

# Super-fine powdered activated carbon (SPAC) for efficient removal of micropollutants from wastewater treatment plant effluent



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## ARTICLE INFO

### Article history:

Received 24 September 2015

Received in revised form

28 November 2015

Accepted 1 December 2015

Available online 10 December 2015

### Keywords:

Powdered activated carbon

Micropollutants

Effluent organic matter

Kinetics

Wastewater

Removal

## ABSTRACT

In an effort to mitigate the discharge of micropollutants to surface waters, adsorption of micropollutants onto powdered activated carbon (PAC) after conventional wastewater treatment has been identified as a promising technology for enhanced removal of pharmaceuticals and pesticides from wastewater. We investigated the effectiveness of super-fine powdered activated carbon, SPAC, (ca. 1  $\mu\text{m}$  mean particle diameter) in comparison to regular-sized PAC (17–37  $\mu\text{m}$  mean diameter) for the optimization of micropollutant removal from wastewater. Adsorption isotherms and batch kinetic experiments were performed for 10 representative micropollutants (bezafibrate, benzotriazole, carbamazepine, diclofenac, gabapentin, mecoprop, metoprolol, ofloxacin, sulfamethoxazole and trimethoprim) onto three commercial PACs and their super-fine variants in carbonate buffer and in wastewater effluent. SPAC showed substantially faster adsorption kinetics of all micropollutants than conventional PAC, regardless of the micropollutant adsorption affinity and the solution matrix. The total adsorptive capacities of SPAC were similar to those of PAC for two of the three tested carbon materials, in all tested waters. However, in effluent wastewater, the presence of effluent organic matter adversely affected micropollutant removal, resulting in lower removal efficiencies especially for micropollutants with low affinity for adsorbent particles in comparison to pure water. In comparison to PAC, SPAC application resulted in up to two-fold enhanced dissolved organic carbon (DOC) removal from effluent wastewater. The more efficient adsorption process using SPAC translates into a reduction of contact time and contact tank size as well as reduced carbon dosing for a targeted micropollutant removal. In the tested effluent wastewater (5 mg/L DOC), the necessary dose to achieve 80% average removal of indicator micropollutants (benzotriazole, diclofenac, carbamazepine, mecoprop and sulfamethoxazole) ranged between 13 and 15 mg/L. These promising results warrant pilot-scale tests using super-fine PAC as an alternative to PAC for more efficient micropollutant removal.

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## 1. Introduction

The incomplete removal of pharmaceuticals and pesticides during conventional wastewater treatment leads to a substantial

input of micropollutants into the aquatic environment. Though the consequences of low levels (ng– $\mu\text{g/L}$ ) of these synthetic substances on the receiving waters are still largely unknown, their adverse ecotoxicological effects are uncontested (Bunzel et al., 2013; Escher et al., 2008; Jobling et al., 1998). In an effort to mitigate the discharge of micropollutants to surface waters, numerous studies have been investigating the use of various advanced treatment processes for micropollutant removal. The issue has also triggered new regulations concerning the discharge and treatment of wastewater. For example, in Switzerland the newly revised water protection act will require large wastewater treatment plants (WWTPs) (>100'000 population equivalent) or WWTPs discharging to sensitive environments to remove 80% of the incoming micropollutant load from the wastewater stream (Eggen et al.,

*Abbreviations:* BZA, bezafibrate; BZT, benzotriazole; CBZ, carbamazepine; DCF, diclofenac; DOC, dissolved organic carbon; DOM, dissolved organic matter; EfOM, effluent organic matter; GAB, gabapentin; LC-OCD, liquid chromatography-organic carbon detection; MCP, mecoprop; MF, microfiltration; MIB, 2-methylisoborneol; MTP, metoprolol; MW, molecular weight; OFL, ofloxacin; PAC, powdered activated carbon; SMX, sulfamethoxazole; SPAC, super-fine powdered activated carbon; TMP, trimethoprim; UF, ultrafiltration; UPLC MS MS, ultra-performance liquid chromatography tandem mass spectrometry; WWTP, wastewater treatment plant.

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2014). As a result, many conventional treatment plants will be upgraded with additional treatment steps to comply with the revised legislation.

As such, the identification of technically and economically feasible advanced wastewater treatment options for the removal of micropollutants from effluent wastewater is gaining importance. Among others, advanced oxidation using ozone or adsorption of micropollutants onto powdered activated carbon (PAC), followed by a final polishing step (sand filtration or ultrafiltration), have shown great potential both in terms of micropollutant removal and regarding large-scale feasibility, treatment efficiency and costs (Acero et al., 2012; Altmann et al., 2014; Hollender et al., 2009; Joss et al., 2008; Margot et al., 2013). Large-scale trials have not only demonstrated excellent removal (>80%) of a broad range of micropollutants, but also contributed to reducing the effluent toxicity (Altmann et al., 2014; Boehler et al., 2012; Hollender et al., 2009; Margot et al., 2013). A greater pathogen reduction was observed with ozonation, but this treatment alternative has the drawback of not completely removing the target compounds from the wastewater stream and generating unknown and potentially toxic by-products (though these may be removed in the final polishing step, generally sand filtration) (Hollender et al., 2009; Zimmermann et al., 2011). On the other hand, activated carbon processes involve physical adsorption onto PAC resulting in the complete removal of all adsorbed contaminants retained by the filtration and the spent carbon must then be disposed of.

In side-by-side comparisons, the two treatment alternatives demonstrated similar removal capacities for broad range of micropollutants at bench and pilot-scale (Altmann et al., 2014; Kovalova et al., 2013b; Margot et al., 2013) and the choice of treatment will therefore be influenced by local considerations. PAC followed by ultrafiltration (PAC-UF) was suggested as the most suitable option for sensitive receiving waters, as it achieved a higher reduction of effluent toxicity due to the good removal of most micropollutants without the formation of problematic by-products (Margot et al., 2013). However, it was also moderately more expensive due to higher energy requirements of ultrafiltration and the relatively high carbon dosage (20 mg/L) necessary to achieve the required 80% micropollutant removal.

When aiming to reduce PAC-UF costs, optimizing the adsorption process is critical. Adsorption processes are influenced by a number of factors, namely the physical-chemical characteristics of the adsorbate, mainly its hydrophobicity, solubility, charge and molecular size; the adsorbent properties, such as the surface area and chemistry; and the solution's chemical properties and its constituents, such as dissolved organic matter (DOM), which also compete for adsorption sites (Delgado et al., 2012; Edzwald, 2010). Though the characteristics of the adsorbate and the solution are intrinsic, an adequate choice of PAC can improve adsorptive removal efficiency as well as the subsequent filtration. For example, the efficient adsorption of foulants can minimize pressure build-up during UF.

The widespread use of PAC for drinking and, more recently, wastewater treatment has triggered numerous studies aiming to understand the factors affecting the adsorption capacity, with the goal of ultimately enhancing adsorption efficiency. It is acknowledged that the equilibrium adsorption capacity is mainly influenced by the extent of oxygen-containing functional groups and by the pore size distribution of PAC (Li et al., 2002; Nowack et al., 2004; Quinlivan et al., 2005). Adsorption tends to occur primarily in pores with similar dimensions as the target compound. As a result, micropollutants favor adsorption in small micropores (<2 nm) on PAC with low oxygen content, whereas a large proportion of DOM adsorbs preferentially in larger pores (>2 nm) (Edzwald, 2010). Given the short contact times typically applied in practice, the adsorption kinetics will also greatly affect the ultimate adsorption

efficiency. Smaller particle diameters have been associated with enhanced uptake rates (Matsui et al., 2013a; Najm et al., 1990), however comparatively few studies have used variations in particle diameter to enhance adsorption kinetics. Recently, promising results were demonstrated with the use of extremely small, finely ground PAC with a particle size of <1  $\mu\text{m}$  (compared to 20–50  $\mu\text{m}$  for regular-sized PAC). Matsui et al. (2006) showed that this super-fine powdered activated carbon (SPAC) applied before microfiltration (MF) allowed important dosage savings (80–90%) compared to normal-sized PAC for similar removal of odor compounds from raw drinking water when contact times were short (Matsui et al., 2006). The grinding of normal-sized PAC to micrometer sized SPAC led to faster adsorption kinetics in various surface water matrices, but also to an enhanced removal of DOM or large molecular weight compounds (Ando et al., 2010; Matsui et al., 2006, Matsui et al., 2005). The greater adsorption capacity of SPAC for DOM was attributed to the larger specific outer surface area compared to PAC (Ando et al., 2010; Matsui et al., 2004). Additionally, SPAC applied before microfiltration did not clog or foul the membrane, but rather reduced membrane fouling as a result of better DOM removal (Matsui et al., 2009b).

If the benefits reported with SPAC for removal of odors and DOM from surface waters – reducing the necessary carbon doses, diminishing contact times and improving membrane permeability – are transferable to advanced wastewater treatment of micropollutants, this would considerably reduce the footprint, operational energy requirements and costs of PAC-UF. To our knowledge, however, the potential of SPAC for removal of micropollutants from wastewater has never been investigated. In this work, we therefore aimed to (1) compare the adsorption kinetics and capacities of three different PACs with their super-fine variant for selected micropollutants, (2) assess the removal of effluent organic matter (EfOM) by SPAC and assess its effect on the micropollutant adsorption capacity, and finally (3) evaluate the feasibility of SPAC-UF for advanced wastewater treatment of micropollutants.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Activated carbons (adsorbents)

Three commercially available PACs were tested: Norit SAE Super (Cabot Norit Activated Carbon, the Netherlands), Sorbopor MV-125 (EnviroLink SA, Switzerland) and Pulsorb FG4 (Chemviron Carbon, Belgium) and will be referred to as Norit, Sorbopor and Pulsorb in the following. Norit (mean particle diameter,  $d_{50} = 17 \mu\text{m}$ ) and Sorbopor ( $d_{50} = 37 \mu\text{m}$ ) were selected in a previous large-scale pilot study among other PACs for their good removal efficiencies (Margot et al., 2013). Pulsorb ( $d_{50} = 21 \mu\text{m}$ ) was chosen to test a relatively low-cost option. Adsorbents were dried at 350 °C for 3 h and subsequently diluted with milliQ to obtain 3 g/L slurries which were kept at 4 °C and sonicated before use. Super-fine PACs (SPACs) were prepared by wet milling to a final  $d_{50}$  of 1  $\mu\text{m}$ . SPACs were dried and stored as slurries like the normal-sized PAC. Characteristics of each commercially available adsorbent and the wet milling method are given in the supplementary information.

#### 2.1.2. Micropollutants (adsorbates)

Ten pharmaceuticals and pesticides were selected based on their physical-chemical properties (structure, charge and hydrophobicity), average WWTP removal and potential ecotoxicity, with the objective of representing the physical-chemical diversity of environmentally relevant micropollutants. The targeted compounds also span a range of removal efficiencies in PAC-UF (Margot et al., 2013). The selection includes the five indicator compounds

selected by the Swiss Federal Office of the Environment for monitoring of wastewater treatment efficiency (benzotriazole (BZT), carbamazepine (CBZ), diclofenac (DCF), mecoprop (MCP), sulfamethoxazole (SMX)), as well as bezafibrate (BZF), gabapentin (GAB), metoprolol (MTP), ofloxacin (OFL) and trimethoprim (TMP). Physical chemical properties and commercial suppliers are given in the supplementary information.

### 2.1.3. Water matrices

To eliminate the variability inherent to distinct water samples, a large volume (70 L) of effluent wastewater (after primary clarification and biological activated sludge treatment) was collected in February 2014 from the Vidy WWTP of the city of Lausanne over 24 h. The large composite sample was homogeneously mixed, stored at  $-20\text{ }^{\circ}\text{C}$  in 2 L polyethylene bottles and thawed at room temperature prior to experiments. The dissolved organic carbon (DOC) content of the water was  $5.1\text{ mg/L}$  as measured by catalytic combustion oxidation method (Shimadzu TOC-V), the pH (measured before each experiment) was  $7.8 \pm 0.2$  and the conductivity was  $685\text{ }\mu\text{S/cm}$ . Moreover, a Liquid Chromatography-Organic Carbon Detection (LC-OCD) analysis of the large composite sample was performed to characterize the organic matter (DOC-LABOR Dr. Huber, Germany).

To evaluate the influence of EfOM on the adsorption of micropollutants onto the PACs and SPACs, experiments were also performed in  $1\text{ mM}$  bicarbonate buffer made with Nanopure water (Millipore Synergy UV purification system) with a pH of 8.1, in effluent wastewater diluted 1:1 with milliQ (DOC =  $2.5\text{ mg/L}$ ) and with non-nitrified wastewater obtained after primary clarification (DOC =  $10\text{ mg/L}$ ).

### 2.2. Kinetic experiments

Kinetic tests were performed with all PACs/SPACs in 500 mL beakers containing 300 mL of carbonate buffer or wastewater spiked with a mixture of 10 micropollutants (in methanol) to a final concentration of  $50\text{ }\mu\text{g/L}$  per micropollutant (0.1% methanol content). After taking a first sample to determine the initial micropollutant concentration, the PAC slurry was added under continuous mixing to obtain a carbon dose of  $15\text{ mg/L}$ . The carbon dose of  $15\text{ mg/L}$  was chosen as a means of comparison to previous work that reported good removal for the same target compounds using doses between 10 and  $20\text{ mg/L}$  (Margot et al., 2013). The SPAC stored as slurries tended to aggregate over time, yielding larger particles ( $3\text{--}7\text{ }\mu\text{m}$ ). Therefore the SPAC slurries were dispersed by sonication before use to yield reproducible results. 12–14 samples (1 mL) were taken at different time points until the adsorption equilibrium was reached. Samples were filtered immediately through  $0.1\text{ }\mu\text{m}$  pore-size PTFE syringe filters (Infochroma AG, Switzerland) to remove the PAC and stored at  $4\text{ }^{\circ}\text{C}$  before analysis of the aqueous phase micropollutant concentration (see section 2.4). The solution pH was measured before and after each experiment and remained stable. Experiments using a  $15\text{ mg/L}$  carbon dose were conducted in duplicate for all adsorbents. In addition, the adsorption kinetics onto Norit PAC and Norit SPAC were evaluated for doses of 5 and  $10\text{ mg/L}$ . Adsorption kinetics were fitted using eqn. (1) (Qiu et al., 2009) and initial uptake rates were compared by means of ANCOVA analysis.

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303} t \quad (1)$$

where  $q_e$  and  $q_t$  (mg/g) are the adsorption capacities at equilibrium and at time  $t$  (min), respectively and  $k$  ( $\text{min}^{-1}$ ) is the pseudo-first-order rate constant of the adsorption process.

Previous work showed that low levels of methanol, added through the micropollutant spike did not influence adsorption of pharmaceuticals onto PAC. Moreover, preliminary experiments were conducted to confirm the absence of any concentration or competition effects among micropollutants at the concentrations and carbon doses chosen.

Similar kinetic experiments (without the micropollutant spike) were performed to assess the kinetics of DOC removal by each adsorbent. Samples taken at various time points were filtered and the residual DOC was quantified by catalytic combustion oxidation method on a Shimadzu TOC-V.

### 2.3. Batch equilibrium tests to determine adsorption isotherms

Adsorption isotherms were established in carbonate buffer and in wastewater. Batch adsorption experiments were performed in crimp head glass vials (Infochroma AG, Switzerland) containing increasing amounts of PAC and 50 mL of matrix water spiked with the micropollutant mixture to a final concentration of  $50\text{ }\mu\text{g/L}$  (0.1% methanol content). Vials were capped with butyl rubber/PTFE stoppers and aluminum crimp caps (Infochroma AG, Switzerland) and rotated ( $35\text{ rpm}$ ) on a carousel rotator Labroller II (Labnet International, Inc., USA) at  $20\text{ }^{\circ}\text{C}$ . After a contact time of 20–24 h, samples were filtered, stored at  $4\text{ }^{\circ}\text{C}$  and the aqueous phase micropollutant concentration was analyzed within 48 h (see section 2.4). Finally, solid-phase concentrations of each adsorbate were calculated by mass balance. Adsorbent-free controls showed that losses by mechanisms other than adsorption were negligible. All batch adsorption experiments were conducted in duplicate for 8 concentrations of powdered activated carbon, ranging from 1 to  $70\text{ mg/L}$ . Linearized isotherms were fitted in Matlab R2015a 8.5.0 (Mathworks).

### 2.4. Analytical method

Micropollutant concentrations in the filtered samples were quantified by ultra-performance liquid chromatography and tandem mass spectrometry (UPLC-MS/MS; Acquity Xevo, Waters). Samples were diluted 1:1 with UPLC eluent A (94% water, 2.5% MeOH, 2.5%  $\text{NH}_4$ -formate 200 mM, 1% formic acid) containing deuterated compounds of each target micropollutant as internal standards. Micropollutant concentrations were calculated based on calibration curves using at least 8 calibration points closest to the sample concentration. Correlation coefficients for the calibration curves were typically  $>0.990$ . The analytical method was adapted from previous work (Margot et al., 2013; Morasch et al., 2010) and details can be found in the supplementary information.

## 3. Results and discussion

### 3.1. Adsorption kinetics

The time to equilibrium was assessed through kinetic tests and showed that the adsorption kinetics of all micropollutants were significantly faster (significance level: 95%) with SPAC compared to PAC for all carbon types. SPAC adsorption equilibrium in wastewater was reached within 7–10 min for all compounds, regardless of their adsorption affinity, compared to over 8–12 h for normal-sized PACs (Fig. 1, Figs. S1–S5 and Table S4). These results are in line with previous work showing that smaller adsorbent particles have faster adsorption kinetics (Matsui et al., 2013a; Najm et al., 1990). The mean particle diameters of all SPACs used herein were between 0.9 and  $1\text{ }\mu\text{m}$ , and accordingly, for the majority of compounds no significant differences were observed in their uptake rates (ancova analysis of slopes, Table S5). The normal-sized PACs,

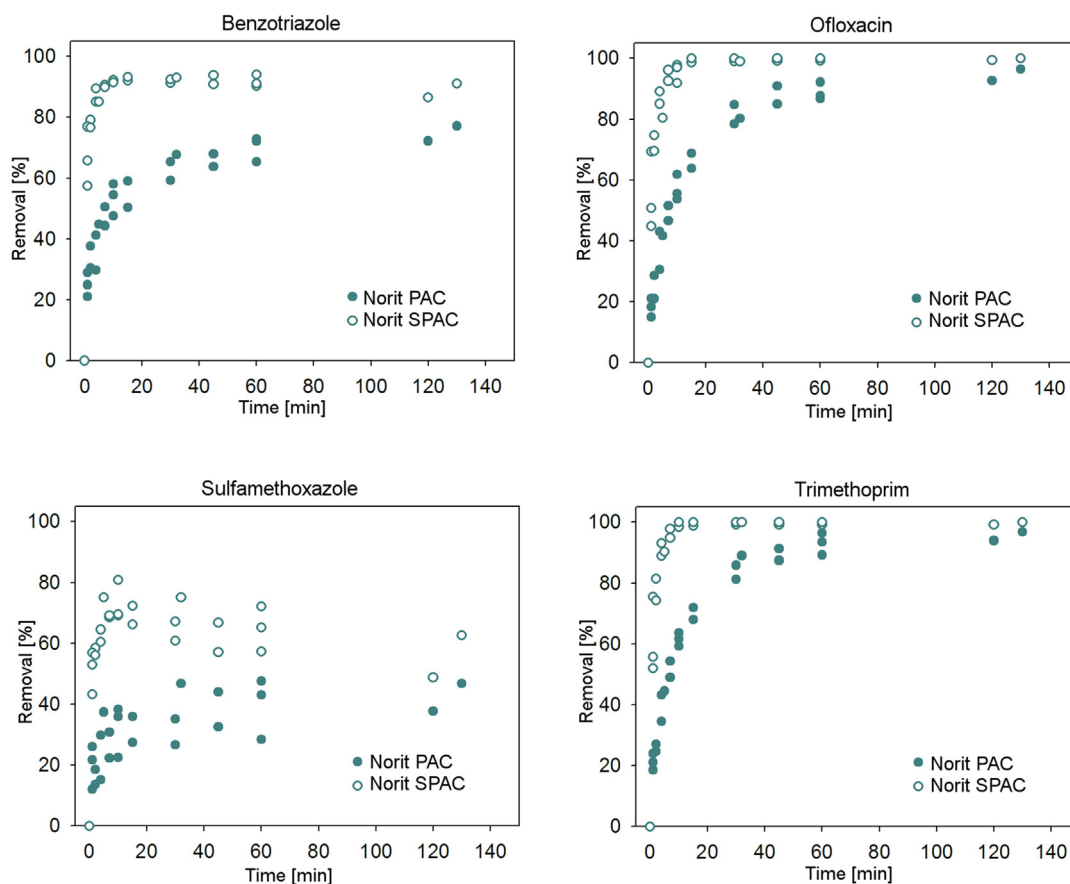


Fig. 1. Adsorption kinetics of selected target micropollutants onto Norit PAC and SPAC with carbon dose of 15 mg/L in effluent wastewater.

Norit PAC ( $d_{50} = 17 \mu\text{m}$ ) and Pulsorb PAC ( $d_{50} = 21 \mu\text{m}$ ), albeit slower than the SPACs, showed considerably faster adsorption of micropollutants compared to Sorbopor PAC ( $d_{50} = 37 \mu\text{m}$ ), which confirms the importance of particle diameter in the adsorption kinetics. In the quest of optimizing PAC-UF removal of methyl-isoborneol (MIB) and geosmin, Matsui et al. determined that for a given contact time the reduction of particle size effectively reduced the carbon dose, due to the faster adsorption onto SPAC. However, grinding of PAC below mean diameters of  $1 \mu\text{m}$  did not provide further benefits (Matsui et al., 2013a). As such, providing the SPAC particles do not aggregate, the current SPAC diameters should represent an optimal particle size for fastest kinetics and limited carbon dosing.

### 3.2. Adsorption isotherms

#### 3.2.1. Adsorption equilibrium in carbonate buffer

To assess the differences in adsorptive capacity of PAC and SPAC for the different target micropollutants Freundlich isotherms were compared for all PACs and target compounds in carbonate buffer. The Freundlich equation

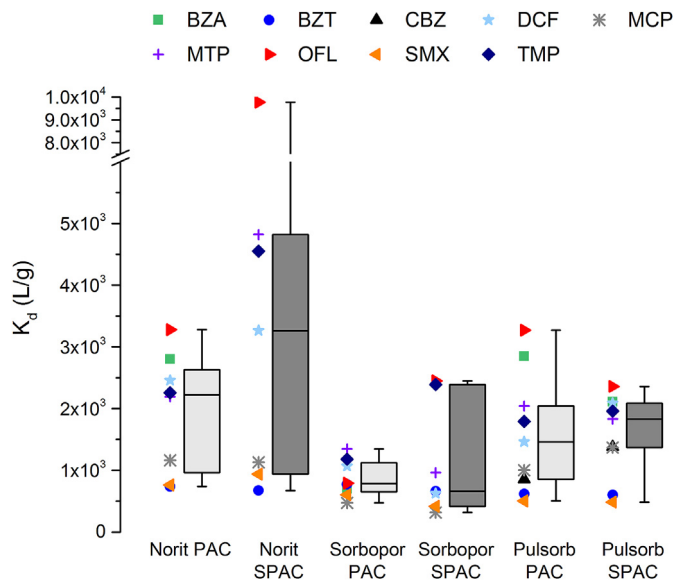
$$q = K_F C^{(1/n)} \quad (2)$$

relates the equilibrium surface concentration,  $q$  (mass adsorbate/mass adsorbent), to the equilibrium solution concentration,  $C$  as a function of the parameters  $K_F$  and  $1/n$  which are constants for a given system. The Freundlich constant  $K_F$  [ $(\mu\text{g}/\text{mg}) (\mu\text{g}/\text{L})^{(1/n)}$ ] determined from the isotherms informs on the adsorption capacity of a given carbon for a given adsorbate and  $1/n$  depends on the

adsorbent heterogeneity. Given the non-linearity of the isotherms ( $K_F$  and  $1/n$  values given in Table S6), we computed the distribution coefficient  $K_d$  (sorbed concentration ( $\mu\text{g}/\text{g}$ )/dissolved concentration ( $\mu\text{g}/\text{L}$ )) for a fixed dissolved micropollutant concentration ( $10 \mu\text{g}/\text{L}$ ) to compare the adsorptive capacities of all tested adsorbents (Fig. 2).

In accordance with previous work (Margot et al., 2013; Rossner et al., 2009), high PAC affinities (high  $K_d$  values) were observed for bezafibrate, metoprolol, ofloxacin and trimethoprim, regardless of carbon type or size. Diclofenac also showed high  $K_F$  values in carbonate buffer, though this compound was generally only moderately well removed in natural waters (Rossner et al., 2009). Mecoprop and carbamazepine showed medium  $K_d$  values relative to the other micropollutants targeted in this study. Low affinities were found for benzotriazole and sulfamethoxazole for all tested carbons. The lowest affinity was observed for the antiepileptic gabapentine, for which no isotherms could be established due to near null adsorption. Considering all compounds except gabapentine, we compared the ranges of  $K_d$  values for each PAC and SPAC by means of a box plot representation (Fig. 2). Generally the majority of  $K_d$  values (25th to 75th percentile box) were distributed over a broader range for the SPACs, mostly due to enhanced adsorption of the compounds which already had high affinity for PAC (ofloxacin, trimethoprim). Overall Norit SPAC had the highest adsorption capacities of the tested carbons in carbonate buffer. However, the observed differences were only small (within a factor of two), demonstrating similar adsorption capacities for the different carbons and their super-fine variants in carbonate buffer. The small differences in the  $1/n$  values that were observed for the different adsorbates, could be indicative of different sorption mechanisms, but this was not further investigated in this work.





**Fig. 2.** Distribution constants,  $K_d$  [L/g] in carbonate buffer (pH 8.1) for all target micropollutants and all tested carbons. Boxes show the range of  $K_d$  values for each carbon type and size (box shows 25<sup>th</sup>, 50<sup>th</sup> and 75<sup>th</sup> percentiles and whiskers the 5<sup>th</sup> and 95<sup>th</sup> percentiles). No isotherms could be determined for gabapentine due to near null adsorption.

### 3.2.2. Adsorption equilibrium in wastewater

In effluent wastewater, approximately two to three-fold lower adsorption capacities were observed for all compounds and PACs/SPACs relative to pure buffered water (Fig. 3), suggesting adverse effects of competing wastewater matrix components on the adsorption of target micropollutant. It is largely acknowledged that background organic matter reduces the number of adsorption sites available for micropollutants, either through direct competition for adsorption sites and/or pore blocking, and consequently decreases the adsorption efficiency of PAC (de Ridder et al., 2011; Delgado et al., 2012; Kovalova et al., 2013a; Mailler et al., 2014; Margot et al., 2013). This effect is well illustrated in Fig. 3, which shows a downward shift of adsorption isotherms in wastewater (empty symbols) due to competition with EfOM, relative to the isotherms in carbonate buffer (solid symbols). The downward trend of the adsorption isotherms with increasing residual liquid phase concentration is another indication of the adverse influence of background organic matter (Kovalova et al., 2013a): at low carbon doses, the limited number of adsorption sites is reduced further by

competing EfOM, leading to a drop of the solid phase concentration. Moreover, for compounds showing a low carbon affinity (e.g. benzotriazole and sulfamethoxazole), this decrease in the solid phase concentration was also observed at low carbon doses in carbonate buffer, where the presence of other target adsorbates hindered the adsorption of the latter.

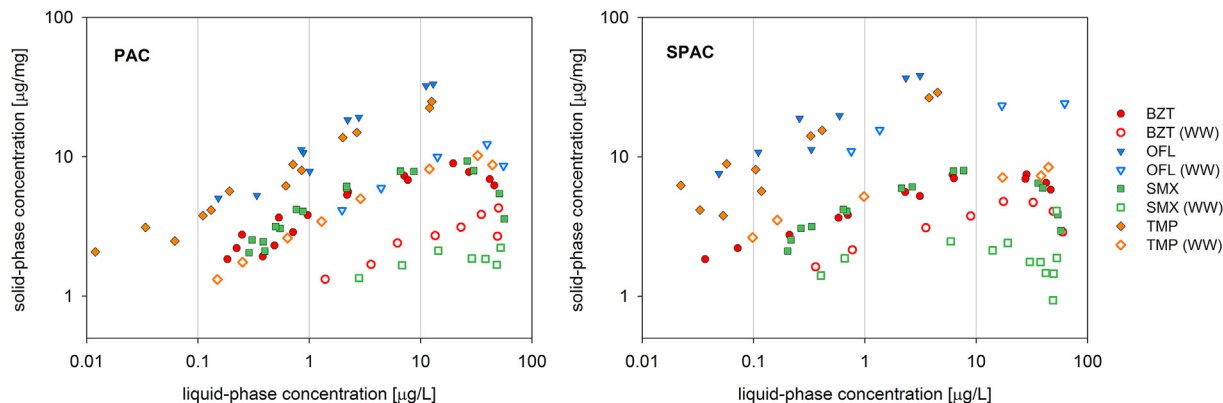
In a complex wastewater matrix, the Freundlich model (eqn. (2)) is too simplistic to accurately capture the adsorption isotherms. Instead, adsorption of micropollutants was more successfully described using an extended model that accounts for the presence of organic matter, the simplified equivalent background compound model (EBC). This model represents competing organic matter as a single compound, the equivalent background compound. It has been shown to effectively describe the adsorption of micropollutants onto PAC in natural waters or wastewater, where the concentration of background organic matter is much greater than that of the target micropollutants (Knappe et al., 1998; Kovalova et al., 2013a; Qi et al., 2007; Rossner et al., 2009; Zoschke et al., 2011). The simplified EBC model relates the relative removal of each micropollutant to the carbon dose in a two parameter equation (eqn. (3)):

$$\ln\left(\frac{C_{1,0}}{C_1} - 1\right) = n_1 \ln\left(\frac{m_A}{V}\right) - \ln(A) \quad (3)$$

where  $n_1$  is the Freundlich exponent of the micropollutant,  $C_{1,0}$  the initial concentration of the micropollutant,  $C_1$  the micropollutant concentration in solution at equilibrium,  $m_A$  the adsorbent mass,  $V$  the volume of solution and  $A$  a parameter which summarizes the adsorption parameters of the trace compound ( $n_1, K_{F,1}$ ) and the EBC (the EfOM). The parameters  $A$  and  $n_1$ , obtained from fitting eqn. (3) to experimental values, allow to determine the adsorbent dose necessary for a given removal of a compound via eqn. (4) (Zoschke et al., 2011):

$$\left(\frac{m_A}{V}\right) = A^{1/n_1} \left(\frac{C_{1,0}}{C_1} - 1\right)^{1/n_1} \quad (4)$$

The validity of this simplified approach has been confirmed for various micropollutants at concentrations ranging from 50 to 200  $\mu\text{g/L}$  in complex wastewater matrices (Kovalova et al., 2013a; Shimabuku et al., 2014; Zoschke et al., 2011). The derivation of eqn. (3), examples of fitted isotherms and the fitted parameters ( $A$  and  $n_1$ ) for each target micropollutant and PAC are given in the supplementary information.



**Fig. 3.** Adsorption isotherms for representative target adsorbates for Norit PAC (left) and SPAC in pure buffered water (full symbols) and effluent wastewater (hollow symbols).

### 3.3. Carbon dose for 80% micropollutant removal from wastewater (at equilibrium)

To quantitatively compare the efficiency of PACs and SPACs in removing micropollutants from wastewater effluent, the dose required for an 80% removal of each targeted adsorbate at equilibrium was calculated using eqn. (4) and results are shown in Table 1 and Fig. 4a. The dose required to remove the compounds with the lowest carbon affinity ranges from 20 to 30 mg/L, whereas approximately 5 mg/L is sufficient for a satisfactory removal of highly adsorbing compounds such as metoprolol, ofloxacin and trimethoprim. The comparison of each PAC with its corresponding super-fine variant showed that differences in the doses required to reach 80% removal were within experimental error for Sorbopor (Fig. 4a, red bars), which indicates that the finely ground Sorbopor did not have superior adsorption capacity relative to normal-sized Sorbopor. The adsorption capacities of Norit PAC and SPAC were also similar for all compounds aside from diclofenac and ofloxacin, which required lower SPAC doses than the parent PAC for 80% removal (Fig. 4b, blue bars). For Pulsorb, lower doses of finely ground Pulsorb were required to achieve 80% removal compared to the Pulsorb PAC (green bars, Fig. 4b). Among the different SPACs, Pulsorb and Norit were approximately equally efficient in removing 80% of each targeted contaminant, whereas Sorbopor was less efficient (Fig. S7, supplementary information). These observations are in line with past work showing that, though the fine grinding of particles increased the adsorption capacity of larger macromolecules such as DOM (Ando et al., 2010; Matsui et al., 2013b, 2009a), the adsorption capacity for small micropollutants such as MIB, geosmin or phenol was not systematically increased, possibly because the adsorption of these smaller molecules occurred on the internal pores of the activated carbon (Ando et al., 2010; Matsui et al., 2013a). The greater adsorption capacity of Pulsorb SPAC relative to its parent PAC, may indicate alterations of the mesoporic structure during the wet milling process, possibly leading to increased numbers of adsorption sites available to the micropollutants. However elucidating the mechanisms behind differences in adsorption capacities was beyond the scope of this work.

The forthcoming Swiss legislation will require large WWTPs to eliminate 80% of the incoming micropollutant load and compliance will be measured based on the average removal of five indicator micropollutants. Thus, assuming five indicator compounds at concentrations of 100 µg/L each in raw wastewater, the initial total load of 500 µg/L would need to be reduced to a total of 100 µg/L in the effluent. In view of this regulation, we calculated the relation

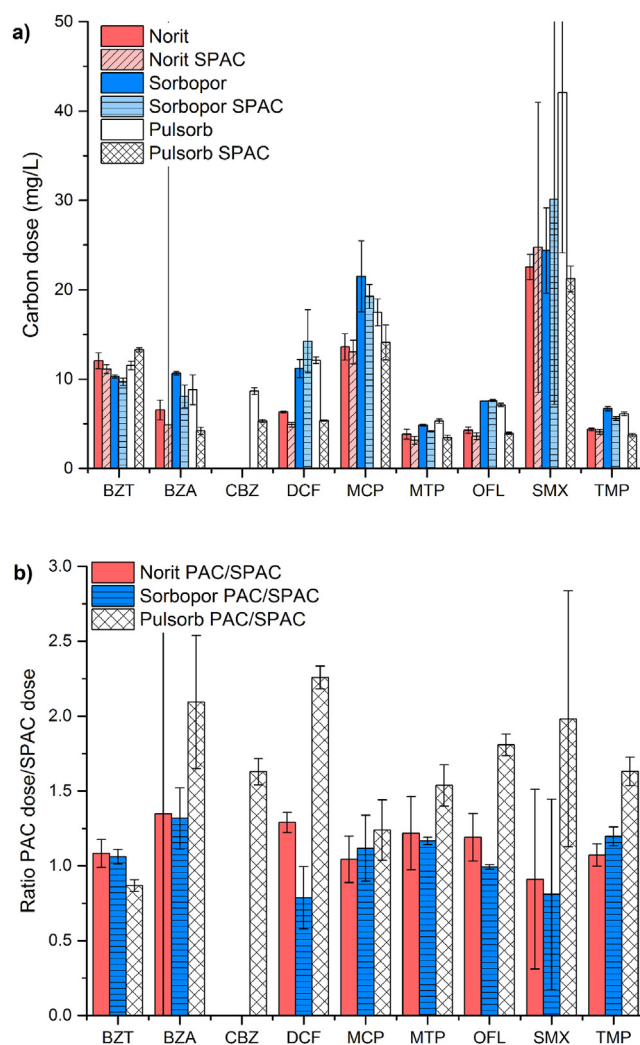


Fig. 4. a) Carbon dose [mg/L] for an 80% removal of each target micropollutant; b) ratio PAC/SPAC of the required dose for an 80% removal; Error bars represent the 95% confidence interval from duplicate experiments.

between the carbon dose and the average removal of all indicator

Table 1

Absolute (mg/L) and specific (mg/mg DOC) doses of PAC and SPAC (at equilibrium) for 80% removal of micropollutants from wastewater (5 mg/L DOC) (doses calculated according to eqn. (4) fitted to equilibrium isotherms) and comparison with doses measured by Altmann et al. for wastewater containing 9–14 mg/L DOC (Altmann et al., 2014).

	Norit PAC		Norit SPAC		Norit PAC (Altmann et al.)	
	Dose 80% removal (12 h)		Dose 80% removal (10 min)		Dose 80% removal (48 h)	
	[mg/L]	[mg/mg DOC]	[mg/L]	[mg/mg DOC]	[mg/L]	[mg/mg DOC]
Benzotriazole	12.0 ± 7%	2.4 ± 9%	12.3 ± 3%	2.5 ± 6%	15 ± 24%	1.19 ± 13%
Bezafibrate	6.6 ± 17%	1.3 ± 18%	4.9	1.0 ± 5%	8 ± 19%	0.68 ± 10%
Carbamazepine <sup>a</sup>	6.4	1.3 ± 5%	4.9	1.0 ± 5%	7 ± 22%	0.56 ± 14%
Diclofenac	6.3 ± 1%	1.3 ± 5%	4.9 ± 5%	1.0 ± 7%	10 ± 8%	0.79 ± 15%
Gabapentine <sup>b</sup>	n.d.					
Mecoprop	13.6 ± 11%	2.7 ± 12%	13.0 ± 10%	2.6 ± 11%		
Metoprolol	3.8 ± 15%	0.8 ± 16%	3.2 ± 14%	0.6 ± 15%		
Ofloxacin	4.3 ± 8%	0.9 ± 9%	3.6 ± 1%	0.7 ± 5%		
Sulfamethoxazole	22.5 ± 6%	4.5 ± 8%	20.6 ± 22%	4.1 ± 23%	28 ± 23%	2.28 ± 8%
Trimethoprim	4.4 ± 3%	0.9 ± 6%	4.1 ± 6%	0.8 ± 8%		

<sup>a</sup> Isotherms for carbamazepine were not measured for Norit materials in wastewater. Values shown represent average of bezafibrate and diclofenac, which matched carbamazepine parameters well in experiments with other materials (Fig. 4), as well as with the values reported by Altmann et al.

<sup>b</sup> No isotherms could be determined for gabapentine (poor adsorption). Values for the other adsorbents Sorbopor and Pulsorb are given in the supplementary information.

compounds combined (Fig. 5; see supplemental information for details). The 80% removal requirement refers to elimination throughout the entire treatment (activated sludge + advanced treatment). Nevertheless, herein we refer to the elimination relative to the activated sludge effluent for better comparison to past work and as a worst-case scenario, assuming no removal of certain recalcitrant compounds may occur during the conventional biological wastewater treatment. To reach an average removal of 80% of these 5 indicator compounds, minimal carbon doses of 13–15 mg/L would be necessary for Norit SPAC, Norit PAC and Pulsorb SPAC. With Pulsorb PAC and Sorbopor PAC/SPAC, higher doses of up to 21 mg/L are needed to attain the required removal. It is important to note that these values assume the adsorption equilibrium has been reached. In comparison to past work, these minimal doses are on the lower end of those used to achieve 80% removal of micropollutants in a pilot-scale PAC-UF system in Switzerland (20 mg/L PAC) when DOC concentrations ranged between 5 and 10 mg C/L (Boehler et al., 2012; Margot et al., 2013) and in batch experiments by Altman et al. (Table 1) (Altmann et al., 2014). The wastewater used for all experiments herein had similar DOC levels (5 mg C/L), but these remain relatively low compared to typical DOC concentrations encountered in other work focused on the removal of micropollutants from effluent wastewater using PAC (Mailler et al., 2014). Generally higher PAC doses (>20 mg/L) were required to achieve similar removal when DOC levels (organic matter) increased (Altmann et al., 2014; Mailler et al., 2014; Margot et al., 2013), due to increased competition of the organic matter for adsorption sites as discussed above. Within a wastewater matrix, the influence of EfOM (measured as DOC) on SPAC removal efficiencies of micropollutants is not known and will be investigated in the following section.

#### 3.4. Influence of effluent organic matter

To compare the effect of effluent organic matter on the micropollutant removal efficiencies of PAC and SPAC, the removal was assessed for effluent wastewaters with varying DOC content. Batch equilibrium experiments were conducted in three different waters with varying DOC content (2.5, 5 and 10 mg C/L) and two different carbon doses of Norit PAC and SPAC (10 and 15 mg/L). Fig. 6 shows

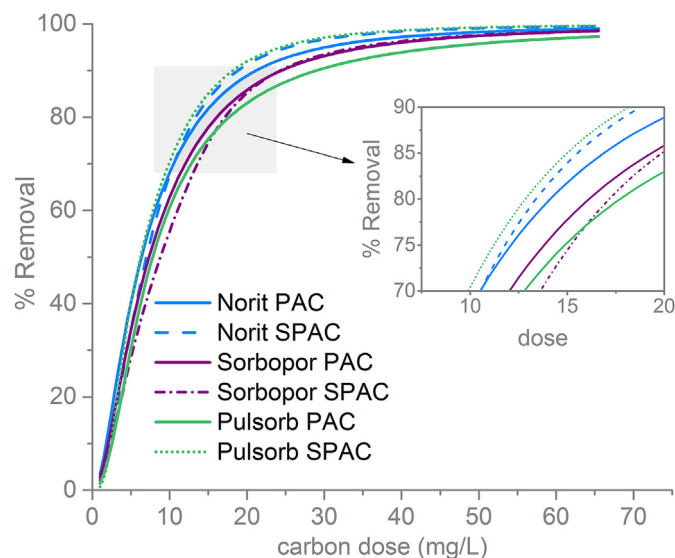


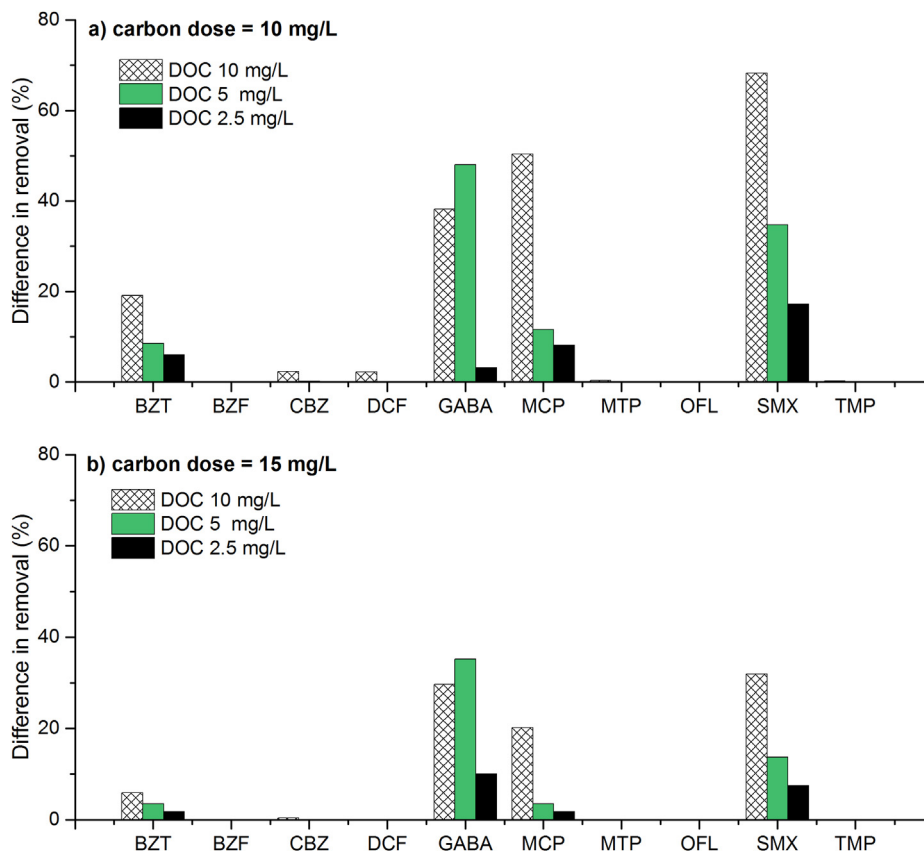
Fig. 5. Carbon dose as a function of average removal of all indicator compounds (benzotriazole, carbamazepine, diclofenac, mecoprop, sulfamethoxazole) for each tested PAC/SPAC.

that increasing DOC concentrations negatively impacted the adsorption capacities of both SPAC and PAC for selected compounds. However, SPAC was more strongly affected than PAC, in particular at the lower carbon dose (10 mg/L) and for weakly adsorbing compounds (e.g. sulfamethoxazole). This suggests that adsorption competition between poorly adsorbing compounds and organic matter was more pronounced for smaller carbon particles. On the other hand, SPAC exhibited up to twice the DOC removal compared to their parent PACs (Fig. 7), which could account for the greater competition with micropollutants. The highest EfOM removal was observed for Norit SPAC (40% mg DOC/L) compared to 20% DOC removal by Norit PAC. Although higher DOM removals with SPAC in comparison to PAC have been reported previously (Ando et al., 2010; Matsui et al., 2013b, 2012, 2004), the same authors also found that low molecular weight (MW) micropollutants, namely geosmin and 2-methylisobornel (MW < 200Da) were not affected by the increased loading of DOM onto SPAC, as most of the DOM did not compete for the same sites as the targeted pollutants. Specifically, the authors suggested that low MW micropollutants preferentially adsorbed onto the interior surfaces of the carbon, whereas the larger MW DOM mainly adsorbs to the carbon surface (Matsui et al., 2013b).

In contrast, in the present study, the higher EfOM loading of SPAC with respect to PAC adversely affected the micropollutant adsorption. Several aspects should be considered to rationalize this finding. First, the nature and size distribution of natural and effluent derived organic matter can differ substantially. LC-OCD analysis of the wastewater used in this work revealed that, compared to typical surface water, the wastewater matrix contained a relatively large fraction of biopolymers (19%, very high MW (>20 kDa) hydrophilic compounds), but also a significant fraction of low MW neutral compounds (MW < 350 Da, 17.3%) that could compete for adsorption sites with the targeted micropollutants. Correspondingly, recent work showed that the fraction of organic matter competing with MIB and sulfamethoxazole for adsorption sites on PAC was significantly higher in wastewater impacted waters than in non-wastewater impacted surface waters (Shimabuku et al., 2014). A larger fraction of competing EfOM should impact both PAC and SPAC, assuming both the micropollutants and the competing EfOM adsorb to internal pores. However, the impact on SPAC should be greater due to its greater overall adsorption capacity for EfOM (Fig. 7). We hypothesize that in addition to competing for adsorption sites, the higher background DOC concentrations combined with a higher fraction of large biopolymers induce a pore-blocking effect, which prevents micropollutants from reaching their adsorption sites. This effect may be enhanced for SPAC and due to a greater number of large molecules at the surface of SPAC. Moreover, as observed previously (de Ridder et al., 2011), increased adsorption of negatively charged organic matter on the surface of the carbon particles can lead to a more negatively charged surface. The increased EfOM loading on SPAC could consequently increase electrostatic repulsion of anionic pharmaceuticals such as sulfamethoxazole. Further work is necessary to i) confirm the increased adverse effect of EfOM for SPACs compared to PACs in batch and up-scaled experiments and ii) understand the competition between the micropollutants and EfOM.

#### 3.5. Feasibility of SPAC-UF for removal of micropollutants

Compared to normal-sized PAC, SPAC offers several advantages that have the potential to lead to important footprint, capital and operational cost reduction. The substantially faster adsorption kinetics of micropollutants onto SPAC translate to a shorter hydraulic residence time for a given carbon dose and micropollutant removal, and consequently the necessary contact tank size can be reduced.

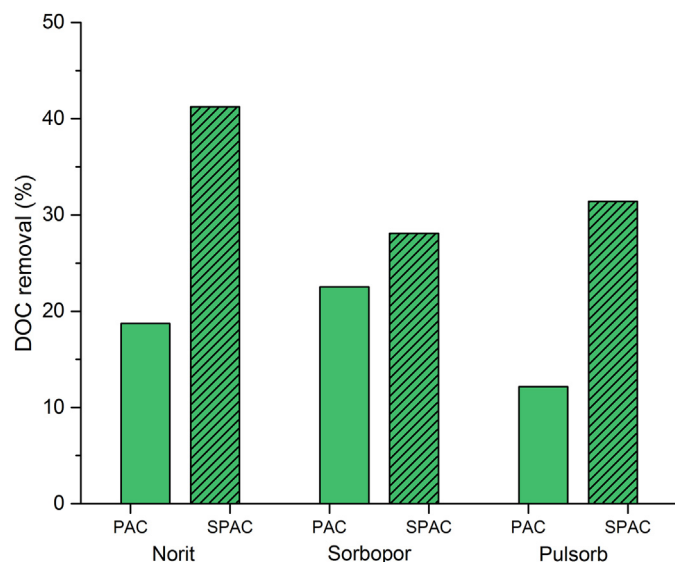


**Fig. 6.** Differences in Norit PAC and SPAC micropollutant removal efficiencies with varying DOC content (difference in removal = % removal PAC - % removal SPAC: positive value indicates better removal by PAC than SPAC). Batch experiments were conducted in 3 different waters with varying DOC content (2.5, 5 and 10 mg DOC/L) and two carbon doses (a) 10 and (b) 15 mg/L PAC or SPAC.

For example, in comparison to pilot PAC-UF systems, where typical contact times ranged from 0.5 to 2 h (Boehler et al., 2012; Löwenberg et al., 2014; Margot et al., 2013), SPAC equilibrium was reached within 7 min. Since the residence time is directly

proportional to the tank size, the use of SPAC thus allows for a reduction in the necessary contact tank size by a factor of 4–17. The total footprint of the treatment can be a limiting factor for small plants (Boehler et al., 2012) or in densely populated areas and could thus potentially be reduced with the use of SPAC.

Further benefits of reaching adsorption equilibrium within 10 min include important carbon dosage savings; in practice, typical PAC-UF contact times of 0.5–2 h (Cook et al., 2001; Zoschke et al., 2011) are too short to reach adsorption equilibrium and thus do not take full advantage of the total adsorptive capacity of PAC. Kinetic experiments showed that for a given carbon dose (15 mg/L), after 0.5–2 h of PAC contact time the adsorption equilibrium had not been reached, yielding an average removal of the indicator compounds of 50–70% (Figs. 1 and S1 and S2). As such, higher doses or PAC recirculation are necessary to fully load the PAC and reach higher removal efficiencies. In comparison, the enhanced SPAC uptake rates result in maximal micropollutant adsorption efficiency as the adsorption equilibrium is reached rapidly (e.g., the 80% removal threshold of indicator compounds is reached after only 7 min using the same SPAC dose). Variations of dose and contact time with SPAC need to be tested at pilot scale and the optimal operation conditions may be influenced by site-specific requirements. In-line dosing of SPAC with short contact times (30–60 s), as applied in drinking water treatment, could be an advantageous option for some plants. Such a set-up (in-line PAC-microfiltration) was previously tested and achieved 80–90% removal of micropollutants from wastewater, but prohibitively high PAC doses (50 mg/L) were required (Pinnkamp et al., 2012). These would likely be greatly reduced using SPAC.



**Fig. 7.** DOC removal from effluent wastewater for a carbon dose of 15 mg/L and an initial DOC concentration of 5 mg C/L.



In previous studies, strong correlations were observed between reduction of UV<sub>254</sub> and adsorptive micropollutant removal. As such, this easily measurable parameter was proposed as a suitable surrogate to monitor real-time micropollutant removal in wastewater using PAC and adjust carbon doses accordingly (Altmann et al., 2014; Zietzschmann et al., 2014). The correlations held true in the present work with both PAC and SPAC (Fig. S8, supplementary information), which indicates that further dosage savings are possible by regulating carbon dose as a function of reduction of UV absorption at 254 nm (UV<sub>254</sub>).

Questions pertaining to the impact of SPAC on the membrane process will need to be investigated at pilot scale. As with PAC, the efficiency of the filtration is influenced by several factors such as membrane properties, operating conditions as well as the water matrix. Transmembrane pressure build-up due to membrane fouling can lead to flux decline and increased energy requirements. Compared to PAC, we expect that SPAC application will be advantageous for the subsequent ultrafiltration process due to enhanced removal of organic matter, a well-acknowledged membrane foulant. Pilot scale trials with surface water comparing both PAC and SPAC – microfiltration found that the latter attenuated reversible and irreversible membrane fouling and minimized the long-term transmembrane pressure increases (Matsui et al., 2007).

In practice, a coagulant is generally applied to ensure adequate retention of the PAC by the membrane and reduce fouling (Altmann et al., 2015; Boehler et al., 2012; Margot et al., 2013). The addition of a coagulant has been shown to improve DOM removal; however it mainly adsorbed the non-competing DOM fraction and, consequently, the elimination of micropollutants using PAC with a coagulant was not enhanced (Altmann et al., 2015). The combined application of SPAC and a coagulant before a membrane was successfully tested by Matsui et al., who found better membrane performance and no influence of the order of the coagulant – PAC/SPAC dosing sequence on the DOM removal from surface waters (Matsui et al., 2004). The effects of a coagulant with SPAC on micropollutant removal from a wastewater matrix still need to be assessed at large scale.

SPAC is currently not commercially available and to date there is no standard production method (Partlan et al., 2016). In view of upscaling, the preparation of finely ground SPAC from PAC warrants more research. Moreover, the onsite preparation of the slurry must be considered along with its sonication before it is put in contact with wastewater, to ensure adequate dispersion of SPAC particles.

#### 4. Conclusion

The removal of micropollutants from effluent wastewater is a growing concern and several European countries are considering the addition of an advanced treatment step after conventional wastewater treatment in order to prevent the discharge of high micropollutant loads to the aquatic environment. The application of powdered activated carbon followed by membrane filtration has demonstrated great potential for this purpose, but remains relatively cost- and energy intensive. Moreover, the typically applied carbon contact times are kinetically unfavorable for efficient adsorption and thus high doses are needed for adequate elimination of micropollutants. In this context, we investigated the effectiveness of super-fine powdered activated carbon (ca. 1 μm mean diameter) in comparison to regular-sized PAC for the optimization of micropollutant removal from wastewater. Bench-scale experiments with three commercial PACs and their finely ground versions highlighted several advantages of using super-fine PACs for the removal of 10 representative micropollutants.

- The total adsorptive capacities of SPAC were similar to those of PAC for two of the three tested carbon materials. However all SPACs showed substantially faster adsorption kinetics and equilibrium was reached within 10 min for all micropollutants, compared to >12h for PAC.
- The faster adsorption process using SPAC translates into a reduction of the necessary contact time and contact tank size as well as reduced carbon dosing for a given targeted micropollutant removal. In the tested effluent wastewater (5 mg/L DOC), the necessary dose to achieve 80% removal of indicator micropollutants (benzotriazole, diclofenac, carbamazepine, mecoprop and sulfamethoxazole) at equilibrium ranged between 13 and 15 mg/L.
- Micropollutant adsorption was adversely affected by effluent organic matter. The detrimental effect of EfOM increased with increasing DOC content (2.5–10 mg C/L), resulting in lower removal efficiencies of those micropollutants with a low affinity for the adsorbent particles (e.g., sulfamethoxazol, gabapentine).
- SPAC application resulted in up to two-fold higher DOC removal compared to PAC, likely owing to the greater surface area available on the smaller particles for the adsorption of organic matter. However, the enhanced uptake of organic matter by SPAC coincided with a more pronounced decrease in the removal efficiencies of selected micropollutants compared to PAC, suggesting that the additionally adsorbed organic matter was competing with micropollutants for adsorption sites. The enhanced competition between micropollutants and effluent organic matter on SPAC warrants further verification and research in other wastewater matrices.
- In a SPAC-UF configuration, we expect the enhanced DOC removal by SPAC to benefit the ultrafiltration process by mitigating membrane fouling and by positively impacting the final water quality and color. Nevertheless, pilot-scale experiments are necessary to confirm these observations at larger scale and determine the influence of smaller PAC particle size on the membrane operation.

#### Acknowledgments

We gratefully acknowledge Dominique Grandjean for assistance with the analytical method, Vidy Wastewater treatment plant for providing wastewater, Daniel Frauchiger for input during the project and Membratec SA, Elemo and EPFL for funding.

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2015.12.001>.

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