and 22.9% of their respective fresh counterparts. However, the BET surface area normalization still did not cause an impact on the order of the $K_{f\text{-}SA}$, which followed the same trend as that on a mass basis. This observation indicates that in addition to the reduced surface area, the accompanying surface chemistry change also played a role in the decreased atrazine adsorption, confirmed by the negative linear correlation (R^2=0.88) between the K_f values and the surface acidic group amounts on the four PACs (Figure 4.3). This correlation agrees with several previous findings, suggesting that an increase in acidic functional groups could attract water adsorption on the carbon surface, thereby reducing the number of available adsorption sites for the target adsorbate (Tennant and Mazyck, 2007; Apul et al., 2013b).

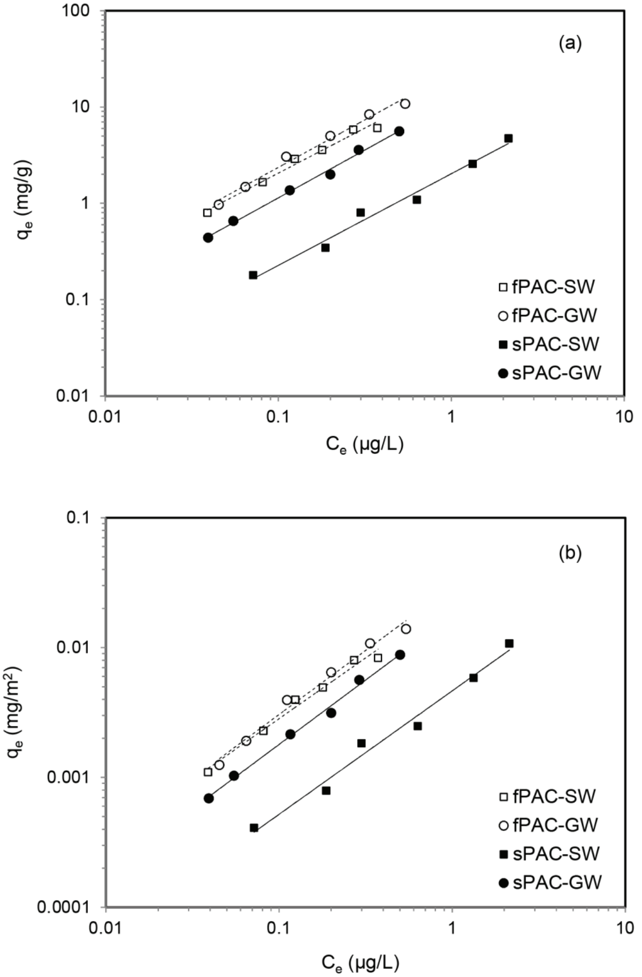

Figure 4.2. *Atrazine adsorption isotherms of the PACs in demineralized water, plotted on the mass basis (a) and plotted on the BET surface area basis (b). Data fitted by the Freundlich model.*

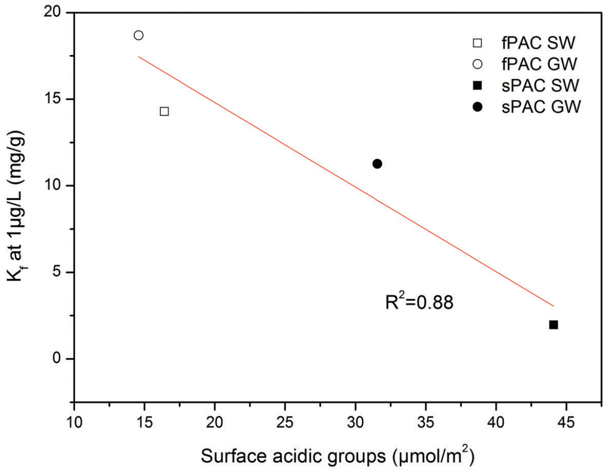

Figure 4.3. *Correlation between the Freundlich K_f values and the amount of surface acidic groups on the four PACs.*

Table 4.3. *The Freundlich best-fit parameters for atrazine adsorption in demineralized water on PACs.*

Samples	Freundlich parameters			R^2
	K_f [a]	$K_{f\text{-}SA}$ [b]	n	
fPAC-SW	14.29 (12.07-16.52)	0.020 (0.017-0.023)	0.80 (0.69-0.90)	0.946
sPAC-SW	1.97 (1.85-2.09)	0.005 (0.004-0.005)	1.12 (1.21-1.85)	0.989
fPAC-GW	18.68 (17.19-20.17)	0.024 (0.022-0.026)	0.83 (0.76-0.90)	0.979
sPAC-GW	11.26 (10.50-12.02)	0.018 (0.017-0.019)	0.99 (0.93-1.05)	0.990

[a]: K_f represents q_e (mg/g) at C_e of 1 μg/L. The values in brackets are 95% confidence interval.

[b]: BET surface area-normalized K_f values, which represents q_e (mg/m^2) at C_e of 1μg/L.

Adsorption kinetics

Atrazine adsorption kinetics on the studied PACs was described by the loading amount as a function of the contact time (Figure 4.4). The fitting parameters for a pseudo-second-order model are summarized in Table 4.4. The model was found to simulate the experimental data well, based on the correlation coefficients (R^2 >0.98). The calculated q_e ($q_{e,\ cal}$) values were consistent with the experimental data ($q_{e,\ exp}$) as well, with the relative standard deviations less than 15%, except for 25% in the case of sPAC-SW. Within the 4 hours contact time, the adsorption rate, k_p, of atrazine on fPAC-SW and fPAC-GW was 5.3 and 3.5 times that of sPAC-SW and sPAC-GW, respectively, reaffirming a more impeded adsorption pathway in the pores of surface water-spent activated carbon.

In view of the pore structure (especially in the mesopore range), the disparate pore size distribution (PSD) between the two fPACs and the similar PSD between fPAC-GW and sPAC-GW were expected to result in significantly different and comparable adsorption kinetics, respectively. However, the obtained data deviate from this expectation and imply that other factors rather than the pore structure were relevant in determining the adsorption kinetic process. It could be attributed to the preloaded NOM moieties on sPACs, which facilitated the formation of water clusters at the pore entrance (Karanfil and Kilduff, 1999; Karanfil et al., 1999); as such, atrazine molecules had to bypass or even displace the previously adsorbed NOM from the pore openings before they accessed the final (equilibrium) adsorption sites (Li et al., 2003b).

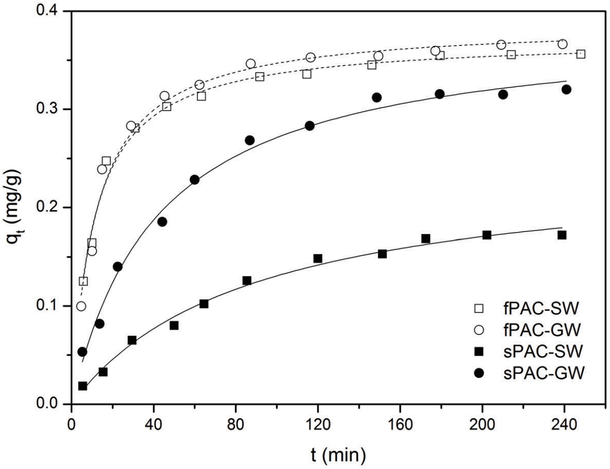

Figure 4.4. *Atrazine adsorption kinetics in demineralized water on PACs. Data fitted by pseudo-second-order kinetic model.*

Table 4.4. *The best-fit parameters of pseudo-second-order model for atrazine adsorption kinetics in demineralized water on PACs.*

Samples	$q_{e,\ exp}$ (mg/g)	Pseudo-second-order kinetic parameters			R^2
		$q_{e,\ cal}$ (mg/g)	RSD [a] (%)	k_p [b]	
fPAC-SW	0.356	0.373 (0.368-0.377)	3.25	0.247	0.988
fPAC-GW	0.366	0.388 (0.382-0.394)	4.13	0.217	0.984
sPAC-SW	0.172	0.245 (0.234-0.256)	24.79	0.047	0.990
sPAC-GW	0.32	0.387 (0.377-0.396)	13.33	0.061	0.991

[a]: The relative standard deviation between $q_{e,\ exp}$ and $q_{e,\ cal}$.

[b]: The pseudo-second-order adsorption rate constant, in the unit of $g \cdot mg^{-1} \cdot h^{-1}$.

4.3.3. Atrazine adsorption in wastewater secondary effluent by PACs

When applying PACs to remove micro-pollutants from the wastewater secondary effluent (e.g. in prior to the tertiary sand filter), the presence of effluent organic matter (EfOM) is a major consideration. Atrazine adsorption isotherms of all PACs in the background of EfOM are presented in Figure 4.5. The corresponding Freundlich isotherm parameters are provided in Table S4.1. As compared to demineralized water, atrazine adsorption capacity decreased considerably for either fPACs or sPAC in the presence of EfOM, which reveals the competition of EfOM molecules with atrazine for the available adsorption sites. For comparison, the percent reductions in the atrazine loading at equilibrium concentrations of 0.1, 0.5 and 1 µg/L (relative to that in demineralized water) were examined (Figure 4.6). The impact of EfOM competition was found to be more serious at equilibrium concentrations exceeding 0.5 µg/L, regardless of the PAC types, indicating that adsorption under relatively low carbon dosage was more sensitive to EfOM competition.

Among the four PACs, sPAC-SW exhibited the least reduction in atrazine loading (particularly at lower equilibrium concentration), with 68% loading reduction in contrast to more than 90% for other PACs at an atrazine concentration of 0.1 µg/L. The reduced competition on sPAC-SW can be explained by its acidic surface chemistry: the higher presence of NOM acidic functional groups would result in less EfOM accessibility due to electrostatic repulsion between the negatively charged EfOM moieties and the sPAC-SW surface (Apul et al., 2013a). Moreover, at the pH of the secondary effluent (i.e. pH=7.8), fPAC-SW (pH_{pzc}=9.7) and fPAC-GW (pH_{pzc}=9.1) carried a positive charge on their surfaces, which could attract EfOM and exacerbate the competition. However, the comparably higher reduction that occurred on the neutral sPAC-GW (pH_{pzc}=7.6) demonstrates the involvement of other competing effects, e.g. site competition and/or pore blockage based on the carbon pore structure characteristics. Previous findings identified the major competing pore region for atrazine as the secondary micropores (0.8-2 nm) (Pelekani and Snoeyink, 1999). It is most likely that the lowest pore volume of this size range on sPAC-GW caused the most severe EfOM-atrazine competition.

The Freundlich K_f of sPAC-SW and sPAC-GW accounted for 13.8% and 60.3% that of fPAC-SW and fPAC-GW in demineralized water (Figure 4.2), respectively; whereas these ratios changed to 27% and 40% in EfOM (Figure 4.6). The resistance of the heavily preloaded sPAC-SW (over sPAC-GW) to EfOM competition demonstrates its suitability for micro-pollutant (i.e. atrazine) removal in the organic matrix, especially in view of an economical concern that spent activated carbons can be reused. However, further investigation is required to confirm the lessened competition on sPAC-SW when a cocktail of micro-pollutants is present in the wastewater secondary effluent.

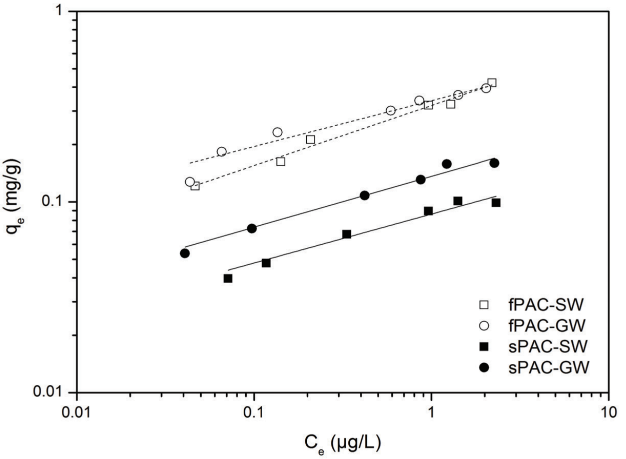

Figure 4.5. *Atrazine adsorption isotherms of the PACs in EfOM on a mass basis. Data fitted by the Freundlich model.*

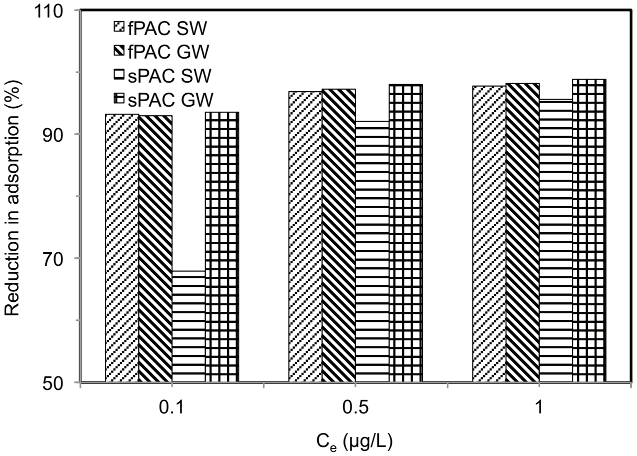

Figure 4.6. *Atrazine adsorption reduction by EfOM presence (in relation to that in demineralized water). The adsorption capacity was calculated based on equilibrium concentrations of 0.1, 0.5 and 1 µg/L, respectively.*

4.4. Conclusion

Two NOM-saturated GACs (after surface water and groundwater treatment, respectively) were evaluated in terms of their physicochemical properties and their reuse potential for atrazine adsorption, both in demineralized water and the wastewater secondary effluent. The pore size distribution results demonstrate a significant pore volume decrease over a wide size range for the surface water preloaded GAC; in particular, its primary micropore region (< 0.7 nm) almost vanished due to the occupation of low molecular weight organic fraction. The reduction in secondary micropores that occurred on both preloaded GACs could be attributed to the common humic substances and building blocks fractions in both surface water and groundwater. Because of a higher NOM loading on the surface water preloaded GAC, a more negatively charged, acidic and hydrophilic surface was obtained as compared to the groundwater preloaded GAC surface.

There were still appreciable adsorption capacity remained on the pulverized spent GACs, and this is particularly obvious for the groundwater-spent activated carbon. The acidic functional groups on a specific surface area basis correlates well with the atrazine adsorbability in demineralized water, with the higher acidic groups amounts (introduced by the preloaded NOM), the less the atrazine adsorbed at equilibrium. Similarly, in addition to the decreased pore surface area/volume, the induced acidity on the carbon surface contributed as well to the impeded adsorption kinetics of atrazine on the pulverized spent GACs. Nonetheless, the pulverized spent GACs, especially the surface water preloaded one, tended to alleviate atrazine adsorption competition in the treated wastewater, possibly due to an electrostatic repulsion of the receiving organic matter by its much more negatively charged surface. This observation demonstrates a possibility of reusing surface water preloaded GAC for micro-pollutant removal in the treated wastewater.

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Supporting information

Chapter 4

Reuse of spent granular activated carbon for organic micro-pollutant removal from treated wastewater

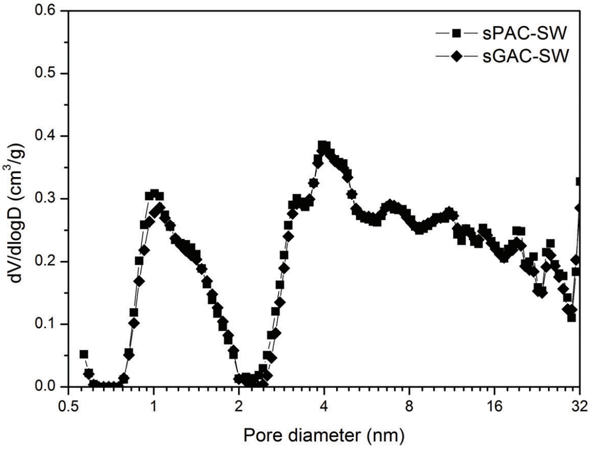

Figure S4.1. *Pore size distribution comparison of the pulverized spent GAC (sPAC) and the original spent GAC (sGAC) used for surface water treatment.*

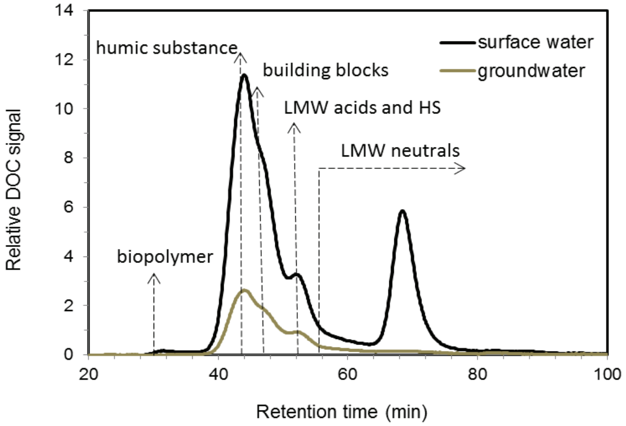

Figure S4.2. *Molecular weight distribution of organic matter in surface water and groundwater by LC-OCD chromatography.*

Table S4.1. *The Freundlich parameters for atrazine adsorption in wastewater secondary effluent on PACs.*

Samples	Freundlich parameters			Loading reduction (%)		
	K_f	n	R^2	at C_e = 0.1 μg/L	at C_e = 0.5 μg/L	at C_e = 1 μg/L
fPAC-SW	0.32 (0.31-0.33)	0.315 (0.292-0.338)	0.981	93.2	96.9	97.8
fPAC-GW	0.34 (0.33-0.35)	0.240 (0.218-0.262)	0.963	92.9	97.3	98.2
sPAC-SW	0.086 (0.084-0.089)	0.256 (0.225-0.288)	0.944	67.9	92.0	95.6
sPAC-GW	0.136 (0.132-0.140)	0.267 (0.237-0.296)	0.959	93.5	98.0	98.8

Chapter 5

Pharmaceutical adsorption from primary and secondary effluent of a wastewater treatment plant by powdered activated carbon

This study investigated powdered activated carbon (PAC) adsorption of thirteen pharmaceuticals from the primary and secondary effluent of a wastewater treatment plant. In addition to fresh PAC, PAC previously used for micro-pollutant elimination from the secondary effluent was also examined for its reuse potential into the primary effluent. Results showed a comparably negligible pharmaceutical uptake by fresh and used PAC in primary effluent, in contrast to a considerable uptake by both PACs in secondary effluent. This indicated a severer adsorption competition induced from the primary effluent organic matter, i.e. the considerably higher constituents of low molecular and hydrophobic components. Furthermore, the competition effect even resulted in a desorption of the negatively charged pharmaceuticals from the used PAC into the primary effluent. It was concluded that adding fresh PAC into the secondary effluent is preferred, while recycling the used PAC into the e.g. activated sludge tank might not be beneficial for an additional pharmaceutical adsorption.

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5.1. Introduction

Conventional wastewater treatment plants are typically not designed to remove the trace-level organic micro-pollutants. Consequently, most of these contaminants are present in wastewater secondary effluent and subsequently enter the receiving aquatic ecosystem if no proper tertiary treatment is implemented (Fent et al., 2006). There are several approaches that have been proposed to update the conventional wastewater treatment for an effective micro-pollutant removal: ozonation, powdered activated carbon (PAC) adsorption and 'dense membrane' filtration (Christian Abegglen, 2009). Among these possible technologies, PAC was highlighted based on its easy implementation, e.g. to integrate into the existing tertiary filter without significant constructional change (Ruhl et al., 2014a; Meinel et al., 2015). Moreover, PAC with its diverse and abundant pores can adsorb a broad spectrum of micro-pollutants with a high efficiency. It was reported that when PAC was combined with ultrafiltration as an advanced tertiary treatment, an average micro-pollutant removal of more than 80% (out of the 70 potentially problematic substances) can be achieved at a PAC dose between 10 to 20 mg/L (Margot et al., 2013).

Different PAC application schemes were attempted in wastewater treatment plants considering a maximum usage of the PAC adsorption capacity and a simultaneous separation of the PAC particles; for example, directly adding PAC into the activated sludge tank, dosing PAC in the secondary effluent before the tertiary filtration, or circulating the backwashed used PAC from the tertiary filter into the activated sludge tank (Boehler et al., 2012). In addition to being capable of disposing the used PAC, the recycling strategy was found to enhance the overall micro-pollutant removal efficiency by 10% to 50% as compared to the single PAC application in the secondary effluent (Boehler et al., 2012). Furthermore, due to the effect of biodegradation and biomass attachment in the activated sludge system (Siegrist and Joss, 2012), the concentration of micro-pollutants is generally higher in the primary effluent than in the secondary effluent. This concentration gradient is expected to yield a higher micro-pollutant loading on the PAC surface accordingly.

However, a crucial factor impacting micro-pollutant adsorption by PAC from a complex background water is the adsorption competition with the co-present organic matter (Zietzschmann et al., 2014b). Since the adsorption competition between micro-pollutants and the organic matter in primary effluent was rarely investigated, the extents to which this adsorption competition could affect the final micro-pollutant uptake is thus largely unknown. Moreover, previous studies demonstrated that the relevant competing organic matter only constitutes a small portion of the bulk organic matter (Matsui et al., 2012). Therefore, identifying the major competing components in the primary effluent is necessary for a better evaluation of the micro-pollutant adsorption efficiency, both on fresh PAC and the recycled used PAC.

In this study, we examined the adsorption of a subset of pharmaceutically active compounds (PhACs) from wastewater primary effluent by the PAC previously used for tertiary treatment. This used PAC was received from the backwash water of a tertiary filter pre-immobilized with fresh PAC for micro-pollutant elimination in the secondary effluent. Also, this study elucidated the adsorption competition between micro-pollutants (i.e. PhACs) and the organic matter originated from primary effluent and secondary effluent. The objectives were to: (1) determine the characteristics of the used PAC (in relation to the fresh PAC), and its potential for reuse in terms of e.g. the available pore surface area; (2) understand the difference between primary effluent and secondary effluent, with respect to the molecular weight distribution of their organic matters which can be linked to PAC adsorption; (3) evaluate the selected PhAC adsorption efficiency on the used and fresh PAC, with primary effluent as the background matrix.

5.2. Methods and materials

5.2.1. The adsorbents

Fresh PAC (Norit SAE SUPER) was obtained from Norit. B.V. (Amersfoort, The Netherlands). Due to its abundant mesopore and micropore volume, this PAC is expected to be able to adsorb both low and high molecular weight pollutants. According to the supplier, the PAC has a grain size d50 of 15 μm, a specific surface area of 1150 m^2/g and a density of 425 kg/m^3. The used PAC was obtained from the backwash water of a rapid dual media filter initially immobilized with ~20 mg/L fresh PAC. The flow diagram of the used PAC recycling system is illustrated in Figure 5.1. Prior to use, the fresh PAC was constantly soaked in demineralized water to discard bubbles inside the PAC pores. The PAC concentrations were defined by measuring the dry PAC mass out of 2 mL of the respective solutions in triplicate.

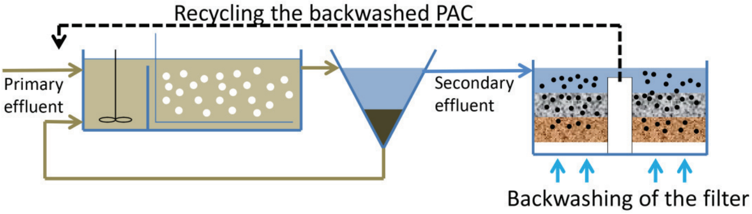


Figure 5.1. *The flow diagram of recycling the backwashed PAC from tertiary filter into the prior activated sludge tank.*

5.2.2. The OMPs and water matrices

A mixture of PhACs with diverse physicochemical properties was chosen for this study. A stock solution of 1.5 g/L PhACs was prepared by adding the pure chemical powders (Sigma Aldrich, The Netherlands) into certain amount of methanol (analytical grade, Sigma Aldrich, The Netherlands). Afterwards, this stock solution was spiked into the primary effluent and secondary effluent to have an additional concentration of 5 μg/L per compound (i.e. on top of the background PhAC concentration). The characteristics of the selected PhACs are presented in the supplemental information Table S5.1.

The primary effluent and secondary effluent water were collected from a domestic wastewater treatment plant in Rotterdam (HHSK, Rotterdam city, The Netherlands). This plant adopts a traditional activated sludge treatment technique: screening, primary clarifier, activated sludge tank, and secondary clarifier. The primary effluent and secondary effluent were then sampled after the primary clarifier and the secondary clarifier, respectively. Upon the water samples' arrival in the lab, 1.2 μm glass fibre membrane discs (Whatman, The Netherlands) were used to separate the solids, and the supernatants were stored in the refrigerator at a temperature of 4 °C, which were then used within 24 hours to avoid biological degradation.

5.2.3. The adsorption tests

PhAC adsorption experiments were conducted for both used PAC and fresh PAC, in primary effluent and secondary effluent, respectively. It has to be pointed out that PhAC adsorption in secondary effluent by the used PAC was conducted to determine the remaining adsorption capacity of the used PAC, which served then as a reference for the used PAC uptake of PhACs in the primary effluent. Specifically, 20 mg/L fresh and used PAC was dosed into 250 mL Erlenmeyer flasks, each containing 200 mL primary effluent or secondary effluent with spiked PhACs. Thereafter, samples were withdrawn after the contact time of 0.5 hour and 48 hours, respectively. It has been suggested that 0.5 hour is a typical contact time encountered in a single stage adsorption reactor, while 48 hours can represent adsorption equilibrium and the maximum capacity (Altmann et al., 2014b). The 0.45 μm glass fibre membrane discs (Whatman, The Netherlands) were used to extract the samples for analysis of the PhAC concentrations.

5.2.4. The analytical methods

The PhAC concentrations were quantified by an ultra-high performance liquid chromatography with tandem mass spectrometry (ultra-HPLC/MS-MS) in Het Waterlaboratorium (Haarlem, The Netherlands), with the aid of a validated multicomponent analysis method (Houtman et al., 2013). Due to the sensitivity of this method (e.g. minimum reporting limit of most compounds was 5 ng/l or lower), samples in this study were diluted five times with ultrapure water before injection into the instrument. Moreover, the matching labelled internal standards were added into each diluted sample to check the recovery during measurement. Additionally, dissolved organic matter (DOC) was determined by a TOC analyser (TOC-VCPH, Shimadzu, Japan), UV_{254} was measured with UV-vis spectrophotometer (Thermo Scientific, Germany). Other wastewater-related parameters, e.g. chemical oxygen demand (COD), NH_4^+-N, NO_2^--N, NO_3^--N, total nitrogen (TN) and total phosphate (TP) were measured with the corresponding Merck kits (Merck, Germany), and pH was detected using a pH meter (Mettler Toledo, USA).

Molecular weight distribution of the organic matter in the primary and secondary effluent were analysed by a liquid size-exclusion chromatography with organic carbon detection (LC-OCD) in the institution of Wetsus (Leeuwarden, The Netherlands). According to LC-OCD, the total DOC was divided into hydrophobic organic carbon (HOC) and hydrophilic organic carbon, i.e. the chromatographic organic carbon (CDOC), which can be further fractionated into biopolymers, humic substances, low molecular weight neutrals (LMW neutrals) and low molecular weight acids (LMW acids). Each fraction has its specific molecular weight and charge characteristics (Huber et al., 2011c; Hu et al., 2014a).

Morphology and elemental composition of the fresh and used PAC were executed using a scanning electron microscopy coupled with an energy dispersive X-ray (SEM-EDX) instrument (Ametek, $EDAX^{TSL}$). Prior to the analysis, PAC samples were introduced under a fume hood for three days. The samples were then scanned in various resolutions for SEM, and at 10 KV accelerating voltage, in 1000× magnification for EDX. The scanning area for EDX detection was approximately 0.3 mm × 0.3 mm, and at least three random areas were selected for this scanning.

Methylene blue and iodine numbers were determined as indicators of specific pore surface area of the PAC samples. As compared to the pore size distribution analysis based on nitrogen gas adsorption/desorption isotherms, wet PAC samples were allowed in this method, which were deemed more accurate, since any dryness technique would destruct the loaded organic matter on the used PAC, and thereby alter the pore structure. The iodine number was measured referring to the Norit Standard Test Methods (ASTM D4607-94), while the methylene blue number was determined following a previously established protocol (Bestani et al., 2008).

5.3. Results and discussion

5.3.1. *The characteristics of used PAC and fresh PAC*

Surface morphology and elemental composition

The surface morphology of used and fresh PAC is given in three different resolutions in the supporting information Figure S5.1. It shows that a large number of ‘brightly white lumps’ was present on the used PAC surface as compared to the fresh PAC, which is likely formed by the developed biomass (Ghosh and Philip, 2005), and the deposited fine suspended solids during the previous filtration of secondary effluent. EDX results reveal that there was no significant difference between used PAC and fresh PAC in terms of the elemental compositions (Figure S5.2). Except for C, the proportion of organic elements (O, S) increased slightly while the inorganic elements (Al and Si) decreased on the used PAC. This reflects the introduction of oxygen complexes on the PAC surface as a result of adsorption (Dong et al., 2014), and deposition of the organic substances as revealed in Figure S5.1.

Porosity

Iodine number was expressed as the amount of iodine adsorbed per gram of PAC at the equilibrium concentration of 0.02 N, based on the approximation that 1 mg of adsorbed iodine molecules corresponds to 1 m^2 of the true micropore (pore diameter ≤ 0.6-0.7 nm) surface area (Bestani et al., 2008), given the small size of the iodine molecule (diameter = 0.532 nm). Whereas the methylene blue number can represent the level of development of sub-micropores with pore diameter between 0.6 to 1.6 nm (Dong et al., 2014), assuming a complete monolayer coverage of the sub-micropores by the methylene blue molecules (diameter= 1.1-1.2 nm) (Bestani et al., 2008). The calculated true micropore and sub-micropore surface area are presented in Figure 5.2. Comparing the fresh and the used PAC, it can be observed that the sub-micropore surface area of the used PAC decreased to a higher extent than the true micropore surface area. This is in consistent with a previous finding that the most loaded pore size range in a full-scale granular activated carbon filter was between 0.7 to 2 nm (Gibert et al., 2013). It can be ascribed to the pore occupancy by organic matter in the secondary effluent, mostly the prevalent humic substances with intermediate molecular size, which tended to fit into the sub-micropores (Gibert et al., 2013). Nevertheless, the residual true micropore surface area of the used PAC indicates its adsorption potential for the small molecular weight substances, e.g. the PhACs.

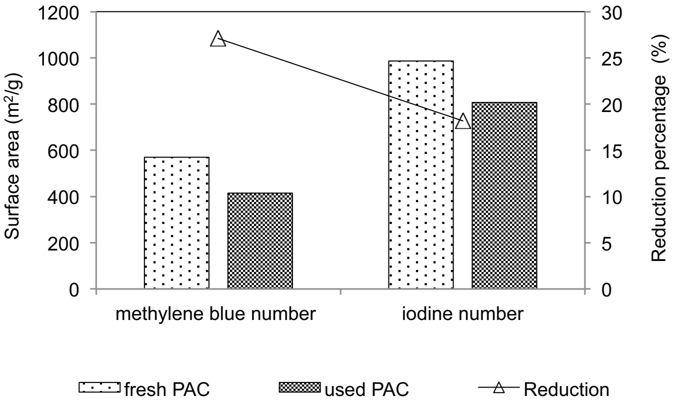


Figure 5.2. *Methylene blue number and iodine number of the fresh PAC and the used PAC.*

5.3.2. The characteristics of primary effluent and secondary effluent

Water quality parameters and the background PhAC concentrations

The basic water quality parameters of primary effluent and secondary effluent are summarised in Table 5.1. It shows that the UV_{254}-represented organic matter was moderately reduced while the bulk organic matter indicators DOC and COD were well reduced. The nutrients (TN and TP) were removed at percentages up to 90%. NH_4^+-N had approximately 100% removal, and was mostly transformed to NO_3^--N. The results demonstrate a complete nitrification/denitrification process in the existing biological treatment.

Table 5.1 also provides an overview of the background concentrations of target PhACs in the primary and secondary effluent. Theophylline, ibuprofen and paracetamol were only detected in the primary effluent rather than in the secondary effluent. Still, these compounds exhibited higher occurrence concentrations than the others in primary effluent; especially, paracetamol had a remarkably high level of 64 µg/L, and this value appeared to be in good agreement with several previous studies (Margot et al., 2013; Sun et al., 2014). PhAC removals during the existing biological process varied between 100% to negligible (i.e. the negative removals) depending on the specific compound. Theophylline, ibuprofen, paracetamol and naproxen turned out to be highly biodegradable, whereas hydrochlorthiazide, carbamazepine and lincomycin showed a recalcitrant characteristic as an even higher concentration was monitored in the secondary effluent than in the primary effluent. This could be attributed to a possible release from the faeces particles during treatment or to analytical uncertainties. According to literature, a high nitrification level was usually associated with a high micro-pollutant removal percentage, due to the high activity of the nitrifying bacteria which are capable of degrading many micro-pollutants (Margot et al., 2013; Tran et al., 2013). In the present study, the detected PhAC concentrations in the secondary effluent can meet the environmental quality criteria proposed in Switzerland (C. Götz, 2010). However, there were still six out of the thirteen compounds that had concentrations above 100 ng/L, which confirmed the demand for an advanced treatment since these PhACs might arouse a potentially detrimental impact on the aquatic organisms and the human body during a chronic exposure.

Table 5.1. *The water quality parameters and the background PhAC concentrations of primary effluent and secondary effluent.*

Parameters	Concentration in primary effluent	Concentration in secondary effluent	Average removal (%)
DOC (mg/L)	32.02	10.78	66.3
UV_{254} (cm^{-1})	0.495	0.274	44.6
COD (mg/L)	154	35	77.3
NH_4^+-N (mg/L)	49.3	1.4	97.2
NO_2^--N (mg/L)	<1.0	<1.0	-
NO_3^--N (mg/L)	0.25 (<0.5)	4.6	-
TN (mg/L)	61	7.1	88.4
TP (mg/L)	20.65	0.68	96.7
pH	7.16	7.21	-
Theophylline (ng/L)	3405±132	ND	~100
Naproxen (ng/L)	2314±43	210±2	90.9
Sulfamethoxazole (ng/L)	313±12	156±9	50.2
Ketoprofen (ng/L)	ND	ND	-
Ibuprofen (ng/L)	5065±329	ND	~100
Clofibric acid (ng/L)	ND	ND	-
Gemfibrozil (ng/L)	613± 30	322±9	47.5
Diclofenac (ng/L)	ND	ND	-
Hydrochlorthiazide (ng/L)	1745±111	1755±163	-0.6
Paracetamol (ng/L)	63905±807	ND	~100
Carbamazepine (ng/L)	339±10	387±20	-14.2
Metoprolol (ng/L)	568±11	451±13	20.6
Lincomycin (ng/L)	14±0.5	15±0.2	-7.1

ND: not detected.

Molecular weight distribution of the organic matter

Molecular weight distributions of the organic matter in primary and secondary effluent are illustrated in Figure 5.3. It shows a predominant CDOC constituent (i.e. the hydrophilic organic matter) in both waters; in which, the intermediate molecules 'humic substances' and the 'low molecular weight neutrals' were two major fractions. Overall, the hydrophobic fraction 'HOC' was completely eliminated during the biological process. Among the four CDOC fractions, 'humic substances' was reduced to the least extent (30%), which was in accordance to the moderate UV_{254} removal (Section 5.3.2). Whereas the low molecules 'LMW neutrals and LMW acids' and the macromolecules 'biopolymers' were considerably reduced, up to 65% and 80%, respectively. It is hypothesized that the high concentration of small molecules in the primary effluent could contribute to a high potential of adsorption competition with the target PhACs, based on several previous findings (Zoschke et al., 2011; Hu et al., 2014a; Zietzschmann et al., 2014b). Furthermore, the HOC component, exclusively present in the primary effluent, might also be responsible for adsorption competition (De Ridder et al., 2011; Hu et al., 2014a), given its higher affinity towards the carbon hydrophobic surface, via, e.g. hydrophobic interactions.

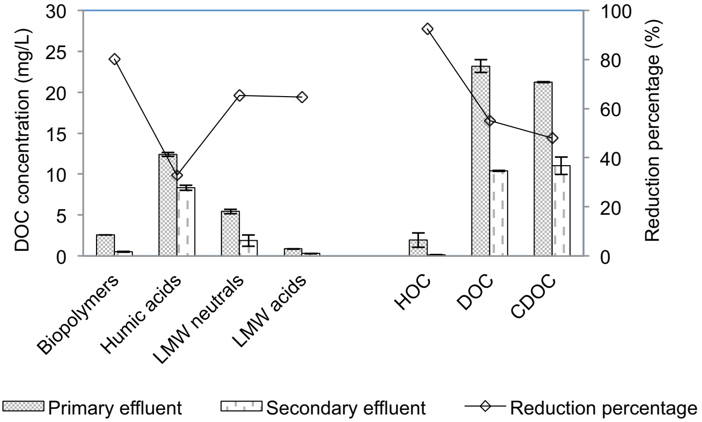
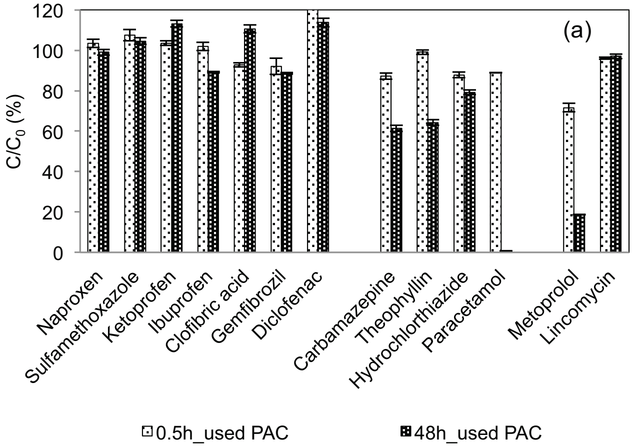
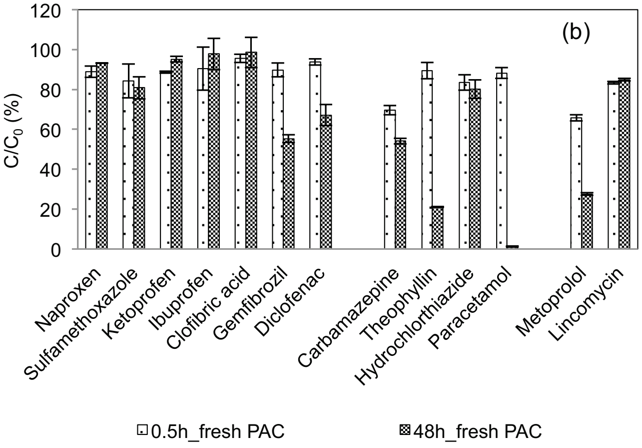


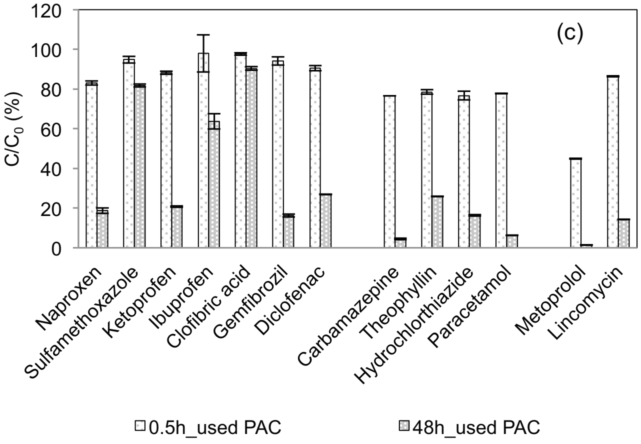
Figure 5.3. *LC-OCD analysis of the molecular weight distribution of organic matter in primary and secondary effluents and the reduction percentage of each organic fraction during the existing biological treatment.*

5.3.3. PhAC adsorption in primary and secondary effluents

The relative PhAC concentrations, after the selected periods of contact time (0.5 hour and 48 hours), from the primary effluent with 20 mg/L used PAC and 20 mg/L fresh PAC are presented in Figure 5.4(a) and 5.4(b), respectively. As references, the corresponding PhAC removal from the secondary effluent by 20 mg/L used PAC and 20 mg/L fresh PAC are presented in Figure 5.4(c) and 5.4(d). In these Figures, PhACs were classified into three groups according to their dissociated species at the investigated pH of around 7.0: the negatively charged group, the neutral group and the positively charged group (from left to right).







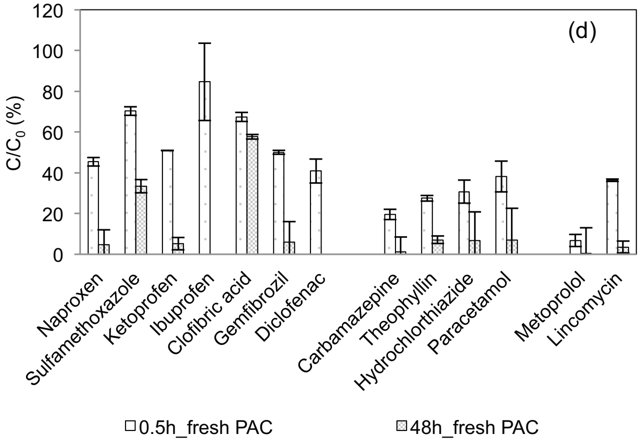


Figure 5.4. *PhAC adsorption in different water matrices by 20 mg/L used PAC (and 20 mg/L fresh PAC): PhAC adsorption at 0.5 hour and 48 hours in primary effluent by 20 mg/L used PAC (a); PhAC adsorption at 0.5 hour and 48 hours in primary effluent by 20 mg/L fresh PAC (b); PhAC adsorption at 0.5 hour and 48 hours in secondary effluent by 20 mg/L used PAC (c) and PhAC adsorption at 0.5 hour and 48 hours in secondary effluent by 20 mg/L fresh PAC (d).*

PhAC adsorption in primary effluent by fresh and used PAC

It can be observed that the PhAC adsorption was negligible in the primary effluent after 0.5 hour: low removals of less than 20% occurred to a majority of the compounds by either fresh PAC or used PAC, with only one exception (i.e. metoprolol) which had approximately 30% removal by both PACs. After 48 hours, six (gemfibrozil, diclofenac, carbamazepine, theophylline, metoprolol and paracetamol) out of the thirteen compounds showed discernible removal improvements as compared to the 0.5 hour contact time with fresh PAC, and there were four compounds (carbamazepine, theophylline, metoprolol and paracetamol) that also had the removal improvement in the case of used PAC. Surprisingly, the negatively charged PhACs (e.g. ketoprofen, clofibric acid) underwent even lower removal as the contact time progressed from 0.5 to 48 hours; and diclofenac, in particular, exhibited a constantly negative removal over the entire adsorption period on the used PAC (Figure 5.4(a)).

The observed unfavourable removal towards negatively charged PhACs indicates a possible replacement of the previously adsorbed negatively charged PhACs on used PAC by the strongly adsorbable components in primary effluent. It could be attributed to the electrostatic repulsion between the negatively charged PhACs and the PAC surface which was concurrently adsorbing, or already loaded with the negatively charged organic matter. On the contrary, apart from the large molecular weight compound (i.e. lincomycin) which was susceptible to size exclusion effect (Moreno-Castilla et al., 2003), the positively charged compound metoprolol had substantial removal improvement with an increase in the contact time from 0.5 to 48 hours. This conforms to some previous findings, in that the electrostatic interaction is prevalent in the wastewater-impacted adsorption process (Mailler et al.; Löwenberg et al., 2014).

Comparing the PhAC adsorption in primary effluent by fresh and used PAC, a statistically significant difference (p-value = 0.01 < 0.05) was found for the adsorption period of 0.5 hour, whereas a statistically insignificant difference (p-value = 0.3 > 0.05) existed for the adsorption period of 48 hours. The results implied a somewhat pore blocking effect on the used PAC, which hindered adsorption kinetics and resulted in less PhAC uptake in the initial adsorption stage. However, the similarity in PhAC removals after 48 hours reflected a similar maximum PhAC adsorption capacity in primary effluent between fresh PAC and used PAC. The comparable true micropore surface area which was more accessible for the PhAC molecules might be a probable explanation for this observation (Section 5.3.1).

PhAC adsorption in secondary effluent by fresh and used PAC

As a reference, Figure 5.4(c) reveals an appreciable remaining capacity of the used PAC for PhAC adsorption in the secondary effluent. Notably, only three compounds (sulfamethoxazole, ibuprofen and clofobric acid) displayed removals of less than 40%, while the rest of the compounds were eliminated approximately at 80% after 48 hours' contact with the used PAC. This is probably due to the additional spiking of PhACs (i.e. 5 µg/L per PhAC) in the batch test which promoted the adsorption. Furthermore, as no pore blocking effect was expected on the fresh PAC, most of the PhACs, especially the neutral and positively charged

PhACs, had already substantial removal percentages (> 60%) after 0.5 hour adsorption in the secondary effluent (Figure 5.4(d)). Moreover, as can be found in Figure 5.4(d), except for 'sulfamethoxazole' and 'clofibric acid', the rest of the compounds exhibited up to 90% removal in the secondary effluent after 48 hours' contact with the fresh PAC.

Comparison of PhAC adsorption in primary effluent and secondary effluent

Comparing Figure 5.4(c) and Figure 5.4(a), a noticeably better PhAC removal can be observed in the secondary effluent than in the primary effluent by used PAC, regardless of the adsorption time (p-value = 0.02 < 0.05 for 0.5 hour and p-value = 0.001 < 0.05 for 48 hours, respectively). This revealed a stronger adsorption competition between PhACs and the primary effluent-associated organic matter, which also appears to be the cause for e.g. the negatively charged PhAC desorption from the used PAC in primary effluent (Figure 5.4(a)). Moreover, this adsorption competition is in agreement with the surmise in Section 5.3.2, and confirms that the hydrophobic organic matter 'HOC' and the low molecular weight organics can be the major competition contributors. On the other hand, it is found that a reduction of these components in the background water can benefit the adsorption of most PhACs, whereas to a lesser degree for the poorly adsorbable compounds, such as sulfamethoxazole (Zietzschmann et al., 2014b) and clofibric acid.

In general, the results suggested that adsorptive removal of PhACs in the primary effluent was not preferred as compared to the secondary effluent, regardless of the fresh PAC and the used PAC. Therefore, adding fresh PAC in the secondary effluent for an advanced treatment instead of in the primary effluent (i.e. followed by the activated sludge tank) would be more beneficial for micro-pollutant removal when a single-stage PAC application is concerned.

5.4. Conclusion

This study evaluated PhAC removal efficiency by PAC adsorption from wastewater primary effluent and secondary effluent. Due to a serious competition induced by the small molecular organics and hydrophobic organics that were largely present in the primary effluent, adding fresh PAC in the primary effluent for PhAC adsorption seems not to be economically feasible. Additionally, the competitive effects even resulted in a desorption of the negatively charged PhACs from the PAC previously used for PhAC removal in the secondary effluent. Thus, recycling the secondary effluent-used PAC into the activated sludge tank might not offer an additional PhAC adsorption.

5.5. References

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Supporting information

Chapter 5

Pharmaceutical adsorption from primary and secondary effluent of a wastewater treatment plant by powdered activated carbon

Table S5.1. *Physicochemical properties of the studied PhACs (molecular weight and charge were obtained from Chemspider (http://www.chemspider.com); pK$_a$ values were obtained from Drugbank (http://www.drugbank.ca) and log Kow were obtained from ACD/I-Lab web software (https://ilab.acdlabs.com/iLab2).*

Compound	Molecular weight (g/mol)	pK$_a$	Log K$_{ow}$	Charge
Naproxen	230.3	4.19	3.00	-1
Sulfamethoxazole	253.3	5.7	0.89	-1
Ketoprofen	254.3	4.29	2.81	-1
Ibuprofen	206.3	4.91	3.72	-1
Clofibric acid	214.6	3.4	2.72	-1
Gemfibrozil	250.3	4.43	4.39	-1
Diclofenac	296.1	4.2	4.06	-1
Carbamazepine	236.3	1; 13.9	2.67	0
Theophyllin	180.2	7.8	-0.17	0
Hydrochlorthiazide	297.7	7.9	-0.07	0
Paracetamol	151.2	9.38	0.34	0
Metoprolol	267.4	9.68	1.79	+1
Lincomycin	406.5	7.6	0.91	+1

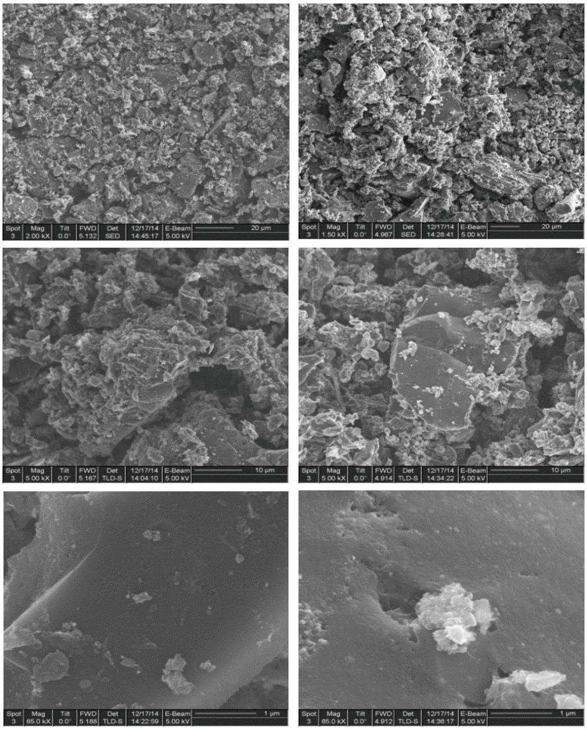

Figure S5.1. *SEM of the fresh PAC (the left side) and the used PAC(the right side).*

Figure S5.2. *Elemental composition of the fresh PAC and the used PAC.*

Chapter 6

Integrating powdered activated carbon into a tertiary filter for micro-pollutant removal from the secondary effluent

Integrating powdered activated carbon (PAC) into wastewater tertiary treatment is a promising technology to reduce organic micro-pollutant (OMP) discharge into receiving waters. To make a use of the existing tertiary filter, PAC was immobilized inside the filter bed acting as a fixed-bed adsorber. The pre-embedding of PAC was realized by direct dosing of a PAC solution on the filter top, which was then promoted to penetrate the filter media by a down-flow of tap water. In order to examine the effectiveness of this PAC pre-embedded filter towards OMP removal, batch adsorption tests, representing PAC contact reactor (with the same PAC mass-to-treated water volume ratio as in the PAC pre-embedded filter) were performed as reference. Moreover, as an alternative dosing option, PAC was dosed continuously with the filter influent (i.e. the studied wastewater secondary effluent with the investigated OMPs). Comparative results confirmed a higher PAC utilization efficiency associated with the PAC pre-embedded filter, as compared to the batch system. While, over a filtration period of 10 hours (approximating a realistic filtration period for tertiary filters), the continuous dosing approach resulted in less OMP removal. Therefore, It was concluded that the pre-embedding approach can be preferentially considered when integrating PAC into the wastewater tertiary treatment for OMP elimination.

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6.1. Introduction

Organic micro-pollutants (OMPs) are emerging as a threat to the aquatic ecosystems and to human health as they can possibly threaten our drinking water quality (Boehler et al., 2012; Zietzschmann et al., 2014a). The effluent of conventional wastewater treatment plant (WWTP) is a major source of OMPs because many OMPs were found to pass the wastewater treatment process without sufficient removal (Reemtsma et al., 2006; Grover et al., 2011). It was reported that after an efficient biological treatment with complete nitrification, on average, only 50% removal of the OMPs (out of 70 potentially problematic solutes) was achieved (Margot et al., 2013). Besides, the use of OMPs, such as pharmaceutical active compounds (PhACs), will even rise in the near future due to the demographic aging (Zietzschmann et al., 2014a). Therefore, there is a need to implement additional treatment steps to eliminate OMP loads in the WWTP effluent, e.g. the secondary effluent.

Powdered activated carbon (PAC) has successfully been applied at full-scale WWTPs for reduction of OMPs and ecotoxicity in the receiving waters (Boehler et al., 2012; Margot et al., 2013). The addition of PAC is preferably located at the tertiary treatment step, because there is a lower competition of the effluent organic matter (EfOM) with the target OMPs for adsorption on the activated carbon. PAC is normally implemented in combination with other technologies for a better exploitation of the adsorption capacity and an easier separation of the waste PAC, e.g. in the flocculation-sedimentation process before the tertiary filter (Boehler et al., 2012), or in a pressurized or submerged ultrafiltration system (Löwenberg et al., 2014). Alternatively, initially immobilizing (pre-embedding) the PAC in an existing tertiary filter can be a cost-effective option, as no extra footprint and constructional change are required, and the original filter packing materials are expected to retain the PAC particles for subsequent OMP adsorption. This approach allows for utilizing PAC in a fixed bed adsorber mode; as compared to the granular activated carbon (GAC), PAC with particle size up to two orders of magnitudes smaller would be advantageous in such case, due to the correspondingly faster adsorption kinetics.

The OMP removal characteristics in a fixed bed adsorber, e.g. the GAC adsorber, is associated with the OMP adsorption capacity (i.e. as determined by the adsorption isotherm), the transport mechanism in the adsorbent particles and the filter operating conditions (Kim et al., 2010). OMP adsorption capacity depends on the availability of carbon micropores which can admit both OMP and the competing organic matter with comparable molecular size (Hu et al., 2014a). The simultaneously favourable adsorption and mass transfer of OMPs has been attributed to a combination of micropores and mesopores (Pelekani and Snoeyink, 2001; Redding and Cannon, 2014). Moreover, pre-adsorbed organic matter, e.g. the EfOM, can result in pore blockage which is dependent on the carbon particle size (Corwin and

Summers, 2010). PAC with smaller particle size is then expected to exhibit much less pore blockage impact if applied in a fixed-bed adsorber mode (Meinel et al., 2015),

To effectively attenuate OMPs from WWTP secondary effluent and to make a full use of the existing tertiary filter (i.e. the anthracite-sand dual media filter), PAC with a proper pore structure was selected and was pre-embedded inside the tertiary filter, which was propelled by a down-flow of tap water before the filtration of secondary effluent started. The effectiveness of the PAC pre-embedded filter towards OMP removal was evaluated in comparison with the related batch test and with the continuous PAC dosing approach (an alternative option of dosing PAC into the filter). Additionally, the PAC distribution profile inside the filter bed was characterized as a function of the pre-embedding down-flow velocity, and the influence of the different PAC distribution profiles on OMP breakthrough was investigated.

6.2. Materials and methods

6.2.1. Powdered activated carbon (PAC)

Commercially available PAC Norit SAE SUPER (Norit B.V., The Netherlands) was selected, as it is manufactured to have abundant micro- and mesopores, and is widely used for WWTP tertiary treatment (Boehler et al., 2012; Margot et al., 2013; Zietzschmann et al., 2014a). According to the supplier, the PAC has an average particle diameter of 15 μm, a specific surface area of 1150 m^2/g and a bulk density of 425 kg/m^3. Before each experiment, PAC was conditioned with demineralized water (a predetermined amount of PAC in 500 mL demineralized water), which was then shaken for full wetting at a speed of 130 rpm for more than 12 hours in an incubator (Innova 44, Eppendorf, USA).

6.2.2. Target OMPs and water quality

A subset of OMPs (purchased from Sigma Aldrich, the Netherlands) was chosen (Table 6.1), and the OMP stock solution was 1.5 g/L per OMP in methanol (analytical grade, Sigma Aldrich, the Netherlands). For each experiment, the spiked OMP stock solution was far below 0.1% (v/v) of the working solution to minimize the co-solvent effect.

The secondary effluent was collected from a conventional WWTP (HHSK, Rotterdam City, The Netherlands) on each experimental day at around 8:00 a.m. using a 1000 L polyethylene portable tank. After its arrival in the lab, OMP stock solution was spiked to reach a nominal concentration of 5 μg/L per OMP (on top of the background concentration in the collected secondary effluent) in the feed tank, which was then referred to as the feed water for the subsequent filter experiments. For the OMP spiking, a 10 L Duran glass bottle was used to transport the prepared OMP solution into the 1000 L feed tank. A submergible pump (Elite 200, AFEC Pump, Taiwan) was placed at the bottom of the tank to circulate the feed water, which was designed to avoid sedimentation of the particulate matter and maintain a homogeneous water quality. In addition, a peristaltic pump (D-4923 extertal, Lenze, Germany) was used to supply the feed water to the top of the filter continuously.

Table 6.1. *Physicochemical properties of OMPs.*

OMPs	MW [a] (g/mol)	Diameter [b] (Å)	Log D [c] (pH=7.2)	pK_a [c]	Charge [a]
Metoprolol	267.4	14.976	-0.17	9.5; 13.9	+1
Paracetamol	151.2	8.847	0.54	1.7; 10.2; 14.6	0
Hydrochlorothiazide	297.7	9.766	-0.17	8.9; 10.2	0
Carbamazepine	236.3	8.157	2.23	0.1;14.3	0
Sulfamethoxazole (SMX)	253.3	10.350	-0.48	1.8; 5.7	-1
Clofibric acid	214.6	10.032	-0.50	4.0	-1

[a]: Data were obtained from Chemspider (http://www.chemspider.com);

[b]: Diameter herein describes the longest distance between atoms in OMP molecular structure, and was calculated using Hyperchem release 7.5.

[c]: Data were estimated/obtained from ACD/I-Lab web software (https://ilab.acdlabs.com/iLab2).

6.2.3. Batch adsorption tests

The feed water for the filter runs was also used for the batch tests. For determining the adsorption isotherm (i.e. OMP removal as a function of PAC dose at adsorption equilibrium), a prepared PAC slurry (2.5 g/L) was pipetted into 7*250 mL Erlenmeyer glass bottles to achieve a varying dosage ranging from 2.5 to 50 mg/L. After 48 hours contact time at a stirring speed of 150 rpm under ambient temperature (20±2 °C), the supernatant waters were collected and filtered through 0.45 µm regenerated cellulose membrane discs (Sartorius, Germany) for OMP measurement. A batch adsorption kinetics experiment was carried out at PAC dosage of 10 and 20 mg/L over a period of 48 hours, respectively; supernatant waters were sampled at fixed time intervals for the OMP measurements, the experimental condition was kept the same as in the batch isotherm test. During each experiment, a blank without PAC addition ran simultaneously to assess any change in the OMP concentrations.

6.2.4. Filter design and operations

The pilot installation is a perspex column with an internal diameter of 67 mm (surface area of 35 cm^2) and a height of ~2 m. The filtration media inside the column consisted of anthracite (on the top) with grain size of 0.8-1.6 mm and sand with grain size of 0.8-1.25 mm. For each filtration cycle, new media was replaced into the column with the same weight and compacted to the same height with both an equal anthracite layer and an equal sand layer. The depth of a fully packed filter bed was 36 cm (896 g) for anthracite and 25.5 cm (1310.7 g) for sand. During filtration, the flow velocity was controlled by a flow meter at the down-stream of the filter bed, water level in the filter was kept constant at the top (i.e. the influent point). The schematic diagram of the setup is illustrated in Figure 6.1.

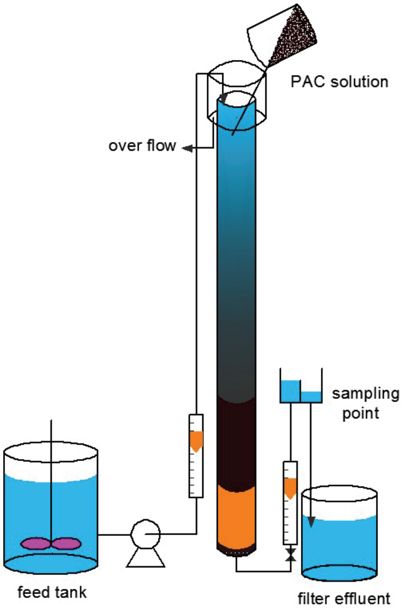

Figure 6.1. *Schematic diagram of the pilot-scale filter with PAC pre-embedding.*

OMP breakthrough was determined in the PAC pre-embedded filter, in which, the directly dosed PAC amount was calculated based on the PAC mass-to-treated water volume ratio (10 and 20 mg/L) as in the batch tests. Specifically, ~3.5 g (and ~7 g) PAC slurry in ~500 mL demineralized water was driven downwards the filter using tap water (Delft City, The Netherlands) at a velocity (pre-embedding velocity) of 10 m/h for ~15 minutes, then filtration of the feed water started in the PAC-immobilized filter at filtration velocity of 10 m/h for 10 hours. As another dosing approach, PAC was continuously added (together with the feed water) to the influent point using an extra peristaltic pump (520U, Watson-marlow, UK). The average PAC dose for this continuous dosing in one filtration cycle (10 hours) was ~20 mg/L with the total PAC mass (~7 g), equal to the pre-embedded experiment, and the filtration velocity was also kept at 10 m/h. The filter effluents in each experiment were periodically sampled and filtered by 0.45 μm regenerated cellulose membrane discs (Sartorius, Germany). Prior to analysis; the PAC particles, which were likely to leak from the filter, were captured on the 0.45 μm membrane disc for observation.

6.2.5. PAC distribution profile

To characterize the PAC distribution over the filter bed, a series of layer-by-layer PAC breakthrough experiments were designed: by increasing the media depth from the top 5.5 cm to 21 cm, 36 cm (anthracite layer) and further to 41.5 cm, 51.5 cm, 61.5 cm (sand layer). For each of the six experiments, PAC slurry (~3.5 g or ~7 g PAC in 500 mL demineralized water) was added initially on top of the filter, by controlling the outflow valve, and different pre-embedding velocities were performed (i.e. 5, 10 and 15 m/h, respectively), expecting to cause an impact on the PAC distribution profiles. The filter effluents were sampled at fixed time intervals, and the PAC concentration in the effluent sample was then determined via turbidity measurement, according to a pre-established calibration curve between turbidity and the PAC concentration (supporting information Figure S6.1). The filter bed was backwashed with tap water after each experiment, which lasted for around 10 minutes, to ensure the PAC particles to be completely flushed out.

To examine the influence of PAC distribution on OMP removal, filtration of the feed water was initiated following the immobilization of PAC inside the filter bed. To avoid redistribution of the PAC particles during the filtration process, filtration velocity was kept either equal to or lower than the pre-embedding velocity. The following combinations were applied for the pre-embedding and filtration velocities, respectively: 15 m/h+5 m/h, 10 m/h+5 m/h and 5 m/h+5 m/h. Sulfamethoxazole (SMX) was selected as an indicator compound for these sets of experiments. The SMX stock solution (1.5 g/L SMX in methanol) was spiked in the WWTP secondary effluent to obtain ~5 μg/L SMX in the feed tank (on top of the background SMX concentration). After one filtration cycle (approximate 8 hours under the filtration velocity of 5 m/h), the filter was replaced with new media, which was pre-soaked in the tap water overnight to remove fines and avoid bubble formation in the next filtration cycle.

6.2.6. Analytical methods

The quantification of SMX was based on an Enzyme-linked immunoassay measurement (Abraxis LLC, USA), the detection limit ranged from 0.025 to 1.0 µg/L, samples with SMX concentration exceeding 1.0 µg/L were diluted and re-measured for accuracy. Quantification of samples with a cocktail of OMPs was executed using UHPLC-HR-Orbitrap-MS (Benchtop Exactive Orbitrap mass-spectrometer, Thermo Fisher Scientific). Specifically, 100 mL OMP samples were spiked with 100 µL of a mixture of the matching labelled internal standards with determined concentrations, afterwards they were concentrated by a factor of 80 (from 100 to 1.25 mL) using the hydrophilic-lipophilic solid phase extraction Oasis HLB cartridges (6 cm^3, 200 mg sorbent, Waters, Ireland), and were then eluted by 2×4mL methanol before injection into the instrument. The analysis details are described in the supporting information of Vanoppen et al. (2015), and the UHPLC-HR-Orbitrap-MS output were interpreted by the Xcalibur 2.1.0.1140 software (Thermo Scientific, USA).

Dissolved organic carbon (DOC) concentration was determined by a TOC analyser (TOC-VCPH, Shimadzu, Japan) and UV_{254} was determined by an UV-vis spectrophotometer (Thermo Scientific, Germany). Turbidity was measured using a turbidimeter (2100N, Hach, USA) and the particle size distribution of the applied PAC was analysed by a particle counter (Model 3000, Pacific Scientific, the Netherlands).

6.3. Results and discussion

6.3.1. Water characteristics of WWTP secondary effluent

The studied WWTP secondary effluent contained an average DOC concentration of ~12 mg/L, and a SUVA value of 2.57 (Table 6.2), which means a non-hydrophobic nature of the studied EfOM (< 4 L/mg·m) (Karanfil et al., 2006). The background OMP concentrations in the secondary effluent ranged from less than 0.05 µg/L for clofibric acid to almost 2 µg/L for hydrochlorothiazide, and the concentration of SMX was slightly lower while that of carbamazepine was much lower than the reported values in the Berlin WWTP effluents, i.e. 0.2-0.6 µg/L and 1.2-2.5 µg/L, respectively (Altmann et al., 2014b). The variation in water quality during the experimental period was not significant as evident from the respective relative standard deviation listed in Table 6.2.

Table 6.2. *The water characteristics of the studied WWTP secondary effluent.*

Parameter	Unit	Average concentration	Relative standard deviation
DOC	mg/L	12.23	±4.2%
UV_{254}	cm^{-1}	0.315	±6.5%
SUVA	L/mg·m	2.57	-
Turbidity	NTU	1.91	±12.3 %
pH	-	7.2	-
Paracetamol	μg/L	ND (n=6)	ND
Hydrochlorothiazide	μg/L	1.80 (n=6)	±17.4%
Metoprolol	μg/L	0.45 (n=6)	±5.9%
SMX	μg/L	0.15 (n=6)	±26.5%
Carbamazepine	μg/L	0.37 (n=6)	±23.4%
Clofibric acid	μg/L	0.014 n=6)	±8.5%

ND: not detected;

n: the number of quantifications/campaigns.

6.3.2. OMP removals in batch test

OMP removal from the feed water (i.e. 5 μg/L spiked OMPs in the background of WWTP secondary effluent) as a function of PAC dose is shown in Figure 6.2. It can be seen that the maximum removal of OMPs enhanced at higher PAC doses. The required minimum PAC dose for e.g. 80% OMP removal differed considerably, from ~5 mg/L for metoprolol and carbamazepine to almost 35 mg/L for SMX and clofibric acid. At a PAC dose of 10 mg/L, metoprolol, carbamazepine and hydrochlorothiazole were removed at above 80%, while paracetamol, clofibric acid and SMX were adsorbed between 30 and 40%. With 20 mg/L PAC, all OMPs were removed up to 60%. The results agree well with a previous finding based on a pilot-scale PAC-ultrafiltration membrane bioreactor system with PAC dosage between 10 to 20 mg/L and a retention time between 2 to 17 days (Margot et al., 2013). 10 and 20 mg/L PAC were considered as appropriate doses for an overall OMP adsorption and served as references for the subsequent investigation of the PAC pre-embedded filter.

Figure 6.3(a) and 6.3(b) show the OMP removal kinetics in the batch system at PAC doses of 10 and 20 mg/L, respectively. It is observed that the time for OMP adsorption equilibrium was independent of the PAC dose and most of OMPs reached adsorption equilibrium after 12 hours (720 minutes). However, in practice, the hydraulic retention time of PAC in a single-stage adsorption system (e.g. the sequencing batch reactor) is in the magnitude of minutes (Zoschke et al., 2011; Ruhl et al., 2014a). which is much less than the observed 12 hours to ensure the PAC maximum adsorption capacity. Immobilizing PAC in the tertiary filter, in this sense, can guarantee longer PAC retention time.

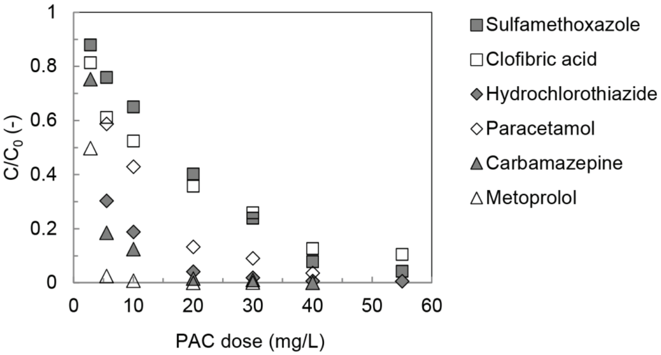

Figure 6.2. *The batch OMP removal (relative OMP concentration at equilibrium) as a function of PAC dose.*

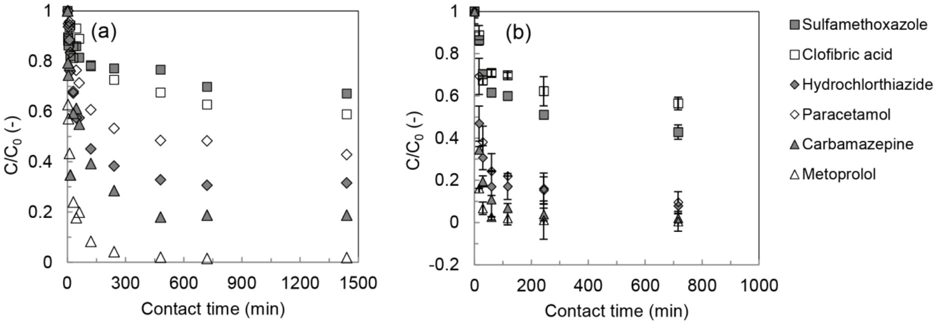

Figure 6.3. *The batch OMP removal (relative OMP concentration) as a function of the contact time at PAC doses of: 10 mg/L (a) and 20 mg/L (b).*

6.3.3. OMP breakthrough in PAC pre-embedded filter

OMP breakthrough under PAC amounts of ~3.5 and ~7 g in the pre-embedded filter (corresponding to 10 and 20 mg/L PAC in the batch kinetic tests, respectively) are depicted in Figure 6.4(a) and 6.4(b), respectively. To compare the OMP removal efficiency in the PAC pre-embedded filter and in the batch system, the cumulative OMP breakthrough (C/C_0) over the investigated 10 hours in the PAC pre-embedded filter was estimated by the best-fit regression of the OMP breakthrough data, e.g. polynomial or power regression type (Figure S6.2, SMX as an example). Next, this cumulative C/C_0 was interpreted in the batch kinetic curve (Figure 6.3) to obtain the contact time required for the same OMP removal target.

Table 6.3 lists the required contact time in the batch system for an equivalent OMP removal as in the PAC pre-embedded filter. It can be seen that the values varied considerably depending on the specific OMP. Except for metoprolol, which showed ~30 minutes, the other OMPs required much longer time exceeding 1 hour for the equivalent OMP removal, making it not applicable for e.g. the conventional sequencing batch reactor where PAC is usually used (Section 6.3.2). It has to be mentioned that, the cumulative OMP removal in the PAC pre-embedded filter was less than the respective equilibrium OMP removal in the batch system, reflecting a non-complete usage of the PAC capacity in the pre-embedded filter. This is most likely due to the short contact time between PAC and the OMPs, i.e. the residence time of feed water in the filter is ~2 minutes. However, unlike the batch system with decreasing OMP concentration along the adsorption process, the constant initial OMP concentration occurring in the PAC pre-embedded filter provided a 'multi-stage' adsorption condition (Zhao et al., 2012), which, still enabled a reasonable exploitation of the PAC adsorption capacity. Nonetheless, this positive effect appears to be less obvious with an increase in the PAC dose (Table 6.3).

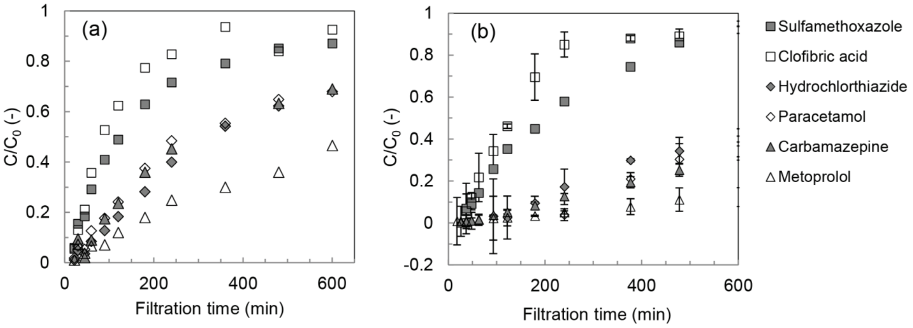

Figure 6.4. *The OMP breakthrough (relative OMP concentration) in the PAC pre-embedded filter as a function of filtration time under PAC amount of: ~3.5 g (a) and ~7 g (b).*

Table 6.3. *Comparing OMP removal efficiency between the PAC pre-embedded filter and the batch system.*

OMPs	Calculated cumulative breakthrough (C/C_0) within 10 h in PAC pre-embedded filter (%)		Required contact time for the same C/C_0 in batch kinetic test (minutes)	
	10 mg/L PAC	20 mg/L PAC	10 mg/L PAC	20 mg/L PAC
SMX	68	60	1140	120
Clofibric acid	77	72	120	60
Hydrochlorothiazide	42	20	180	75
Paracetamol	46	14	850	240
Carbamazepine	45	15	80	45
Metoprolol	25	6	30	30

6.3.4. OMP removal in the filter with continuous PAC dosing

OMP breakthrough under continuous PAC dosing is given in Figure 6.5. This adsorption process consists of a primary adsorption onto the freshly dosed PAC in the filter supernatant, and an additional adsorption onto the retained PAC in the filter bed (Altmann et al., 2014a; Altmann et al., 2015a). In this study, however, only 7 minutes contact time was available during PAC transport in the filter supernatant, explaining the low OMP removal (less than 25% except for metoprolol) in the initial filtration stage. Whereas, as the filtration progressed, a steady decrease in the relative OMP concentration was observed, which emphasizes the importance of the retained PAC for OMP removal. However, the observed OMP removal trend deviated from what was found by (Altmann et al., 2015a), where OMP removal stabilized after 4 hours of filtration. This was due to the higher PAC dose in the present study (20 *versus* ~7.2 mg/L), which resulted in more unexhausted PAC in the filter bed.

To compare the OMP removal between continuous PAC dosing and the pre-embedding, the cumulative OMP breakthrough (C/C_0) in Figure 6.5 was estimated over the same filtration time of 10 hours as in the PAC pre-embedded filter, the comparative results are shown in Table 6.4. It is clear that PAC pre-embedded filter exhibited less OMP breakthrough than the continuous dosing in the given period, regardless of the type of OMP. However, as the continuous dosing offered a better OMP removal in the later filtration period, while the pre-embedding offered a better OMP removal in the initial filtration period, an equal OMP removal could be possibly expected after a more prolonged filtration run, given the same total amount of PAC added. However, Table 6.4 reveals that, except for SMX and clofibric acid which are less hydrophobic (with lower log D values), the other four OMPs had cumulative breakthrough less than or close to 20% after 10 hours' running of the ~7 g PAC pre-embedded filter, indicating the effectiveness of the PAC pre-embedded filter for such OMPs.

From the experiments it was observed that PAC constantly leaked from the filter effluent under the continuous dosing; while this leakage was indiscernible in the effluent of the pre-embedded filter (Figure S6.3). This can be partly attributed to the much higher PAC input concentration under pre-embedding, which enabled PAC particles to occupy the attachment sites of the filter media more rapidly (Sun et al., 2015), and hindered the downward transport of the subsequent PAC, thus enhancing their retention inside the filter.

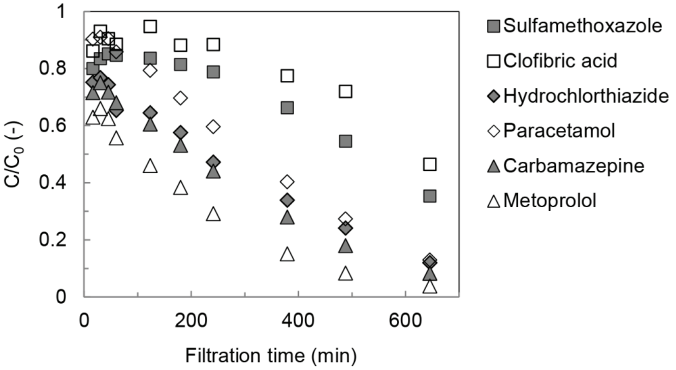

Figure 6.5. *The OMP breakthrough (relative OMP concentration) in PAC continuous dosing filter. PAC dose: 20mg/L; filtration period: ~10.75 h, filtration velocity: 10m/h.*

Table 6.4. *The comparison of OMP removal between PAC continuous dosing and pre-embedding over the filtration time of 10 hours at an equivalent PAC does of 20 mg/L.*

OMPs	Calculated cumulative breakthrough (C/C_0) under PAC continuous dosing (%)	Calculated cumulative breakthrough (C/C_0) under PAC pre-embedding (%)
SMX	70	60
Clofibric acid	81	72
Hydrochlorothiazide	44	20
Paracetamol	53	14
Carbamazepine	39	15
Metoprolol	27	6

6.3.5. PAC distribution and the influence on OMP breakthrough

In consideration of an easy implementation and an effective OMP removal (during ~10 hours' operation), the PAC pre-embedding approach was preferred in this study. From the particle size distribution analysis, it is shown that the employed PAC has a dominant size less than 5 μm (Figure S6.4). The PAC distribution, expressed by the cumulative mass percentage along the filter height, is illustrated in Figure 6.6(a) and 6.6(b), with the direct PAC dose amount of ~3.5 and ~7 g, respectively.

Apparently, the PAC particles were driven more downwards to the filter end with an increase in the pre-embedding velocity, and a more heterogeneous PAC distribution was created consequently. It was found in Figure 6.6(a) that, ~80 wt% PAC was retained in the first 5.5 cm anthracite layer under a flow of 5 m/h as compared to ~54 and ~36 wt% under 10 and 15 m/h, respectively; the latter two even drove PAC deeper down into the sand layer (~4 wt%). This phenomenon recurred in the filter when the PAC dose was doubled (Figure 6.6(b)). However, a less scattered PAC distribution was observed with an increase in the dosed PAC amount under the respective pre-embedding velocities. When ~7 g PAC was added, the mass percentage in the first 5.5 cm anthracite layer were ~90, ~ 65 and ~56 wt% under flows of 5, 10 and 15 m/h, respectively; all higher than the corresponding values in the ~3.5 g PAC added filter. This dose-dependent distribution appears to comply with the finding of Section 6.3.4, and confirms that a higher PAC input concentration was able to increase the potential for PAC retention on the filter top. Moreover, after passing through 10 L tap water, a negligible amount of PAC (< 1 wt%) was present in the effluent, indicating the immobilization of PAC in the filter bed.

Due to the poorly adsorbing character, SMX was selected as a first breakthrough indicator to test the influence of PAC distribution on OMP breakthrough. SMX breakthrough as a function of the specific throughput (the treated effluent volume divided by the dosed PAC mass) is shown in Figure 6.6(c) and 6.6(d), with the filter pre-embedding conditions corresponding to Figure 6.6(a) and 6.6(b), respectively. The results show that, a retarded SMX breakthrough was associated with a higher pre-embedding velocity, although SMX breakthrough overlapped somehow at pre-embedding velocities of 10 and 15 m/h under PAC dose of ~3.5 g, and of 5 and 10 m/h under PAC dose of ~7 g. For example, to achieve 80% SMX removal (i.e. 20% SMX breakthrough), the specific throughput increased by a factor of 2, from ~ 5 L/g at 5 m/h pre-embedding velocity to ~ 9 L/g at 15 m/h pre-embedding velocity (Figure 6.6(c)). The same increase occurred in the case of ~7 g PAC pre-embedded filter, from ~6 L/g at 5 m/h pre-embedding velocity to ~11 L/g at 15 m/h pre-embedding velocity (Figure 6.6(d)). The extension of OMP breakthrough by a higher pre-embedding velocity can be correlated to a more homogeneous distribution of the PAC particles, allowing for a better contact between PAC and the target compound, and thus better adsorption kinetics.

Given a complex EfOM background in the secondary effluent, the OMP removal was inevitably subject to an adsorption competition effect, which explained the 9 times less specific throughput for 20% breakthrough of SMX than the reported values in the study of Altmann et al. (2015a), where tap water was used as a background. However, a similar increase rate (i.e. two times) of the specific throughput for 20% breakthrough of SMX was found in this study and in Altmann et al.'s study, where an even more homogenous PAC distribution was established by an up-flow pre-embedding in the backwash direction. This implies that a homogeneous PAC distribution might be more beneficial for OMP removal with a complex organic matter background where adsorption competition is involved.

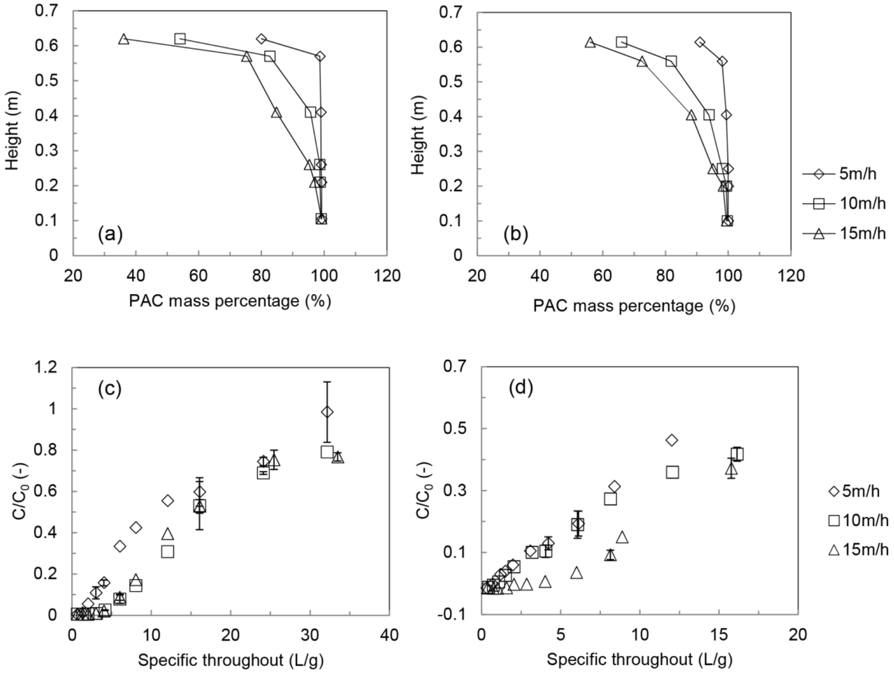

Figure 6.6. *The cumulative PAC mass percentage along the filter height under different pre-embedding velocities, with the PAC dose amount of ~3.5 g (a) and ~7 g (b). The corresponding relative concentration of SMX in the filter effluent under a fixed filtration velocity of 5 m/h, with the PAC dose amount of ~3.5 g (c) and ~7 g (d).*

6.4. Conclusion

In this study, PAC was integrated into a pilot tertiary dual media filter for OMP removal from the WWTP secondary effluent. As an economic approach, direct dosing of PAC on top of the filter to immobilize PAC inside the filter bed was proposed. OMP adsorption in batch tests were performed as references to evaluate the effectiveness of the PAC pre-embedded filter. Comparative results confirmed a higher OMP removal efficiency in the PAC pre-embedded filter than in the batch system employing an equal PAC mass-to-treated water volume ratio. As another dosing approach, continuous dosing PAC caused a constant leakage of the PAC particles from the filter bed. In addition, as compared to the PAC retained in the filter bed, the suspended PAC in the filter supernatant contributed marginally to the OMP adsorption, offering lower OMP removals in the case of PAC continuous dosing than PAC pre-embedding during the investigated filtration time of 10 hours. Furthermore, the distribution profile of the embedded PAC was identified as an important factor governing OMP removal efficiency. A more homogeneous PAC distribution created by a higher pre-embedding velocity was able to extend the OMP breakthrough. For example, by tripling the pre-embedding velocity from 5 to 15 m/h, the volume of the treated effluent with higher than 80% SMX removal can be increased by a factor of two.

6.5. References

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Supporting information
Chapter 6

Integrating powdered activated carbon into a tertiary filter for micro-pollutant removal from the secondary effluent

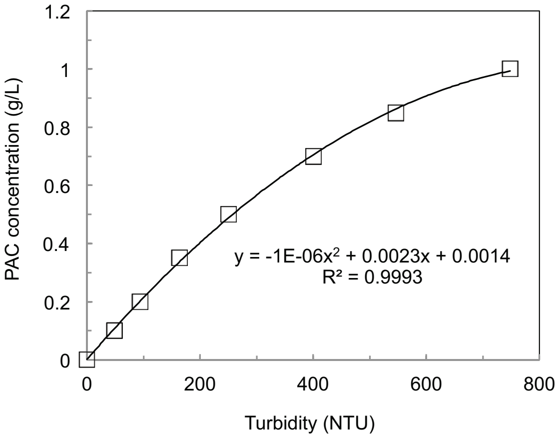

Figure S6.1. *The relationship between the measured turbidity and PAC concentration.*

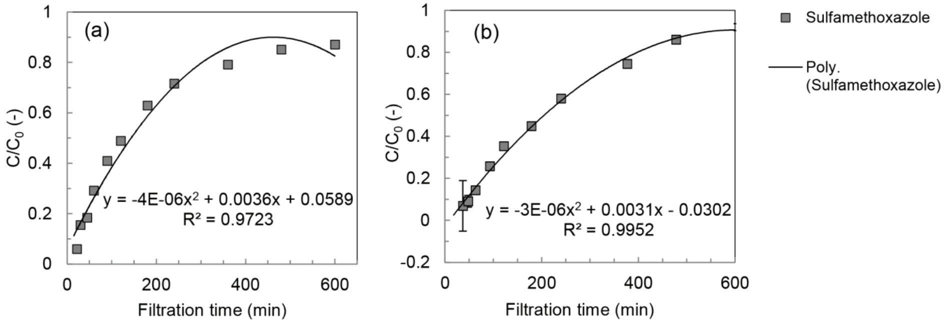

Figure S6.2. *The best-fit polynomial regression of SMX breakthrough over 10 hours' running of the PAC pre-embedded filter, under PAC amount of ~3.5 g (a) and ~7 g (b).*

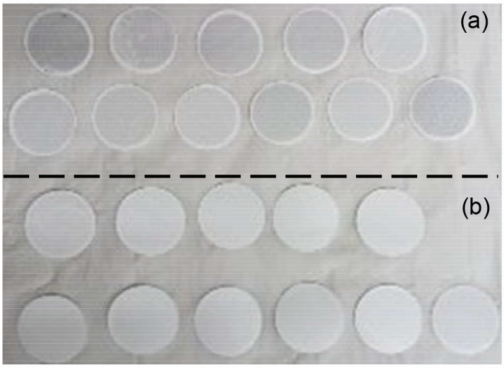

Figure S6.3. *PAC leaking from the filter during ~10 hours' filtration of the feed water: the periodical effluent samples in the PAC continuous dosing experiment (a), and the periodical effluent samples in PAC pre-embedding experiment (b).*

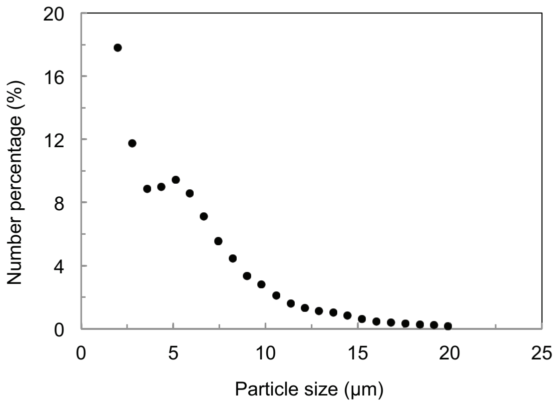

Figure S6.4. *Particle size distribution of the employed PAC.*

Chapter 7

Conclusions and recommendations

7.1. Conclusions

In this thesis, the mechanisms of adsorption competition between the trace-level (e.g. µg/L) micro-pollutants and background organic matter (BOM) on activated carbon were elucidated in chapters 2-4. The factors such as molecular compositions of the BOM, pore structure and surface chemistry of the employed activated carbons, charge and hydrophobicity of the investigated micro-pollutants were all taken into consideration for their possible impacts on the adsorption competition. Meanwhile, site competition and pore blocking as two major competition pathways were differentiated, the predominant pathway in the particular application system was identified, and was related to the aforementioned factors for a better control of the system to mitigate adsorption competition. Based on the results obtained, a proper activated carbon type was employed for the studies in the latter two chapters, which were more established from a practical point of view. The questions with respect to where and how to apply the activated carbon into the wastewater treatment processes have been further addressed, in order to provide the waterworks with strategies to advance the wastewater treatment for eliminating micro-pollutants in an economic and efficient way.

Overall, it was concluded that the small molecular weight BOM, although with a relatively lower concentration, is the most competitive fraction interfering with micro-pollutant adsorption on activated carbon. Techniques such as anionic exchange as pre-treatment turned out not to be promising for removal of this BOM fraction, while biodegradation e.g. for groundwater treatment, showed certain efficacy. Activated carbon with a higher volume of micropore was favoured for less occurrence of site competition, especially when employed in a batch system. The size of activated carbon is important dictating its utilization efficiency; for example, by grinding saturated granular activated carbon (GAC) from a drinking water treatment plant, the adsorption capacity can be restored for e.g. micro-pollutant adsorption from the wastewater treatment plant (WWTP) effluent. Together with the merits of easy implementation and fast adsorption kinetics, it is suggested to apply powdered activated carbon (PAC), rather than GAC, into the wastewater treatment for micro-pollutant removal. Due to a higher adsorption competition associated with the primary effluent, the secondary effluent is then preferred for PAC application. Furthermore, it was found that immobilizing PAC inside the tertiary filter bed can achieve a comparatively higher micro-pollutant removal, reflecting a simple while effective dosing approach.

The specific conclusions in responses to the research questions raised in chapter 1 are as follows:

7.1.1. What type of activated carbon is less subjected to adsorption competition?

In chapter 2, batch simultaneous adsorption experiments were conducted, where the site competition was demonstrated to be the main competition mechanism. Among three employed PACs, the one with the highest amount of primary and secondary micropores performed the best, due to a less occurrence of site competition, as the lowest amount of this PAC was required to reach the same micro-pollutant (i.e. atrazine and caffeine) removal in the given water matrix. In chapter 3, two GACs with different pore structures were preloaded with the wastewater effluent organic matter (EfOM) in a batch system, to investigate the preloading effect on the subsequent uptake of micro-pollutants (i.e. a subset of pharmaceutically active compounds, PhACs). The GAC having a wider pore size distribution of both micropores and mesopores was found to be subjected to a higher preloading effect. This was due to its easy accessibility for the EfOM, which occupied the PhAC adsorption sites to a higher extent.

7.1.2. Which fraction of the BOM contributes most to the adsorption competition?

In chapter 2, it was found that pre-treatment of the background waters using an strong-base anionic exchange resin (AER) did not improve micro-pollutant (i.e. atrazine and caffeine) adsorption by the studied powdered activated carbons (PACs). The liquid chromatography coupled with organic carbon detection (LC-OCD) analysis revealed that, it was the organic fraction of ‘low molecular weight neutrals’ that was most refractory to the AER treatment; which was then postulated to be the main contributor to site competition during the batch adsorption process. However, the AER pre-treatment removed larger organic molecules e.g. humic substances and building blocks, which were the possible pore-blocking contributors during a dynamic filtration test with GAC (i.e. the rapid small-scale column test). The removal of these components, therefore, served to increase the treated water volume before a certain breakthrough of the investigated micro-pollutants. In chapter 3, EfOM was separated by a nanofiltration membrane to differentiate its size into: a small-sized range (similar to the PhACs) in the NF permeate, and another with both the larger-sized range and the small-sized range in the NF feed water. Overlapping PhAC adsorption isotherms on the GACs preloaded by the two size fractions demonstrated that, the larger-sized organics were irrelevant to PhAC equilibrium adsorption, while the small-sized organics contributed mostly to site competition.

In chapter 4, the change of carbon characteristics were correlated with the molecular compositions of the influent organic matter after a full operational cycle of the GAC filters, which were used for surface water and groundwater treatment, respectively. The LC-OCD analysis of the influents revealed that surface water contained a broader molecular weight distribution than groundwater, which blocked both the micropores and mesopores of the

GAC. Compared to the groundwater, the surface water-preloaded carbon had a reduced capacity as well as a hindered kinetic for the subsequent micro-pollutant (atrazine) adsorption in a batch system.

7.1.3. How the physicochemical properties of the target micro-pollutants relate to the adsorption competition?

In chapter 3, PhAC adsorption capacity of the EfOM-preloaded GACs and the respective fresh GACs were compared, the reduced adsorption capacity was correlated to the physicochemical properties of PhACs. Results showed that, the adsorption of positively charged PhACs was less reduced than the negatively charged PhACs, which indicates the relevance of an electrostatic interaction. In addition, it was found that within each charge group, hydrophobic PhACs generally exhibited less adsorption reduction (i.e. less EfOM preloading impact), revealing an hydrophobic partitioning effect. Therefore, the negatively charged hydrophilic PhACs represent the most problematic compounds for activated carbon adsorption, additional techniques that can effectively remove these compounds is suggested to supplement the activated carbon process.

7.1.4. Can recycling the secondary effluent-used PAC into the activated sludge tank offer an additional micro-pollutant adsorption?

In chapter 5, primary effluent and secondary effluent of a WWTP were compared for their suitability of adding PAC to efficiently remove PhACs. The results showed a negligible PhAC uptake in the primary effluent in contrast to a significant PhAC uptake in the secondary effluent by fresh PAC. This was due to a serious site competition derived from the higher concentration of low molecular and hydrophobic organics in the primary effluent (as compared to the secondary effluent). Moreover, it was observed that recycling the PAC previously used for wastewater tertiary treatment to the primary effluent (e.g. into the activated sludge tank) could result in a desorption of the negatively charged PhACs from the used PAC phase.

7.1.5. What strategy of dosing PAC, directly or continuously, to the WWTP tertiary filter enables a later micro-pollutant breakthrough?

Based on the conclusions in chapter 5, in chapter 6, fresh PAC was integrated into the tertiary treatment step (i.e. a dual media filter), as less BOM would interfere with micro-pollutant adsorption. Apart from a continuous dosing strategy, in which the fresh PAC was dosed together with the filter influent (i.e. the secondary effluent), PAC was pre-embedded inside the filter bed for a better utilization. It was found that a large portion of the directly dosed PAC accumulated on the filter top; however, an increase in the pre-embedding velocity served to promote the PAC transporting deep down to the filter end, creating a more homogeneous PAC distribution. The subsequent micro-pollutant (e.g. sulfamethoxazole) breakthrough under varying PAC distributions demonstrated that, a homogeneous distribution can prolong the sulfamethoxazole breakthrough. For example, by tripling the pre-embedding velocity from 5 to 15 m/h, the treated effluent volume with 80% sulfamethoxazole removal was increased by a factor of two.

7.2. Recommendations

From the literature and the results in this study, it is concluded that activated carbon (e.g. PAC), with a large volume of micropores and mesopores is preferred for micro-pollutant adsorption. Mesopores are important as they can offer fast adsorption kinetics and compensate for the insufficient contact time usually encountered in practice. However, the presence of mesopores favours BOM adsorption with larger molecular sizes, thus probably blocking the adsorption pathways of the micro-pollutants. Therefore, reduction of the activated carbon particle size would help to create more surface area, which enables more adsorption sites for the BOM while not compromising the internal adsorption sites for micro-pollutants. Additionally, the shortened adsorption pathway by reducing the carbon particle size would facilitate micro-pollutant adsorption kinetics. Although studies relating the ‘superfine activated carbon’ have been carried out in the research group of Prof. Matsui. Y. (Ando et al., 2010; Matsui et al., 2012; Matsui et al., 2013), further investigations regarding the adsorption behaviour of a cocktail of representative PhACs in the treated wastewater would be necessary. Furthermore, PAC with smaller particle size is expected to penetrate deeper inside a tertiary filter bed if a pre-embedding dosing approach is implemented (chapter 6), accordingly, the homogenous PAC distribution can provide a better micro-pollutant removal. However, the PAC size needs to be optimized in order to prevent the PAC leakage from the filter effluent.

Regarding the BOM, the findings in this thesis together with the available literature demonstrate the importance of small-sized organic fraction for direct site competition with the micro-pollutants. A proper pre-treatment which can remove this organic fraction would thus be beneficial. The LC-OCD analysis in chapter 4 revealed a very small amount of the low molecular weight organics present in the groundwater, possibly due to the biodegradation effects during the soil passage process. Also, in chapter 5, it was observed that the low molecular weight organics were reduced to a higher extent than the other fractions after the biologically activated sludge system. It is then recommended that an advanced biological treatment should be investigated as a robust barrier before the application of activated carbon for efficient micro-pollutant removal from the treated wastewater.

Regarding the application of PAC in WWTP for micro-pollutant removal, it is recommended to dose PAC in the secondary effluent instead of the primary effluent, due to a less adsorption competition induced from the secondary effluent. Furthermore, it is recommended to immobilize the PAC inside the tertiary filer bed before the filtration of secondary effluent, so as to achieve a higher PAC utilization efficiency for micro-pollutant adsorption. In the pre-embedded tertiary filter, it was discovered that a more homogeneous PAC distribution formed by a higher pre-embedding velocity can lead to a prolonged micro-pollutant breakthrough. As such, the optimal pre-embedding velocity needs to be further determined to ensure that, the most homogenous PAC distribution can be established before the PAC particles are leaking through the filter. In addition, chapter 4 proposed a cheaper PAC source (i.e. sPAC, by grinding the drinking water-spent GAC), as a placement of the fresh PAC for application in the tertiary treatment. Thus, integrating sPAC into the tertiary filter would be an intriguing alternative. Further investigation is then encouraged to test the effectiveness of the sPAC pre-embedded tertiary filter for micro-pollutant removal from wastewater secondary effluent.

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Matsui, Y., Yoshida, T., Nakao, S., Knappe, D.R.U., Matsushita, T. 2012. Characteristics of competitive adsorption between 2-methylisoborneol and natural organic matter on superfine and conventionally sized powdered activated carbons. Water Research, 46(15), 4741-4749.

Summary

In the recent years, the removal of micro-pollutants from treated wastewater has been highly advocated throughout Europe and the rest of the world. The relevant regulations and the suitable techniques have been proposed accordingly, which promoted the innovation of the conventional wastewater treatment plants (WWTPs). Activated carbon adsorption and advanced oxidation are regarded as the most promising technologies to attenuate micro-pollutant concentration in the treated wastewater (i.e. the secondary effluent). In this thesis, activated carbon adsorption of micro-pollutants was systematically studied with respects to the adsorption competition mechanisms and the practical applications for advancing wastewater tertiary treatment. Different forms and types of activated carbons were adopted in the particular operational system, the associated adsorption competitions between target micro-pollutants and the background organic matter (BOM) were illustrated with the aid of various BOM separation methods. Moreover, for a better exploitation of the activated carbon adsorption capacity (i.e. when integrating into the existing WWTPs), the appropriate dosing location and the dosing approach have been identified, respectively.

In literature, there were two well-established pathways for BOM interfering with the target micro-pollutant adsorption on activated carbon: site competition and pore blocking. To differentiate these two pathways and examine which BOM fraction contributes most to the competition; batch adsorption tests and rapid small-scale column tests (RSSCTs) were performed, and an strong-base anionic exchange resin (AER) was used to separate the BOM. Results revealed that the AER was not effective to remove the site competition organics which interfered mostly with the micro-pollutants in the batch isotherm tests. These site competition organics appeared to be hydrophobic, and have a low molecular weight character. Moreover, the powered activated carbon (PAC) with the highest amount of primary and secondary micropores was subjected to the least site competition, and was thus selected for the subsequent RSSCTs, where, site competition and pore blocking occurred concurrently. In contrast to the batch adsorption tests, the retarded micro-pollutant breakthrough after AER pre-treatment indicated the relevance of AER removed organics for interfering with micro-pollutant adsorption in the dynamic filtration. This can be attributed to a less pore blocking effect due to the reduced amounts of ‘humic substances’ and ‘building blocks’ in the BOM.

During the operation of granular activated carbon (GAC) filter, the preloading of BOM is a normal phenomenon before GAC contacts with the target micro-pollutants, this leads to

an occupation of the adsorption sites and/or makes adsorption sites in small pores practically unavailable to the target micro-pollutants. To understand the preloading effects from wastewater effluent organic matter (EfOM) on the subsequent micro-pollutant (e.g. pharmaceutically active compounds, PhACs) adsorption. EfOM were differentiated by a nanofiltration (NF) membrane into fractions with size similar to or higher than that of the investigated PhACs. These two size fractions were pre-adsorbed onto two GACs with different pore structures. Comparison of the PhAC adsorption isotherms between the fresh GACs and the preloaded GACs reflected a significant reduction in the PhAC adsorption capacity after EfOM preloading, while the EfOM fraction which was rejected by the NF had a negligible impact. This observation emphasized the importance of the NF-permeating, low molecular organics for a direct site competition with the PhACs. Regarding the GAC pore structure, the one with a broad pore size distribution including both micropores and mesopores was able to adsorb an higher amount of EfOM, thus causing a higher PhAC adsorption reduction on the preloaded GAC. Furthermore, the PhAC adsorption reduction were correlated to their molecular physicochemical properties. PhACs with positive charge were found to have a less adsorption reduction than the neutral and negatively charged PhACs, due to the electrostatic attraction with the preloaded GAC surface. Additionally, hydrophobic PhACs within each charge group were generally more resistant to the preloading effects.

Concerning the change of the GAC characteristics by a continuous preloading of the influent organic matter, spent GACs treating surface water and groundwater over a full operational cycle were collected, respectively. Comparing to the groundwater-spent GAC, which had a loss of only the secondary micropores, the surface water-spent GAC exhibited pore volume reduction covering a wide size range, due to the higher organic carbon concentration and also a broad molecular weight distribution of the organic matter in surface water. Specially, the higher amount of low molecular weight organics in surface water resulted in a diminishing of the primary micropores. Micro-pollutant (atrazine) adsorption tests were conducted to evaluate the reuse potential of the two spent GACs (after pulverizing). It was found that in addition to the reduced adsorption sites, the heavily loaded organic matter on surface water-spent carbon decreased atrazine adsorption capacity and hindered the adsorption kinetics (in a demineralized water), likely due to the induced water adsorption and water cluster formation on the spent carbon surface. However, a less adsorption competition was observed for atrazine adsorption in an organic matrix (i.e. the wastewater secondary effluent) on the surface water-spent carbon, because of the repulsion of the like-charged organic matter. This implies the suitability of reusing the surface water-spent carbon into the treated wastewater for micro-pollutant removal.

When applying activated carbon e.g. PAC into the wastewater treatment processes for micro-pollutant adsorption, a better dosing location needed to be selected. The primary effluent and secondary effluent of a WWTP were considered in this respect. Primary effluent generally has a higher micro-pollutant concentration than the secondary effluent, and was thus supposed to facilitate the micro-pollutant adsorption onto PAC, while secondary effluent has less BOM concentration and was expected to cause less adsorption competition. Results showed a negligible PhAC uptake in the primary effluent in contrast to a significant PhAC uptake in the secondary effluent by fresh PAC, and this was mainly due to the site competition induced by the low molecular and hydrophobic organics, which were largely present in the primary effluent as compared to the secondary effluent. Moreover, these competing organics were able to replace the pre-adsorbed micro-pollutants (e.g. the negatively charged PhACs) from the PAC which was used for secondary effluent treatment. As such, recycling the PAC used for tertiary treatment into the e.g. activated sludge tank might not help to improve the overall micro-pollutant adsorption.

The (fresh) PAC was thus utilized for the secondary effluent treatment and was integrated into a dual media tertiary filter (instead of recirculating into the activated sludge tank). As a simple and economic approach, PAC was directly added and immobilized inside the tertiary filter bed. In comparison to the batch adsorption tests where PAC was suspended, the immobilized PAC inside the filter bed can offer a better micro-pollutant removal, due to a constant micro-pollutant concentration gradient under the dynamic filtration condition. Analogously, a constantly improved micro-pollutant removal was observed as the immobilized PAC amount increased in the filter during PAC continuous dosing. In addition to the approach how PAC was added, the profile how PAC was distributed inside the filter bed also played a role in the micro-pollutant breakthrough. By manipulating the filter effluent valve, different ‘pre-embedding’ velocities were achieved, which can propel the PAC to transport downwards to the filter end. A higher pre-embedding velocity served to create a more homogeneous PAC distribution inside the filter bed, consequently, prolonging the micro-pollutant (e.g. sulfamethoxazole) breakthrough.

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Curriculum Vitae

Jingyi Hu (胡婧逸) was born in Tianmen City, Hubei Province, China, on Aug 16th, 1986. She had her four years' bachelor study in Huazhong University of Science and Technology (HUST), majoring in Water Supply and Drainage Engineering. In 2008, she started her master in the college of Environmental Science & Engineering in Tongji University, where she got the chance to transform knowledge into practice.

From Aug, 2009 to Oct 2010, she worked in a drinking water treatment plant in Shangyu City, Zhejiang Province, mainly in charge of a membrane bioreactor system for production of drinking water. She managed to solve the technical problems during the system operation, and successfully defended her master thesis in Jan, 2011.

After the Spring festival of 2011, she set off for the Netherlands to have a reunion with her husband, and also to start her own PhD in the same research group at TU Delft. Under the supervision of Luuk and Bas, she was able to explore the beauty of activated carbon, and performed her experiments on micro-pollutant adsorption by various activated carbons (from the treated wastewater). She carried out her research in the framework of Agentschap NL- Innowater Program 'Integrated Filter Technology', and this thesis is the final product of her PhD work.