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A comparison of adsorption of organic micropollutants onto activated carbon following chemically enhanced primary treatment with microsieving, direct membrane filtration and tertiary treatment of municipal wastewater

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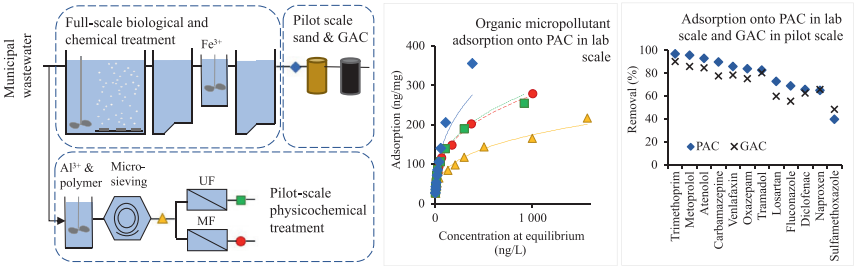
HIGHLIGHTS

- Micropollutants were adsorbed onto PAC after direct membrane filtration.
- Similar adsorption of micropollutants after MF and UF.
- Higher adsorption of micropollutants seen in tertiary treated wastewater.
- Higher adsorption of micropollutants related to lower adsorption of DOC.
- Similar adsorption by PAC and GAC.

GRAPHICAL ABSTRACT



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ABSTRACT

The adsorption of organic micropollutants onto powdered activated carbon (PAC) was investigated in laboratory scale based on samples from four wastewater process streams (matrices); three from a pilot-scale plant with different degrees of physicochemical treatment of municipal wastewater and one from a full-scale activated sludge plant with post-precipitation. The pilot-scale treatment consisted of chemically enhanced primary treatment with microsieving followed by direct membrane filtration as microfiltration or ultrafiltration. The results showed highest adsorption of micropollutants in the tertiary (biologically and chemically) treated wastewater and lowest adsorption in the microsieve filtrate. Adsorption of micropollutants in the direct membrane microfiltration (200 nm) permeate was generally similar to that in the direct membrane ultrafiltration (3 nm) permeate. The higher adsorption of micropollutants in the tertiary treated wastewater could be related to a lower concentration of dissolved organic carbon (DOC) and lower affinity of DOC for PAC at low dosage (<15 mg PAC/L) in this matrix. At a PAC dose of 10 mg/L, sulfamethoxazole was removed by 33% in the tertiary treated wastewater and 7% in the direct membrane microfiltration permeate. In addition to the PAC experiments, a pilot scale sand filter and a proceeding GAC filter was operated on tertiary treated wastewater from the full-scale treatment plant. Similar removal trends in the PAC and GAC experiments were observed when studying a weighted average micropollutant removal in the GAC filter and a similar dose of activated carbon for both PAC and GAC. Positively charged micropollutants were removed to a higher extent than negatively charged ones by both PAC and GAC.

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1. Introduction

Conventional wastewater treatment, such as the activated sludge process, is not designed to remove organic micropollutants like pharmaceutical residues, and only contributes to partial removal of these substances (Joss et al., 2008). Adsorption onto activated carbon is one option to reduce the discharge of micropollutants via municipal wastewater without producing any by- or transformation products (Margot et al., 2013).

The adsorption onto activated carbon is affected by numerous factors, such as the activated carbon surface chemistry and pore structure (Alves et al., 2018; Moreno-Castilla, 2004). Its porous structure has been classified into micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm) (Sing et al., 1985). Micropores make up at least 90–95% of the surface area, and are the most important pores for the adsorption of micropollutants (Radovic, 2001), whereas macropores and mesopores function mainly as passages for micropollutants. Powdered activated carbon (PAC) has a higher fraction of mesopores than granular activated carbon (GAC), and thus allows for more rapid intraparticle diffusion (Real et al., 2017; Suzuki, 1991).

Dissolved organic matter (DOC) in wastewater has a negative influence on micropollutant adsorption due to competition for micropore adsorption sites and macro- and mesopore blocking (Jarvie et al., 2005; Yu et al., 2009). The molecular weight of DOC can vary from a few hundred Da to over 100 kDa, and low-molecular weight DOC influence the adsorption of micropollutants more than high-molecular weight DOC (Zietzschmann et al., 2014). Aromatic DOC, as indicated by UVA_{254}, has further been seen to correlate with micropollutant removal by activated carbon (Altmann et al., 2014; Zietzschmann et al., 2016). Since the DOC composition of the effluent varies in different types of wastewater treatment processes (Krasner et al., 2009; Wang and Chen, 2018), the degree of adsorption will also vary. Adsorbate (micropollutants) properties, such as functional groups, polarity, aromaticity, hydrophobicity, charge and molecular weight, are also important factors determining adsorption (Yu et al., 2009; de Ridder et al., 2011; Knappe et al., 2003; Quinlivan et al., 2005). Anyhow, for a high adsorption of micropollutants it is advantageous to have a low concentration of DOC, which depends on the treatment processes preceding the adsorption step (Boehler et al., 2012).

Treatment with activated carbon can be applied after or integrated with an existing process at a wastewater treatment plant. PAC or GAC adsorption after biological treatment and subsequent separation have been examined in several studies (Altmann et al., 2015; Kårelid et al., 2017; Löwenberg et al., 2014; Margot et al., 2013). Integrated processes where PAC is added into a biological reactor would require less space and exhibit potential synergistic effects (Boehler et al., 2012; Cimbritz et al., 2019; Gutiérrez et al., 2021; Meinel et al., 2016; Serrano et al., 2011; Streicher et al., 2016).

An alternative option to conventional wastewater treatment is chemical precipitation and microsieving followed by direct membrane filtration. Chemical precipitation and microsieving can be used to increase treatment efficiency and reduce foot-print (Ljunggren et al., 2007; Väänänen et al., 2016). Direct membrane filtration, by micro- or ultrafiltration, is an abiotic process where wastewater is filtered directly using a porous membrane (Ravazzini et al., 2005) and has the potential of treating wastewater with small footprint and low energy consumption (Hey et al., 2017, 2018; Nieuwenhuijzen et al., 2000). A combination of the two treatment processes has previously shown the potential to produce permeates with organic contents of ~40 mg/L COD (Hey et al., 2017), which is in the same range as for biologically treated wastewater, 20–50 mg/L COD (Ekblad et al., 2019). However, micro- or ultrafiltration is not efficient for the removal of micropollutants and thus an additional process would be needed, such as activated carbon adsorption. Whether micropollutant adsorption onto PAC or GAC after direct membrane filtration can be combined has however not been fully investigated.

The main objective of this study was to investigate micropollutant adsorption onto PAC using real wastewater at actual micropollutants concentrations (no spiking) after pilot scale treatment of influent municipal wastewater by (1) physicochemical treatment (coagulation, flocculation and microsieving (100 μm pore size)), (2) physicochemical treatment and subsequent microfiltration (200 nm pore size), (3) physicochemical treatment and subsequent ultrafiltration (3 nm pore size), and (4) full-scale activated sludge treatment with post-precipitation (tertiary treatment). The micropollutant adsorption in the PAC experiments for the tertiary treated wastewater (4) was further compared with the micropollutant removal in a pilot-scale plant based on sand- and GAC filtration.

2. Materials and methods

A pilot-scale plant with microsieving, microfiltration (MF), ultrafiltration (UF) and a GAC filter was operated at Svedala wastewater treatment plant (Sweden), as shown in Fig. 1, and described in detail in Sections 2.1 and 2.3. Svedala treatment plant has a treatment capacity for 18,500 population equivalents and is treating municipal wastewater with the majority being domestic wastewater, and small contributions of industrial wastewater and stormwater run-off. During the pilot-scale plant operation period, the incoming wastewater was of the character medium-to-strong with average concentrations around 350 mg/L suspended solids, 650 mg/L COD, 180 mg/L total organic carbon (TOC), 70 mg/L notal nitrogen and 9 mg/L total phosphorus (n = 8–19). The adsorption of 12 organic micropollutants onto PAC was investigated in laboratory-scale experiments in wastewater from each treatment step, and onto GAC in pilot scale, as described in Sections 2.2 and 2.3.

2.1. The direct membrane filtration pilot-scale plant

The microsieving and direct membrane filtration pilot-scale treatment plant received 3 m^3/h of wastewater from the sand trap. Treatment was initiated by pre-precipitation with 12 mg Al^{3+}/L poly aluminium chloride (Kemira, Sweden) and 3 mg/L anionic polymer (Veolia, France) and microsieving in a drum filter (100 μm pore size, Hydrotech, Sweden). Subsequent membrane filtration was performed in two parallel lines: one with MF (0.2 μm pore size, MFP2, Alfa Laval, Denmark) and one with UF (10 kDa molecular weight cut-off, ~3 nm pore size, UFXpHt10, Alfa Laval, Denmark).

2.2. Lab-scale PAC experiments

Wastewater for the PAC experiments was collected as grab samples after microsieving, MF, UF and after biological and chemical treatment at the full-scale treatment plant (tertiary effluent). Suspended solids, TOC and COD were analysed prior to the adsorption experiments, which were initiated within 24 h. PAC (SAE Super, Norit, Netherlands; BET surface area 1150 m^2/g, particle size ~20 μm) was prepared as a suspended stock solution in deionized water. Wastewater (40 mL) with pH 7.7 was transferred into Falcon tubes (50 mL) and PAC was added at 12 concentrations (0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 80, 100 mg/L). After 24 h of agitation on a horizontal shaker at 20 °C, PAC was separated from the water by centrifugation (4000 rpm for 10 min) and subsequent filtration (0.45 μm, Minisart RC, Sartorius, Germany). DOC and ultraviolet absorbance at 254 nm (UVA_{254}) were determined within 24 h. Filtered samples for micropollutant analysis were stored at −20 °C in 100 mL HDPE bottles.

2.3. Pilot-scale GAC filtration

A 19-l filter containing GAC (AquaSorb™ carbon 5000, Jacobi Carbons, Germany; BET surface area 1200 m^2/g, particle size ~1 mm) was operated downstream of 19-l sand filter fed with tertiary treated wastewater. An empty bed contact time (EBCT) of 10 min was maintained by controlling the flow (114 L/h). Backwashing of the sand filter was usually performed weekly and the maximum pressure was 5 bar. The GAC filter was backwashed twice per month and the maximum pressure was 3 bar. Flow proportional 24-h composite samples were collected after approximately 3000, 8000, 18,000 and 23,000 bed volumes. DOC and UVA_{254} were determined within 24 h after each sampling. Removal efficiencies at different

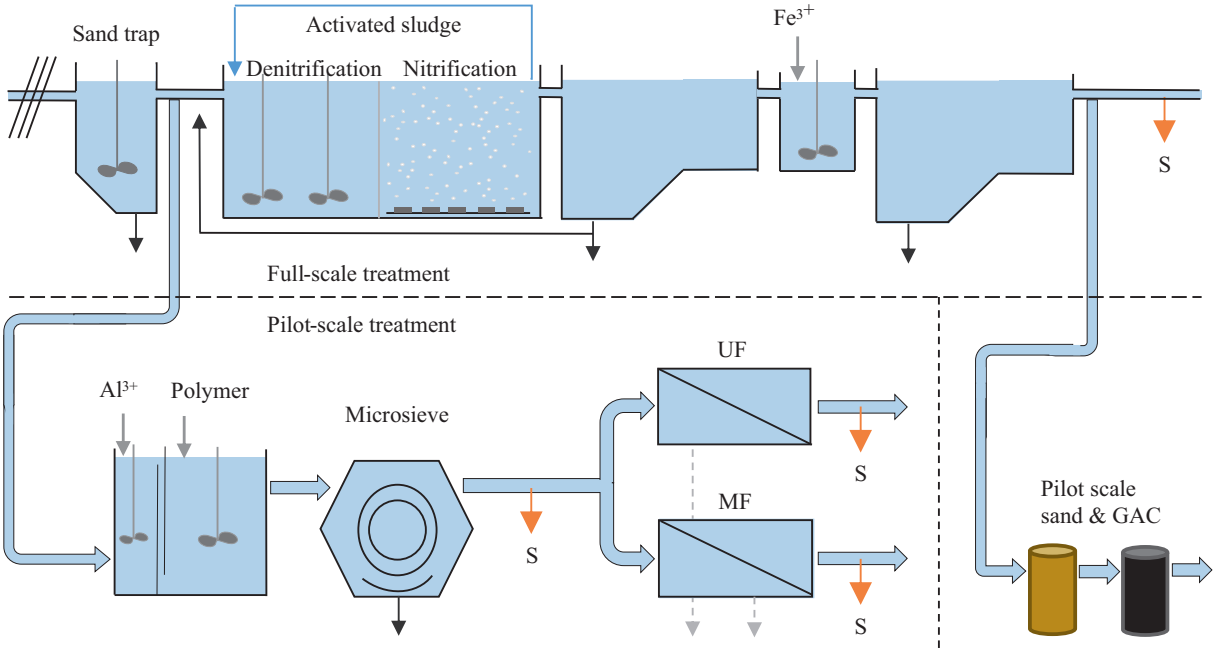


Fig. 1. Process scheme of Svedala wastewater treatment plant, the microsieve and direct membrane filtration pilot-scale plant and the pilot-scale GAC treatment. Sampling locations for the PAC experiments are marked with "S".

EBCTs (5, 10, 20 and 30 min) were evaluated at 8000 bed volumes by changing the flow through the GAC filter and by grab sampling. Samples for micropollutant analysis were stored at −20 °C in 100 mL HDPE bottles.

2.4. Analytical methods

2.4.1. Analysis of wastewater constituents

Analysis of DOC and UVA_{254} was performed on filtered samples (0.45 μm filters, Minisart RC, Sartorius, Germany). UVA_{254} was measured using a UV-VIS spectrophotometer (Hach DR 6000). COD, TOC and DOC were analysed with Hach cuvettes (LCK314, LCK385) using spectrometry (Hach DR2800). The suspended solids concentrations were determined according to Swedish standard (SS-EN ISO 5667-3:2004).

2.4.2. Analysis of organic micropollutants

12 micropollutants were selected for analysis based on their presence in wastewater treatment plant effluents (Svahn and Björklund, 2017): atenolol, carbamazepine, diclofenac, fluconazole, losartan, metoprolol, naproxen, oxazepam, sulfamethoxazole, tramadol, trimethoprim and venlafaxine. In brief, the frozen HDPE bottles were thawed and 40 mL of each sample was concentrated and purified on an Oasis HLB 200 mg solid phase extraction column. After drying, elution and evaporation, each sample was reconstituted in methanol and 1 μL was analysed by ultra-performance liquid chromatography (UPLC) coupled to tandem mass spectroscopy (MS/MS) (Waters Acquity UPLC H-Class, Xevo TQS Waters Micromass, Manchester, UK) as described by Svahn and Björklund (2016, 2019).

The analysis of micropollutants with low to moderate micropollutant concentrations in wastewater with a high interfering background matrix requires thorough sample preparation and optimized mass spectrometer parameters to achieve precision, accuracy, and low limits of quantification. By using a low injection volume (1 μL) and three separate chromatographic methods (acid, alkaline, neutral) (Svahn and Björklund, 2019) in the UPLC, it is possible to achieve high precision and elevated sensitivity, which is required for the analysis of micropollutants at low concentrations. Traditionally, this kind of analysis has been conducted by spiking samples with micropollutants at relatively high concentrations (Delgado et al., 2012). The limits of quantification and relative standard deviations for the 12 investigated micropollutants are given in Table S1. The molecular properties of the micropollutants (Table S2) were determined using Chemaxon software (Swain, 2012).

2.5. Calculations based on Freundlich isotherms

Freundlich isotherms (Freundlich, 1906) were fitted to the PAC adsorption data according to Eq. (1).

$$q_e = K_F * C_e^{1/n} \quad (1)$$

q_e is the concentration of micropollutants in the solid phase (ng/mg), K_F the Freundlich constant (ng/mg)/(ng/L)$^{1/n}$, C_e the micropollutant concentration at equilibrium (ng/L), and $1/n$ the Freundlich intensity parameter (dimensionless).

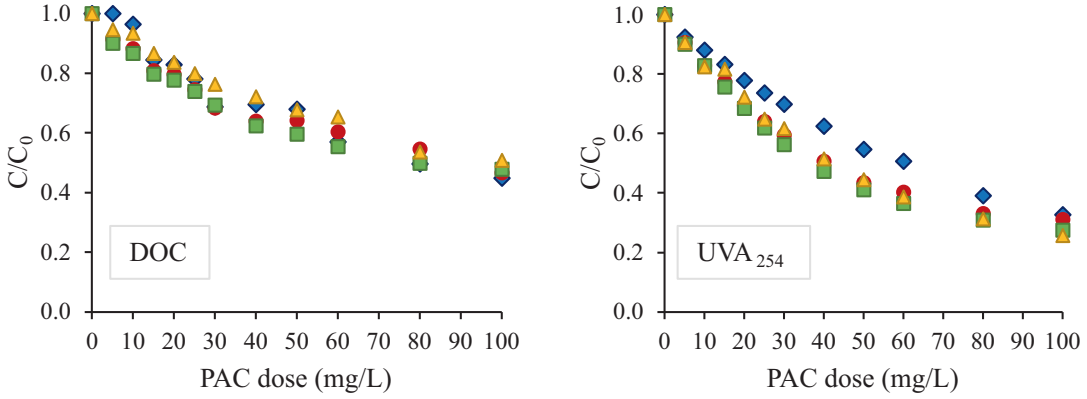
Freundlich parameters were determined through linear fitting of adsorption data on a log-log scale, as described previously by Hamdaoui and Naffrechoux (2007). As the initial micropollutant concentrations, C_0, were constant and the concentration of the adsorbent (PAC) was systematically increased, the maximum adsorption capacity, q_m (ng/mg), for the micropollutants could be estimated (Hamdaoui and Naffrechoux, 2007) according to Eq. (2).

$$q_m = K_F * C_0^{1/n} \quad (2)$$

3. Results and discussion

3.1. Wastewater characteristics and DOC removal in the PAC experiments

The concentrations of DOC, UVA_{254} and SUVA, and the relative decrease of DOC and UVA_{254} in the lab-scale experiments are given in Fig. 2 and Table S3. DOC is a measurement of the dissolved organic content, while UVA_{254} can be used to estimate the aromatic content in a solution, and SUVA is the ratio of UVA_{254} to DOC. The tertiary effluent showed the lowest DOC concentration and UVA_{254} (without PAC), indicating that the abundance of aromatic DOC was lower in this matrix (Fig. 2). All matrices had similar specific UVA_{254} (SUVA), indicating that the proportions of DOC with an aromatic backbone and aromatic moieties were similar in all



Reference values (C_0)	Microsieving filtrate	MF permeate	UF permeate	Tertiary effluent
DOC (mg/L)	16.4	12.4	11.9	10.7
UVA_{254} (m^{-1})	29.0	21.8	20.7	18.9
SUVA (L/(m*mg))	1.8	1.8	1.7	1.8

Fig. 2. Relative decrease of DOC and UVA_{254} in the laboratory PAC experiments, including the values of DOC, UVA_{254} and SUVA without PAC, as single measurements.

matrices. The concentrations of suspended solids, COD, TOC, SUVA, UVA_{254} and DOC (without PAC) are compiled in Table S4.

Both DOC and UVA_{254} decreased in all experiments when PAC had been added. For most PAC doses, a higher removal of DOC was observed in the membrane permeates compared to that in the other matrices, however the differences between the matrices were relatively small (Fig. 2). The removal of DOC by adding PAC was generally lower in the microsieving filtrate than in both the MF and UF permeates due to possible adsorption and pore blocking by the relatively high concentration of TOC (41.5 mg/L) (Table S4). The difference between removal of UVA_{254} in the matrices was greater than that of DOC. The lowest removals of UVA_{254} were observed in the microsieve filtrate.

Since membrane filtration is based on size exclusion, it was assumed that only compounds smaller than the membrane pores were present in the MF and UF permeates. By subtracting the concentration of DOC in the MF permeate (12.4 mg/L) from the concentration of DOC in the microsieving filtrate (16.4 mg/L), it was determined that about 4 mg/L of the DOC in the microsieve filtrate had a diameter > 200 nm (Fig. 2). This fraction of DOC could have contributed to pore blocking of PAC macropores >50 nm. The concentrations of DOC in the MF and UF permeates revealed that most DOC molecules (11.9 mg/L) had a diameter < 3 nm, and that only a small fraction of the DOC (0.5 mg/L) had a diameter of 3–200 nm.

3.2. Organic micropollutant adsorption isotherms

Initial micropollutant concentrations, micropollutant removal with a PAC dose of 10 mg/L and Freundlich isotherm parameters in the lab-scale experiments are given in Table 1. The initial concentration of micropollutants varied from 57 ng/L (fluconazole) to 8653 ng/L (naproxen), and the micropollutant removal with a PAC dose of 10 mg/L varied between 3% (sulfamethoxazole) and 96% (trimethoprim). The adsorption of micropollutants in the four matrices (Figs. 3 and S1) appeared to be related to the concentration of DOC and UVA_{254} (Fig. 2); the removal of micropollutants in the tertiary effluent (10.7 mg/L DOC, 18.9 m^{-1} UVA_{254}) was usually the highest while removal in the microsieving filtrate (16.4 mg/L DOC, 29.0 m^{-1} UVA_{254}) was the lowest. High concentration of DOC and UVA_{254} could indicate high competition for adsorption sites by aromatic, organic compounds. Both DOC and UVA_{254} measurements have been suggested as suitable to estimate micropollutant adsorption by PAC (Altmann et al., 2014, 2016). The removal could also be related to the molecular properties of the micropollutants, which is further discussed in Section 3.3.

The removal of micropollutants in the MF (200 nm) and UF (3 nm) permeates (Figs. 3 and S1) were, in most cases, similar and this could be due to the comparable DOC concentrations (Fig. 2). UF only retained 0.5 mg/L more DOC than MF which suggested that most DOC in the MF permeate was smaller than 3 nm. The results indicated that the small fraction of DOC between 3 and 200 nm did not significantly influence adsorption of micropollutants onto PAC.

Freundlich isotherms could be fitted ($R^2 \geq 0.90$) to most of the positively charged and uncharged micropollutants, but only to a few negatively charged micropollutants (Figs. 3 and S1). The two negatively charged micropollutants, diclofenac and sulfamethoxazole, showed negative adsorption trends at increasing equilibrium concentrations, i.e. with decreasing PAC dose, in most wastewater matrices. Similar adsorption trends were seen for all low-adsorbing compounds: diclofenac, sulfamethoxazole, fluconazole, losartan and naproxen (Fig. S1), which accords well with previous studies where such trends have been related to competitive adsorption by DOC (Altmann et al., 2014; Zietzschmann et al., 2014). Furthermore, these results could be explained by the low affinity of these micropollutants for activated carbon, which would be especially important when the available adsorption sites are limited, and the DOC content is high. The adsorption of sulfamethoxazole could be fitted with an isotherm ($R^2 \geq 0.90$) in the tertiary effluent but not in any of the other matrices, possibly due to the lower affinity of the DOC for PAC in that matrix.

The micropollutant maximum adsorption capacities of PAC were generally higher in the matrices with less DOC, as in the following order: tertiary effluent > UF permeate ≈ MF permeate > microsieving filtrate (Table 1). The lowest maximum adsorption capacity was found for fluconazole (4 ng/mg) in MF permeate, and the highest for naproxen (551 ng/mg) in UF permeate (Table 1). The differences in adsorption capacities were partly related to the initial concentrations of the micropollutants. Since this study was performed without spiking micropollutants, a variation in the initial concentration and adsorption capacities was expected. Especially noteworthy are the differences in concentration for naproxen in the tertiary effluent compared to the other matrices which is due to the biodegradability of naproxen (Lahti and Oikari, 2011). However, the differences in initial concentration could not alone explain the variations in the adsorption capacities. Sulfamethoxazole and trimethoprim had similar initial concentrations in the tertiary effluent, yet the latter showed much higher absorption capacity of PAC, probably as a result of the differences in molecular charges, as is discussed in Section 3.3.

To further analyse the influence of DOC and UVA_{254} on the adsorption of micropollutants, the PAC dose was normalized to the initial

Table 1
Initial concentrations, removal with a PAC dose of 10 mg/L and Freundlich isotherm parameters (only given for isotherm fits $R^2 \geq 0.90$) for the adsorption of micropollutants onto PAC in the four wastewater matrices. Initial concentration and the removal with 10 mg/L PAC were based on one analysis per wastewater sample. Freundlich isotherms were based on 5–11 PAC doses (n) depending on the limit of quantification.

Compound (and charge)	Matrix	Initial concentration (ng/L)	Removal with 10 mg/L PAC (%)	Freundlich parameters K_F ((ng/mg)(ng/L)$^{-1/n}$)	1/n	q_m (ng/mg)	R^2	n
Metoprolol (+)	Microsieving filtrate	2653	62	19.0	0.32	239	0.99	11
	MF permeate	2392	84	28.1	0.33	367	0.99	9
	UF permeate	2188	86	27.5	0.34	372	0.99	10
	Tertiary effluent	2160	95	28.1	0.38	537	0.91	10
Atenolol (+)	Microsieving filtrate	1940	47	10.4	0.33	125	0.94	11
	MF permeate	875	61	–	–	–	<0.90	9
	UF permeate	1557	73	13.8	0.35	182	0.99	8
	Tertiary effluent	1562	89	16.7	0.40	327	0.99	8
Tramadol (+)	Microsieving filtrate	991	34	7.0	0.26	42	0.94	11
	MF permeate	1021	65	9.0	0.34	94	0.99	11
	UF permeate	923	61	10.3	0.29	77	0.98	11
	Tertiary effluent	819	82	7.8	0.42	131	0.99	11
Trimethoprim (+)	Microsieving filtrate	319	67	5.0	0.31	30	0.98	9
	MF permeate	154	81	4.3	0.31	20	0.99	7
	UF permeate	197	85	5.5	0.33	32	0.99	6
	Tertiary effluent	222	96	6.2	0.54	117	0.99	6
Venlafaxin (+)	Microsieving filtrate	736	44	5.7	0.29	39	0.99	11
	MF permeate	606	65	6.5	0.34	56	0.99	11
	UF permeate	416	61	5.5	0.30	34	0.96	10
	Tertiary effluent	539	78	5.0	0.46	88	0.99	10
Oxazepam (0)	Microsieving filtrate	484	34	4.5	0.25	22	0.96	11
	MF permeate	328	61	5.5	0.26	25	0.96	9
	UF permeate	359	67	–	–	–	<0.90	11
	Tertiary effluent	465	80	7.3	0.33	57	0.93	11
Carbamazepine (0)	Microsieving filtrate	652	50	5.7	0.31	42	0.99	11
	MF permeate	451	70	6.5	0.32	45	0.97	10
	UF permeate	436	73	7.7	0.30	49	0.99	9
	Tertiary effluent	505	86	6.5	0.43	96	0.99	9
Fluconazole (0)	Microsieving filtrate	58	8	–	–	–	<0.90	11
	MF permeate	105	37	1.5	0.23	4	0.9	11
	UF permeate	105	35	1.6	0.23	5	0.97	11
	Tertiary effluent	57	60	1.0	0.38	5	0.98	10
Losartan (−)	Microsieving filtrate	1750	32	14.8	0.20	64	0.96	11
	MF permeate	854	53	–	–	–	<0.90	10
	UF permeate	830	61	–	–	–	<0.90	9
	Tertiary effluent	1545	65	19.4	0.25	120	0.91	10
Diclofenac (−)	Microsieving filtrate	707	45	–	–	–	<0.90	10
	MF permeate	440	50	–	–	–	<0.90	7
	UF permeate	413	62	–	–	–	<0.90	11
	Tertiary effluent	429	52	–	–	–	<0.90	9
Naproxen (−)	Microsieving filtrate	8653	21	–	–	–	<0.90	11
	MF permeate	6869	43	–	–	–	<0.90	11
	UF permeate	7238	60	62.0	0.25	551	0.97	9
	Tertiary effluent	333	53	–	–	–	<0.90	5
Sulfamethoxazole (−)	Microsieving filtrate	198	3	–	–	–	<0.90	11
	MF permeate	216	7	–	–	–	<0.90	11
	UF permeate	246	16	–	–	–	<0.90	11
	Tertiary effluent	269	33	2.3	0.26	9	0.94	11

DOC concentration and to the initial UVA_{254} (Figs. S2, S3). After the normalization, the adsorption profiles were more similar but the difference in DOC could not fully explain the observed difference as the general order (tertiary effluent > UF permeate ≈ MF permeate > microsieving filtrate) was preserved. The normalization for UVA_{254} gave more similar removals than the normalization for DOC. The higher adsorption in the effluent wastewater could be due to that the biological treatment changed the composition of the DOC (Wang and Chen, 2018) by decreasing the content of low- molecular weight fractions (Park et al., 2010) which are more competitive for adsorption sites (Zietzschmann et al., 2014).

3.3. Influence of the molecular properties of organic micropollutants on adsorption

Differences in the affinity of micropollutants for activated carbon may be related to their individual physicochemical properties. Fig. 4 shows micropollutant removal from the tertiary effluent as a function of PAC dose, together with selected molecular properties of the 12 micropollutants studied. The 12 micropollutants were almost completely removed (>85%) at high PAC doses (>40 mg/L). The three micropollutants showing the highest adsorption were trimethoprim, metoprolol and atenolol, which are all positively charged at the experimental pH of 7.7. The three micropollutants showing the lowest adsorption were sulfamethoxazole, naproxen and diclofenac, which are all negatively charged at this pH. This effect was most pronounced at low PAC doses (<15 mg/L) at which the number of adsorption sites are more limited. Uncharged micropollutants showed both poor and good adsorption onto PAC.

It has been reported that electrostatic interactions between micropollutants and PAC significantly influence adsorption (de Ridder et al., 2011; Guillossou et al., 2020). Slightly basic experimental conditions (e.g. pH 7.7) results in a negatively charged activated carbon surface due to dissociation of oxygen complexes of acid character, such as carboxylic and phenolic groups on the graphene-like surface (Moreno-Castilla, 2004). This would explain both the high removal of positively charged compounds and the low removal of negatively charged compounds.

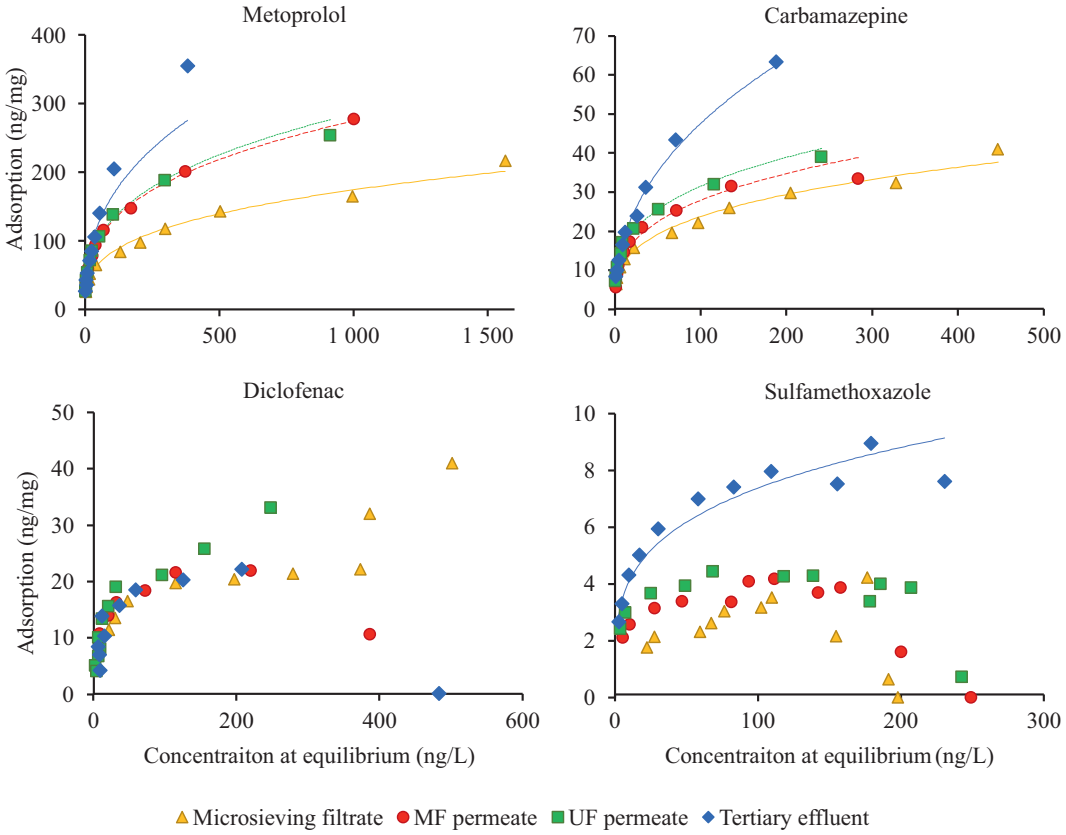
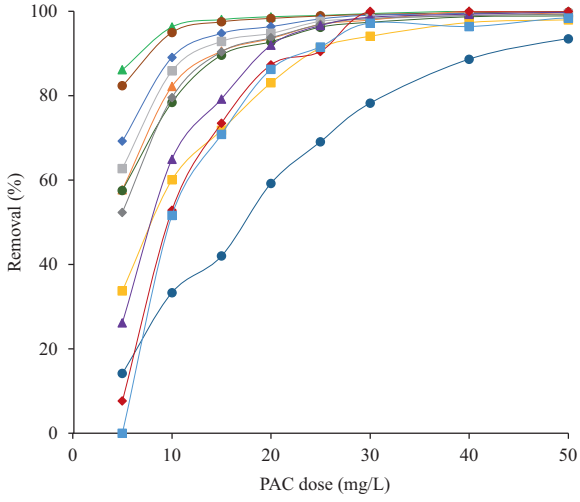


Fig. 3. Adsorption of four micropollutants onto PAC in four wastewater matrices together with Freundlich isotherms. Freundlich isotherms are only shown for $R^2 \geq 0.90$. Note the different scales on the axes.

Water solubility showed negative correlation with removal within the groups of negatively charged and uncharged micropollutants while the octanol-water partitioning coefficient, log P_{OW}, which is a measurement of hydrophobicity of a compounds neutral form, correlated positively with removal within those groups. Log P_{OW} showed higher correlation to the removals of micropollutants than log D_{OW}, which is a measurement of hydrophobicity of a compounds neutral and ionized forms, altogether. Values for log P_{OW} and log D_{OW} are given in Table S2. Hydrophobicity has been reported to be an important factor influencing micropollutant adsorption onto activated carbon (de Ridder et al., 2010; Hamdaoui and Naffrechoux, 2007; Moreno-Castilla, 2004; Quinlivan et al., 2005; Rodriguez et al., 2016). As an example, carbamazepine, an uncharged compound with a high value of log P_{OW} (2.8), showed high affinity for PAC in the present study. In contrast, the uncharged compound fluconazole was poorly adsorbed, which could be explained by the low value of log P_{OW} (0.6) in combination with its high water solubility (1.39 mg/mL).

Diclofenac, losartan and naproxen all showed low affinity for PAC, mainly due to their negative charge. Moreover, they all have high log P_{OW} values (Fig. 4), which could cause the formation of complexes between micropollutants and hydrophobic DOC (Hernandez-Ruiz et al., 2012; Mott,



	Molecular weight (g/mol)	Charge	Log P_{OW}	Water solubility (mg/mL)
Trimethoprim	290	+	1.3	0.615
Metoprolol	267	+	1.8	0.402
Atenolol	266	+	0.4	0.429
Carbamazepine	236	0	2.8	0.152
Tramadol	263	+	2.5	0.750
Venlafaxin	277	+	2.7	0.230
Oxazepam	287	0	2.9	0.088
Fluconacole	306	0	0.6	1.390
Losartan	423	-	5.0	0.005
Sulfamethoxazole	253	-	0.8	0.459
Naproxen	230	-	3.0	0.051
Diclofenac	296	-	4.3	0.004

Fig. 4. Organic micropollutant removal vs. PAC dose in the tertiary effluent (left) and organic micropollutant molecular properties (right). ChemAxon software Chemicalize was used to determine molecular weight, charge, hydrophobicity (log P_{OW}) at pH 7.7. Water solubility was found on the drugbank.com website.

2002). Micropollutant-DOC complexes could further co-adsorb onto the PAC surface (Guillossou et al., 2020). Interestingly, these three micropollutants demonstrated relatively high adsorption in the MF and UF permeates (Fig. S2). Formation of micropollutant-DOC complexes could be possible after MF and UF because of the different composition of DOC in these permeates compared to the DOC in the tertiary effluent. This is supported by the low but existing removal of these three micropollutants by UF and MF, seen in the column Initial concentration in Table 1.

3.4. Removal of organic micropollutants in a pilot-scale GAC column

The GAC filter column was operated for 23,000 bed volumes and the removal of micropollutants and DOC at four different bed volumes are presented in Fig. 5a. The influence of EBCT on micropollutant removal is presented in Fig. 5b. Like in the PAC experiments, the positively charged micropollutant showed a higher removal than the negatively charged micropollutants at all investigated bed volumes. Moreover, the breakthrough of the negatively charged micropollutants occurred at earlier time points than that of the positively charged micropollutants. Similar observations have been reported in previous studies (Benstoem et al., 2017; Meinel et al., 2015; Nguyen et al., 2013). A DOC removal of only 20% was observed around 8000 bed volumes. This indicated an almost complete saturation of DOC and that the entire GAC bed had been pre-loaded with DOC. At 18000, and 23,000 bed volumes, the removal of DOC was close to 0%.

At 23000 bed volumes, the removal of sulfamethoxazole was negative (Fig. 5a) which indicated that, at this time-point, the capacity of GAC to adsorb sulfamethoxazole had been reached. Already at 18000 bed volumes, the estimated adsorbed amount (q) of sulfamethoxazole was 9 ng/mg GAC which is comparable with the maximum adsorption capacity (q_m) of 9 ng/mg PAC from the lab-scale batch experiments (Table 1). At 23000 bed volumes, the other micropollutants showed removals between 14% and 49% (Fig. 5a) and the adsorbed amounts (Table S5) were all below those achieved in the lab-scale batch experiments (Table 1).

Different types of carbons were used in the PAC and the GAC experiments (PAC SAE Super and AquaSorb™ carbon 5000) which could have influenced the results. Both carbon types has similar BET surface areas (1150 m^2/g and 1200 m^2/g respectively), points of zero charge (pH_{PZC}) of 9.8 and 8 respectively (Ersöz et al., 2013; Kovalova et al., 2013; Türgay et al., 2011) but different pore size distributions. PAC SAE Super has a lower proportion of micropore to mesopore volume (1.4:1) (Mestre et al., 2019; Rúa-Gómez et al., 2012) than AquaSorb™ carbon 5000 (2.8:1) (Villars et al., 2020) which may have influenced the adsorption and competition by dissolved organic matter (Ebie et al., 2001; Pelekani and Snoeyink, 1999).A change in EBCT had a greater effect on the removal of compounds with low affinity for GAC than on compounds with high affinity for GAC. As seen in Fig. 5b, a more distinct drop in removal of negatively charged micropollutants and the uncharged fluconazole was observed when the EBCT was decreased. A sufficiently long EBCT seems to be more important for the removal of micropollutants with low affinity, than for those with high affinity to GAC.

3.5. Comparison of weighted organic micropollutant removal in by GAC with removal by PAC

The adsorption by PAC and GAC was investigated by comparing the removal of micropollutants by a DOC-normalized dose of 1.2 g activated carbon/g DOC using both PAC and GAC (Fig. 6). The removal for the different micropollutants was relatively similar for both types of activated carbon. Negatively charged micropollutants showed low removals in both applications. Sulfamethoxazole demonstrated higher removal by GAC than by PAC. This could be due to a low competitive environment in the lower part of the GAC column at low bed volume throughput. In the beginning of filtration with new GAC, the top zone in the GAC column adsorbs compounds with high affinity for the GAC, such as metoprolol and carbamazepine. Subsequently, the lower part of the GAC column receives lower concentration of these highly adsorbable compounds. This enables higher adsorption of compounds with low affinity for GAC, such as sulfamethoxazole, in the lower part of the GAC column.

4. Conclusions

The adsorption of 12 micropollutants onto PAC was investigated in laboratory-scale experiments with four different wastewater matrices, and onto GAC in pilot scale with tertiary treated wastewater. Based on our findings, we could conclude that there is a potential of integrating micropollutant adsorption onto activated carbon following direct membrane filtration of municipal wastewater treatment. Ultrafiltration did not provide a better permeate for the adsorption of micropollutants than microfiltration. The following conclusions were also drawn:

- The majority of micropollutants were adsorbed to the highest extent in the tertiary effluent and to the lowest extent in the microsieve filtrate.
- Micropollutant adsorption in microfiltration (200 nm) and ultrafiltration (3 nm) permeates were similar; the fraction of DOC of 3–200 nm (0.5 mg/L) did not significantly influence the adsorption of micropollutants.

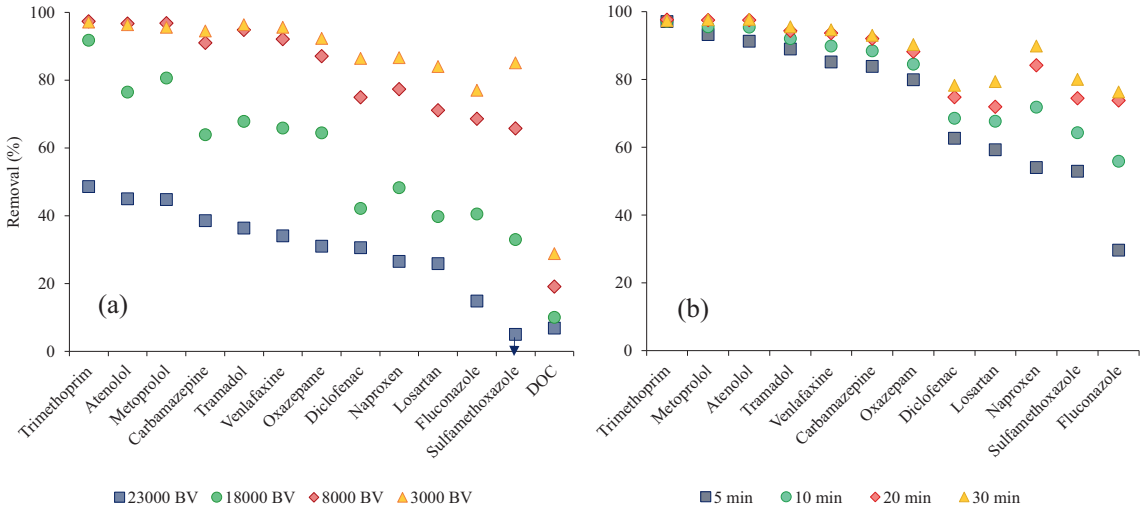


Fig. 5. Influence of throughput in bed volumes (BV) (a) and EBCT (b) on micropollutant removal in a pilot-scale GAC filter when treating a tertiary effluent. Sulfamethoxazole showed negative removal at 23000 bed volumes. Panel a is based on 24-h time-proportional samples and Panel b on paired grab samples.

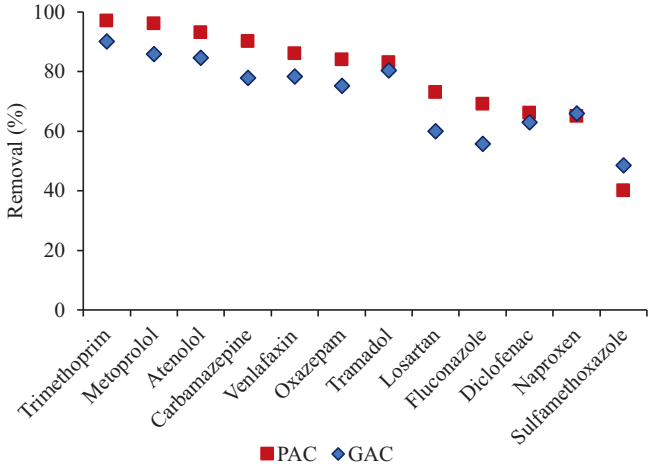


Fig. 6. Comparison of the removal of micropollutants by PAC and GAC at a dose of 1.2 g activated carbon/g DOC. The removal by GAC is based on the weighted mean micropollutant removal during the GAC process from 0 to 23,000 bed volumes.

- The higher adsorption of micropollutants in the tertiary treated wastewater could be related to the lower concentration of DOC and the lower affinity of DOC for PAC in this matrix.
- Micropollutant removal in the PAC experiments of tertiary treated wastewater was similar to micropollutant removal by GAC filtration.

CRediT authorship contribution statement

Simon Gidstedt: Conceptualization, Formal analysis, Investigation, Writing – original draft, Visualization. **Alexander Betsholtz:** Conceptualization, Methodology, Formal analysis, Investigation, Writing – review & editing, Visualization. **Per Falås:** Methodology, Formal analysis, Writing – review & editing. **Michael Cimbritz:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition. **Åsa Davidsson:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition. **Federico Micolucci:** Writing – review & editing. **Ola Svahn:** Formal analysis, Investigation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.152225.

References

Altmann, J., Ruhl, A.S., Zietzschmann, F., Jekel, M., 2014. Direct comparison of ozonation and adsorption onto powdered activated carbon for micropollutant removal in advanced wastewater treatment. Water Res. 55, 185–193. https://doi.org/10.1016/j.watres.2014.02.025.

Altmann, J., Sperlich, A., Jekel, M., 2015. Integrating organic micropollutant removal into tertiary filtration: combining PAC adsorption with advanced phosphorus removal. Water Res. 84, 58–65. https://doi.org/10.1016/J.WATRES.2015.07.023.

Altmann, J., Massa, L., Sperlich, A., Gnirss, R., Jekel, M., 2016. UV254 absorbance as real-time monitoring and control parameter for micropollutant removal in advanced wastewater treatment with powdered activated carbon. Water Res. 94, 240–245. https://doi.org/10.1016/j.watres.2016.03.001.

Alves, T.C., Cabrera-Codony, A., Barceló, D., Rodriguez-Mozaz, S., Pinheiro, A., Gonzalez-Olmos, R., 2018. Influencing factors on the removal of pharmaceuticals from water with micro-grain activated carbon. Water Res. 144, 402–412. https://doi.org/10.1016/j.watres.2018.07.037.

Benstoem, F., Nahrstedt, A., Boehler, M., Knopp, G., Montag, D., Siegrist, H., Pinnekamp, J., 2017. Performance of granular activated carbon to remove micropollutants from municipal wastewater—a meta-analysis of pilot- and large-scale studies. Chemosphere 185, 105–118. https://doi.org/10.1016/j.chemosphere.2017.06.118.

Boehler, M., Zwickenpflug, B., Hollender, J., Ternes, T., Joss, A., Siegrist, H., 2012. Removal of micropollutants in municipal wastewater treatment plants by powder-activated carbon. Water Sci. Technol. 66 (10), 2115–2121. https://doi.org/10.2166/wst.2012.353.

Cimbritz, M., Edefell, E., Thörnqvist, E., El-taliawy, H., Ekenberg, M., Burzio, C., Modin, O., Persson, F., Wilén, B.M., Bester, K., Falås, P., 2019. PAC dosing to an MBBR – effects on adsorption of micropollutants, nitrification and microbial community. Sci. Total Environ. 677, 571–579. https://doi.org/10.1016/j.scitotenv.2019.04.261.

de Ridder, D.J., Villacorte, L., Verliefde, A.R.D., Verberk, J.Q.J.C., Heijman, S.G.J., Amy, G.L., van Dijk, J.C., 2010. Modeling equilibrium adsorption of organic micropollutants onto activated carbon. Water Res. 44 (10), 3077–3086. https://doi.org/10.1016/j.watres.2010.02.034.

de Ridder, D.J., Verliefde, A.R.D., Heijman, S.G.J., Verberk, J.Q.J.C., Rietveld, L.C., Van Der Aa, L.T.J., Amy, G.L., Van Dijk, J.C., 2011. Influence of natural organic matter on equilibrium adsorption of neutral and charged pharmaceuticals onto activated carbon. Water Sci. Technol. 63 (3), 416–423. https://doi.org/10.2166/wst.2011.237.

Delgado, L.F., Charles, P., Glucina, K., Morlay, C., 2012. The removal of endocrine disrupting compounds, pharmaceutically activated compounds and cyanobacterial toxins during drinking water preparation using activated carbon-a review. Science of the Total Environment. Vols. 435–436. Elsevier, pp. 509–525. https://doi.org/10.1016/j.scitotenv.2012.07.046.

Ebie, K., Li, F., Azuma, Y., Yuasa, A., Hagishita, T., 2001. Pore distribution effect of activated carbon in adsorbing organic micropollutants from natural water. Water Res. 35 (1), 167–179. https://doi.org/10.1016/S0043-1354(00)00257-8.

Ekblad, M., Falås, P., El-taliawy, H., Nilsson, F., Bester, K., Hagman, M., Cimbritz, M., 2019. Is dissolved COD a suitable design parameter for ozone oxidation of organic micropollutants in wastewater? Sci. Total Environ. 658, 449–456. https://doi.org/10.1016/j.scitotenv.2018.12.085.

Ersöz, G., Napoleoni, A., Atalay, S., 2013. Comparative study using chemical wet oxidation for removal of reactive black 5 in the presence of activated carbon. J. Environ. Eng. 139 (12), 1462–1469. https://doi.org/10.1061/(asce)ee.1943-7870.0000757.

Freundlich, H., 1906. Over the adsorption in solution. J. Phys. Chem. 57, 385–470.

Guillossou, R., Le Roux, J., Mailler, R., Pereira-Derome, C.S., Varrault, G., Bressy, A., Vulliet, E., Morlay, C., Nauleau, F., Rocher, V., Gasperi, J., 2020. Influence of dissolved organic matter on the removal of 12 organic micropollutants from wastewater effluent by powdered activated carbon adsorption. Water Res. 172, 115487. https://doi.org/10.1016/j.watres.2020.115487.

Gutiérrez, M., Grillini, V., Mutavdžić Pavlović, D., Verlicchi, P., 2021. Activated carbon coupled with advanced biological wastewater treatment: a review of the enhancement in micropollutant removal. Sci. Total Environ. 790, 148050. https://doi.org/10.1016/J.SCITOTENV.2021.148050.

Hamdaoui, O., Naffrechoux, E., 2007. Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon. Part I. Two-parameter models and equations allowing determination of thermodynamic parameters. J. Hazard. Mater. 147 (1–2), 381–394. https://doi.org/10.1016/j.jhazmat.2007.01.021.

Hernandez-Ruiz, S., Abrell, L., Wickramasekara, S., Chefetz, B., Chorover, J., 2012. Quantifying PPCP interaction with dissolved organic matter in aqueous solution: combined use of fluorescence quenching and tandem mass spectrometry. Water Res. 46 (4), 943–954. https://doi.org/10.1016/j.watres.2011.11.061.

Hey, T., Väänänen, J., Heinen, N., la Cour Jansen, J., Jönsson, K., 2017. Potential of combining mechanical and physicochemical municipal wastewater pre-treatment with direct membrane filtration. <sb:title>Environ. Technol. (United Kingdom)</sb:title><sb:volume-nr></sb:volume-nr> 38 (1). https://doi.org/10.1080/09593330.2016.1186746.

Hey, T., Bajraktari, N., Davidsson, Å., Vogel, J., Madsen, H.T., Hélix-Nielsen, C., Jansen, J.la C., Jönsson, K., 2018. Evaluation of direct membrane filtration and direct forward osmosis as concepts for compact and energy-positive municipal wastewater treatment. Environ. Technol. (United Kingdom) 39 (3), 264–276. https://doi.org/10.1080/09593330.2017.1298677.

Jarvie, M.E., Hand, D.W., Bhuvendralingam, S., Crittenden, J.C., Hokanson, D.R., 2005. Simulating the performance of fixed-bed granular activated carbon adsorbers: removal of synthetic organic chemicals in the presence of background organic matter. Water Res. 39 (11), 2407–2421. https://doi.org/10.1016/j.watres.2005.04.023.

Joss, A., Siegrist, H., Ternes, T.A., 2008. Are we about to upgrade wastewater treatment for removing organic micropollutants? Water Sci. Technol. 57 (2), 251–255. https://doi.org/10.2166/wst.2008.825.

Kårelid, V., Larsson, G., Björlenius, B., 2017. Pilot-scale removal of pharmaceuticals in municipal wastewater: comparison of granular and powdered activated carbon treatment at three wastewater treatment plants. J. Environ. Manag. 193, 491–502. https://doi.org/10.1016/j.jenvman.2017.02.042.

Knappe, D.R.U., Li, L., Quinlivan, P., Wagner, T., 2003. Effects of Activated Carbon Characteristics on Organic Contaminant Removal. IWA Publishing.

Kovalova, L., Knappe, D.R.U., Lehnberg, K., Kazner, C., Hollender, J., 2013. Removal of highly polar micropollutants from wastewater by powdered activated carbon. Environ. Sci. Pollut. Res. 20 (6), 3607–3615. https://doi.org/10.1007/s11356-012-1432-9.

Krasner, S.W., Westerhoff, P., Chen, B., Rittmann, B.E., Nam, S.N., Amy, G., 2009. Impact of wastewater treatment processes on organic carbon, organic nitrogen, and DBP precursors in effluent organic matter. Environ. Sci. Technol. 43 (8), 2911–2918. https://doi.org/10.1021/es802443t.

Lahti, M., Oikari, A., 2011. Microbial transformation of pharmaceuticals naproxen, bisoprolol, and diclofenac in aerobic and anaerobic environments. Arch. Environ. Contam. Toxicol. 61 (2), 202–210. https://doi.org/10.1007/s00244-010-9622-2.

Ljunggren, M., Alm, L.-G., Nilsson, B., Persson, E., Strube, R., Svensson, L., la Cour Jansen, J., 2007. Microscreening in chemically enhanced primary treatment. Chemical Water and Wastewater Treatment IX. Proceedings of the 12th Gothenburg Symposium 2007. IWA Publishing https://doi.org/10.2166/9781780402079.

Löwenberg, J., Zenker, A., Baggenstos, M., Koch, G., Kazner, C., Wintgens, T., 2014. Comparison of two PAC/UF processes for the removal of micropollutants from wastewater treatment plant effluent: process performance and removal efficiency. Water Res. 56, 26–36. https://doi.org/10.1016/J.WATRES.2014.02.038.

Margot, J., Kienle, C., Magnet, A., Weil, M., Rossi, L., de Alencastro, L.F., Abegglen, C., Thonney, D., Chèvre, N., Schärer, M., Barry, D.A., 2013. Treatment of micropollutants in municipal wastewater: ozone or powdered activated carbon? Sci. Total Environ. 461–462, 480–498. https://doi.org/10.1016/j.scitotenv.2013.05.034.

Meinel, F., Ruhl, A.S., Sperlich, A., Zietzschmann, F., Jekel, M., 2015. Pilot-scale investigation of micropollutant removal with granular and powdered activated carbon. Water Air Soil Pollut. 226. https://doi.org/10.1007/s11270-014-2260-y.

Meinel, F., Sperlich, A., Jekel, M., 2016. Pilot-scale study of powdered activated carbon recirculation for micropollutant removal. Water Sci. Technol. 74 (4), 927–934. https://doi.org/10.2166/WST.2016.273.

Mestre, A.S., Hesse, F., Freire, C., Ania, C.O., Carvalho, A.P., 2019. Chemically activated high grade nanoporous carbons from low density renewable biomass (Agave sisalana) for the removal of pharmaceuticals. J. Colloid Interface Sci. 536, 681–693. https://doi.org/10.1016/J.JCIS.2018.10.081.

Moreno-Castilla, C., 2004. Adsorption of organic molecules from aqueous solutions on carbon materials. Carbon 42 (1), 83–94. https://doi.org/10.1016/j.carbon.2003.09.022.

Mott, H.V., 2002. Association of hydrophobic organic contaminants with soluble organic matter: evaluation of the database of Kdoc values. Adv. Environ. Res. 6 (4), 577–593. https://doi.org/10.1016/S1093-0191(01)00104-6.

Nguyen, L.N., Hai, F.I., Kang, J., Price, W.E., Nghiem, L.D., 2013. Coupling granular activated carbon adsorption with membrane bioreactor treatment for trace organic contaminant removal: breakthrough behaviour of persistent and hydrophilic compounds. J. Environ. Manag. 119, 173–181. https://doi.org/10.1016/j.jenvman.2013.01.037.

Nieuwenhuijzen, A.F., Evenblij, H., van der Graaf, J., 2000. Direct wastewater membrane filtration for advanced particle removal from raw wastewater, pp. 235–244 https://doi.org/10.1007/978-3-642-59791-6_22.

Park, M.H., Lee, T.H., Lee, B.M., Hur, J., Park, D.H., 2010. Spectroscopic and chromatographic characterization of wastewater organic matter from a biological treatment plant. Sensors 10 (1), 254–265. https://doi.org/10.3390/s100100254.

Pelekani, C., Snoeyink, V.L., 1999. Competitive adsorption in natural water: role of activated carbon pore size. Water Res. 33 (5), 1209–1219. https://doi.org/10.1016/S0043-1354(98)00329-7.

Quinlivan, P.A., Li, L., Knappe, D.R.U., 2005. Effects of activated carbon characteristics on the simultaneous adsorption of aqueous organic micropollutants and natural organic matter. Water Res. 39 (8), 1663–1673. https://doi.org/10.1016/j.watres.2005.01.029.

Radovic, L.R., 2001. Chemistry & Physics of Carbon. A Series of Advances. Vol 27. Marcel Dekker.

Ravazzini, A.M., van Nieuwenhuijzen, A.F., van der Graaf, J.H.M.J., 2005. Direct ultrafiltration of municipal wastewater: comparison between filtration of raw sewage and primary clarifier effluent. Desalination 178 (1–3 SPEC. ISS.), 51–62. https://doi.org/10.1016/j.desal.2004.11.028.

Real, F.J., Benitez, F.J., Acero, J.L., Casas, F., 2017. Adsorption of selected emerging contaminants onto PAC and GAC: equilibrium isotherms, kinetics, and effect of the water matrix. J. Environ. Sci. Health A 52 (8), 727–734. https://doi.org/10.1080/10934529.2017.1301751.

Rodriguez, E., Campinas, M., Luis Acero, J., João Rosa, M., 2016. Investigating PPCP removal from wastewater by powdered activated carbon/ultrafiltration. Water Air Soil Pollut. 227 (177). https://doi.org/10.1007/s11270-016-2870-7.

Rúa-Gómez, P.C., Guedez, A.A., Ania, C.O., Püttmann, W., 2012. Upgrading of wastewater treatment plants through the use of unconventional treatment technologies: removal of lidocaine, tramadol, venlafaxine and their metabolites. (2012, Vol. 4, Pages 650-669) Water 4 (3), 650–669. https://doi.org/10.3390/W4030650.

Serrano, D., Suárez, S., Lema, J.M., Omil, F., 2011. Removal of persistent pharmaceutical micropollutants from sewage by addition of PAC in a sequential membrane bioreactor. Water Res. 45 (16), 5323–5333. https://doi.org/10.1016/J.WATRES.2011.07.037.

Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J., Siemieniewska, T., 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure Appl. Chem. 57 (4), 603–619. https://doi.org/10.1351/pac198557040603.

Streicher, J., Ruhl, A.S., Gnirß, R., Jekel, M., 2016. Where to dose powdered activated carbon in a wastewater treatment plant for organic micro-pollutant removal. Chemosphere 156, 88–94. https://doi.org/10.1016/j.chemosphere.2016.04.123.

Suzuki, M., 1991. Application of fiber adsorbents in water treatment. Water Sci. Technol. 23 (7–9), 1649–1658. https://doi.org/10.2166/wst.1991.0619.

Svahn, O., Björklund, E., 2016. Increased electrospray ionization intensities and expanded chromatographic possibilities for emerging contaminants using mobile phases of different pH. J. Chromatogr. B Anal. Technol. Biomed. Life Sci. 1033–1034, 128–137. https://doi.org/10.1016/j.jchromb.2016.07.015.

Svahn, O., Björklund, E., 2017. Pharmaceutical Emissions From Scanian Wastewater Treatment Plants in 2017: A Development And Collaborative Project at Kristianstad University - In Cooperation With Skåne And six Scanian Treatment Plant Operators (Kristianstad University Report; 58 pages).

Svahn, O., Björklund, E., 2019. High flow-rate sample loading in large volume whole water organic trace analysis using positive pressure and finely ground sand as a spe-column in-line filter. Molecules 24 (7). https://doi.org/10.3390/molecules24071426.

Swain, M., 2012. chemicalize.orgchemicalize.orgby ChemAxon Ltd. J. Chem. Inform. Model. 52 (2), 613–615. https://doi.org/10.1021/ci300046g.

Türgay, O., Ersöz, G., Atalay, S., Forss, J., Welander, U., 2011. The treatment of azo dyes found in textile industry wastewater by anaerobic biological method and chemical oxidation. Sep. Purif. Technol. 79 (1), 26–33. https://doi.org/10.1016/j.seppur.2011.03.007.

Väänänen, J., Cimbritz, M., La Cour Jansen, J., 2016. Microsieving in primary treatment: effect of chemical dosing. Water Sci. Technol. 74 (2), 438–447. https://doi.org/10.2166/wst.2016.223.

Villars, K., Huang, Y., Lenhart, J.J., 2020. Removal of the cyanotoxin microcystin-LR from drinking water using granular activated carbon. Environ. Eng. Sci. 37 (9), 585–595. https://doi.org/10.1089/EES.2020.0017.

Wang, M., Chen, Y., 2018. Generation and characterization of DOM in wastewater treatment processes. Chemosphere. Vol. 201. Elsevier Ltd., pp. 96–109. https://doi.org/10.1016/j.chemosphere.2018.02.124.

Yu, Z., Peldszus, S., Huck, P.M., 2009. Adsorption of selected pharmaceuticals and an endocrine disrupting compound by granular activated carbon. 1. Adsorption capacity and kinetics. Environ. Sci. Technol. 43 (5), 1467–1473. https://doi.org/10.1021/es801961y.

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

Zietzschmann, F., Stützer, C., Jekel, M., 2016. Granular activated carbon adsorption of organic micro-pollutants in drinking water and treated wastewater - aligning breakthrough curves and capacities. Water Res. 92, 180–187. https://doi.org/10.1016/j.watres.2016.01.056.