Removal of organic micropollutants in a drinking water treatment plant by powdered activated carbon followed by rapid sand filtration

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ABSTRACT

Powdered activated carbon (PAC) is a promising technology to reduce organic micropollutants (OMPs) in drinking water treatment plants and combined with biological treatment processes such as rapid sand filters (RSFs), has the potential to remove a broad range of OMPs during water treatment. However, the removal of OMPs by a combination of two treatments (PAC-RSF) is not fully understood. 49 OMPs were spiked in PAC followed by RSF pilot plant treatment and the effluent was measured after 1, 4 and 7 day(s). Also, in a separate experiment 29 OMPs (out of 49) were dosed into the RSF column to assess the removal of OMPs by just RSF. Statistical analyses were performed and the OMPs were classified according to their charge and hydrophobicity. The results showed that OMPs were removed at the highest percentage after the first 24 h of dosing. The highest removal was observed for the neutral and hydrophobic compounds (80.0%–99.5%). The removal of neutral and hydrophilic compounds varied (0.14%–98.5%) depending on the possibility of forming π-π interactions and hydrogen bonds. Electrostatic repulsion between anionic OMPs and negatively charged PAC led to a decrease in the removal of anionic compounds. In contrast, electrostatic attraction led to an increase in the removal of cationic OMPs. Regarding OMPs removal by RSF, some compounds were removed by the sand filter depending partly on their physical-chemical properties and more dominantly on their functional groups. By comparing the OMPs removal by PAC-RSF with RSF, it was possible to determine the contribution of biological processes in the sand filter in the removal of some OMPs.

1. Introduction

The presence of organic micropollutants (OMPs) in both the aquatic environment and finished drinking water have raised concerns about their potential effects on the environment and public health [1,2]. For many years, the removal of OMPs has been the subject of study for researchers [2,3,53] as it is important to eliminate them from drinking water with appropriate treatment technology. Recently various technologies have been used to eliminate OMPs from drinking water, such as reverse osmosis and nanofiltration [4,5], advanced oxidation processes [3], and activated carbon adsorption [6–8].

Based on scientific research, adsorption onto activated carbon is regarded as one of the most effective steps to remove OMPs from water [9] due to the affinity of activated carbon for a wide range of

compounds, the large internal surface area [10] resulting in high adsorption capacities, low cost, simple operating design [11] and absence of oxidation by-products [8]. Commonly, activated carbon is applied in the form of powdered activated carbon (PAC) which is dosed as a powdered slurry. Based on the literature, the adsorption of OMPs into PAC varies regarding OMPs characteristics, e.g. molecular weight, polarity, pKa, molecular size, functional groups, hydrophobicity, charge [8,12], water matrix characteristics, e.g. pH [13], natural organic matter [14] and type of PAC e.g. pore size, area and surface chemistry [15–17].

The majority of previous studies on PAC were focused on the adsorption isotherms [18,19]. Other studies mostly reported the removal of OMPs by PAC in wastewater treatment plants [20,21], and some studies were considered the removal of only specific pollutants by PAC [22–24]. Few studies reported the OMPs removal by PAC in

Table 1
List of compounds and their physical-chemical properties; compounds dosed into the only sand filter are in bold.

Classes	Compound	MW (Da)	Charge [a]	Log K_{ow} [b]	pKa (pKb) [a]	Log D [b] (pH = 8)	Category [c]
Herbicide	*Atrazine*	215.7	neutral	2.61	15.8	2.2	1
ICPs[d]	Bisphenol A	228.3	neutral	3.32	9.6	4.04	1
PHARM[d]	*Carbamazepine*	236.3	neutral	2.45	15.96	2.77	1
Herbicide	*Chlortoluron*	213	neutral	2.4	13.5	2.5	1
ICPs	Dibutyl phthalate (DBP)	278.3	neutral	4.57	−6.7	4.68	1
ICPs	Diethyl phthalate (DEP)	222.2	neutral	2.42	−6.7	2.69	1
Herbicide	Dimethenamid	275.8	neutral	2.15	16.73	2.92	1
Herbicide	*Diuron*	233	neutral	2.7	13.2	2.5	1
PHARM	Estrone	270.4	neutral	3.13	10.4	3.38	1
Herbicide	*Isoproturon*	206	neutral	2.9	13.8	2.3	1
Herbicide	*S-Metolachlor*	284	neutral	3.13	NA	3.22	1
PCPs[d]	1,4-dioxane	88.1	neutral	−0.27	−3.9	−0.09	2
ICPs	*4-Methyl-1H-benzotriazole*	133	neutral	1.7	9.15	1.8	2
ICPs	*5-Methyl-1H-benzotriazole*	133	neutral	1.7	8.85	0.9	2
pesticide	Carbendazim	191.2	neutral	1.52	9.7	1.8	2
Herbicide	*Chloridazon*	222	neutral	1.1	−1.8	1.1	2
ICPs	Diglyme	134.2	neutral	−0.36	−3.7	−0.32	2
ICPs	Ethyl-t-butylether (ETBE)	102.2	neutral	1.92	NA	1.54	2
PHARM	Iopamidol	777	neutral	−2.42	11	−2.31	2
ICPs	Methyl tert-butyl ether (MTBE)	88.1	neutral	1.18	−4.1	1.18	2
PHARM	*N*-Nitrosodimethylamine (NDMA)	74	neutral	−0.57	3.52	0.04	2
PHARM	N-Nitrosomorpholine (NMOR)	116.1	neutral	−0.44	3.14	−0.18	2
PHARM	*Pentoxifylline*	278	neutral	0.3	19.64	0.54	2
ICPs	T-butylalcohol (TBA)	74.1	neutral	0.35	18.09	0.72	2
ICPs	Tris (2-chloroethyl) phosphate (TCEP)	285.5	neutral	1.44	−9.1	1.42	2
ICPs	Triglyme	178.2	neutral	−0.76	−3.5	−0.38	2
ICPs	*2,4-D*	221	negative	2.8	−4.9	−0.83	3
ICPs	*Acesulfame-K*	201	negative	−2.67	3.02	−3.21	3
PHARM	Amidotrizoic acid (diatrizoate)	613.9	negative	1.37	2.17	−0.63	3
ICPs	*Bisphenol S*	250.3	negative	1.65	8.2	1.97	3
PHARM	*Diclofenac*	294	negative	4.26	4.15	1.1	3
PHARM	Erythromycin	733.5	positive	3.06	9.69	1.69	3
PHARM	*Guanylurea*	102	positive	−3.6	13.62	−3.85	3
PHARM	Ibuprofen	206.3	negative	3.97	4.8	1.7	3
PHARM	*Metformin*	129	positive	−1.4	12.3	−3.8	3
PHARM	*Metoprolol*	267.37	positive	1.88	14.09	−0.47	3
ICPs	*Naphthalene-1,3,6-trisulfonic acid (NTS)*	368	negative	−1.9	NA	−6.3	3
ICPs	*Naphthalene-1,5-disulfonic acid (NDS)*	288	negative	−0.9	NA	−4.6	3
Herbicide	*Nicosulfuron*	410	negative	0.01	4.5	−2.31	3
PCPs	*Nitrilotriacetic acid (NTA)*	191	negative	−3.8	1.97	−5.92	3
PERF[d]	*Perfluorobutanoic acid (PFBA)*	214	negative	2.4	1.6	−1.2	3
PERF	*Perfluorobutanesulfonic acid (PFBS)*	300	negative	2.4	−3.3	0.2	3
PERF	*Perfluorohexanoic acid (PFHA)*	314	negative	4.4	−0.16	0.15	3
PERF	*Perfluorohexanesulfonic acid (PFHS)*	400.12	negative	4.34	0.14	0.15	3
PERF	*Perfluorononanoic acid (PFNA)*	464	negative	7.3	−0.21	2.84	3
PERF	*Perfluorooctanoic acid (PFOA)*	414.07	negative	4.81	−4.2	1.6	3
PERF	*Perfluorooctanesulfonic acid (PFOS)*	500.13	negative	4.49	0.1	0.66	3
PHARM	*Sotalol*	293.81	positive	0.24	10.07	−1.63	3
PHARM	Sulfamethoxazole	253.3	negative	0.89	6.2	0.1	3

[a] Calculated with ChemAxon software; when pKa (strongest acidic) was not available pKb (strongest basic) was considered.

[b] Calculated with PubChem database and ChemAxon software.

[c] Properties category 1: neutral and hydrophobic (log D > 2); category 2: neutral and hydrophilic (log D < 2); category 3: anionic and cationic OMPs (see Section 2.2).

[d] ICPs: Industrial and consumer products; PHARM: Pharmaceutical; PCPs: Personal care products; PERF: Perfluorinated substances.

drinking water [8,25] and if so, the combination of PAC with other treatments in drinking water treatment plants for removing OMPs received less attention in previous studies.

Usually, for better exploitation of the adsorption capacity and removing the PAC waste easier, the PAC system is designed in combination with other technologies such as biological processes and sand filtration This combination is used in drinking water treatment plants in the Netherlands. Rapid sand filtration (RSF) is an important treatment step in drinking water treatment plants [26]. Although rapid sand filters are not specifically designed for the removal of OMPs, many studies indicated that they have the potential to degrade several different OMPs

[26,27]. These studies reported that for most OMPs adsorption onto sand material [28] and biodegradation by bacteria (autotrophic and heterotrophic) ([26,29] are the most important removal mechanisms by RSF. Although it is challenging to separate the OMPs removal by adsorption from biodegradation in RSF [28], the studies showed that biodegradation is the dominating removal process in RSF [27,30].

As it was mentioned, the removal of OMPs by activated carbon has been of interest to researchers for many years, as well as the capability of RSFs to remove OMPs. However, there is still a lack of information concerning the removal of OMPs by the combination of these treatments: PAC followed by RSF in drinking water treatment. Since PAC –

RSF is used as an important water treatment step in full-scale drinking water treatment plants in the Netherlands, any improvement in the understanding regarding the effect of activated carbon on the adsorption process of OMPs as well as influencing rapid sand filtration in the removal of compounds could be essential for the further understanding of the robustness of this combined PAC – RSF treatment either in the Netherlands or other countries.

In this study, the removal from drinking water of a wide range of OMPs (charged-uncharged) with different physical-chemical properties in PAC followed by RSF treatment was examined. Few studies investigated the removal of OMPs by PAC in drinking water either on a pilot-scale or a full-scale and if so, there is no study in which the removal of OMPs by the combination of PAC with RSF in drinking water has been reported. Therefore, this study is an innovative investigation among drinking water treatment studies focusing on OMP removal. Also, the removal efficiencies of selected OMPs over time which is extremely important in a pilot study were quantified in order to assess the treatment effectiveness. Compounds were classified based on their charge and hydrophobicity. The removal efficiencies of each group by PAC-RSF were quantified and the removal mechanisms of each category were discussed. For achieving these goals, statistical analyses were also applied.

In addition, the influence of biodegradation and adsorption during RSF individually and in combination with PAC treatment has been assessed. To the best of our knowledge, the removal of OMPs by PAC followed by RSF treatment in drinking water has not been reported in any studies and also there is no study considering the removal of charged (anionic or cationic) and uncharged compounds with different physical-chemical properties by PAC-RSF in drinking water treatment. Moreover, with this paper, we report the removal of some specific OMPs by RSF which have never been measured in sand filtration (e.g., naphthalene-1,3,6-trisulfonic acid and naphthalene-1,5-disulfonic acid).

2. Materials and methods

2.1. OMPs selection

The robustness of combined drinking water treatments against emerging substances has been studied for several years in the Netherlands [3,4]. All the measurements in this study were carried out in a pilot plant in which 49 OMPs were dosed, and the removal was measured. The pilot plant used in this study had the same process set up as a full-scale plant (PAC and RSF) applied by the Dunea water company in the Netherlands which supplies drinking water in the province of South Holland. The presented data were extracted from extended pilot trials carried out at Dunea company between 2006 and 2013. The Dunea study was based on PAC followed by RSF at the pilot scale. The OMPs have been selected based on their presence in natural freshwater, their toxicological relevance, their interest in water utilities, and their variation in polarity, molecular weight, and hydrophobicity (Table 1). The

structure and functional groups of the investigated compounds in this study are presented in Section 1 of supplementary materials. Moreover, in order to examine the removal efficiency of OMPs by RSF alone, 29 compounds (out of 49) were dosed into the sand filter column which are shown in Table 1 and have been identified in 'Bold'. These compounds were selected based on substances proposed by the water utilities and exceedance of the drinking water standard or target value in several years between 2008 and 2011 more than twice a year, or frequent detection in concentrations above 50% of the standard or target value.

2.2. OMPs classification

In this study, the selected OMPs were classified based on their charge and hydrophobicity into three categories (Table 1). For describing the hydrophobicity of compounds, the pH-dependent octanol-water distribution coefficient (log D_{OW}) was used. A cut-off value of 2 was used to distinguish between hydrophobic compounds (log D $_{(pH\ 8)} \geq 2$) and hydrophilic compounds (log D $_{(pH\ 8)} < 2$) in line with previous literature [8,54]. Therefore, the OMPs were classified as (1) neutral and hydrophobic compounds (neutral HP); (2) neutral and hydrophilic compounds (neutral HL); and (3) charged (anionic and cationic) compounds. Category (1) included eleven neutral hydrophobic compounds, category (2) included fifteen neutral hydrophilic OMPs, and category (3) consisted of twenty-three charged compounds (Table 1). The physical-chemical properties of the investigated compounds such as molecular weight (MW), charge, water-octanol partition coefficient (log K_{ow}), pKa, and log D are also described in Table 1. Log K_{ow} values were obtained from software KOWWIN and values of pKa, log D and compounds' charge were calculated with ChemAxon software.

2.3. OMPs stock solutions

When creating the stock solutions, it was checked whether the solubility in water of the individual substances was exceeded. Not all substances were an experimental solubility, in which case a theoretical solubility (calculated based on log K_{ow}) was used. Therefore, based on their solubility, selected compounds were divided into three groups. These groups were a soluble group (1) and poorly soluble group (2) and stock solutions were made accordingly. Stock solution (3) consisted of volatile compounds which were added on the day of dosage. Stock solutions 1 and 2 were prepared in 20 L stainless steel tanks filled with 10 L of demineralized water. The weighted compounds were added sequentially and, then, before obtaining a final volume of ~20 L, the demineralized water was added. Stock solutions were kept at 35–40 °C under constant stirring for 4 h, and 4 h at room temperature. However, complete dissolving could not be achieved. Stock solution (3) was prepared in a 20 L stainless steel tank filled with ~15 L of demineralized water. Subsequently, all stock solutions were filtered through a 0.45 μm filter, and demineralized water was added to 20 L by weight in jerry cans. Stock solutions were stored at 3 ± 2 °C until the day of dosage.
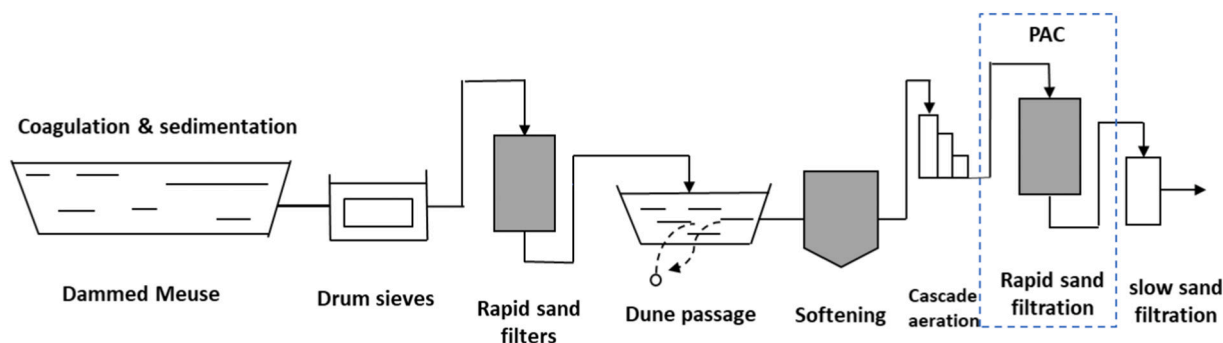

Fig. 1. Schematic diagram of the full-scale drinking water treatment at Dunea water company; dash line shows the PAC-RSF pilot installation.

Table 2
Feed water characteristics of the PAC-RSF pilot installation.

Parameter	Unit	Average concentration	Std. deviation
pH	[−]	8.6	0.07
Temperature	[°C]	13	2.76
Conductivity	[mS/m]	51	4.24
Colour	[mg/L Pt]	8.2	0.28
UV ext. 254 nm	[ext/m]	7.3	0.14
Turbidity	[FTU]	1.7	0.28
DOC	[mg/L C]	2.6	0.07
Ca^{2+}	[mg/L]	45	1.41
Mg^{2+}	[mg/L]	7.7	0.21
HCO_3^-	[mg/L]	182	2.83
O_2	[mg/L]	2.1	0.85
Orthophosphate	[mg/L]	0.2	0.02

Table 3
Physical properties of the used PAC type; Norit SA-super.

Parameters	PAC (Norit)
Skeletal density (g/cm^3) [a]	2.32
Specific pore volume (cm^3/g) [a]	0.52
Avg. particle size diameter (μm) [b]	15
C/H ratio [c]	790
BET surface area (m^2/g) [d]	957
Point of zero charge (PZC) [d]	6.8
Pore size distribution (nm) [d]	0.95 and 10
Specific micropore volume (cm^3/g) [d]	0.30
Specific mesopore volume (cm^3/g) [d]	0.17

[a] [17].
[b] [32].
[c] [35].
[d] [23].

2.4. Analytical method

Spike-in concentrations of the selected compounds (Table 1) were based on the detection limit of the target method, the flow rate of the installation, dosing time, and the maximum removal efficiency. The OMPs were dosed to an influent concentration of 1 μg/L each, except for the perfluorinated compounds, which were dosed to an influent concentration of 0.1 μg/L each. The detailed information about the analytical methods and limit of quantification (LOQ) are described in supplementary materials Section 2. Regarding feed water quality, pH was measured by using the inoLab_IDS multimeter with the WTW pH-Electrode Sentix 940 probe. Electric conductivity (EC) was measured by using the inoLab_IDS measurement as well but with a WTW TetrCon 324 probe. Dissolved organic carbon (DOC) was measured by using a HACH kit (LCK380 range 2–65 mg/L) for the total organic carbon (TOC) kit after the sample was filtered with a 0.45-μm filter. Turbidity was measured by using a turbidity meter (HACH 2100 N). Absorbance was measured using a spectrophotometer (GENESIS 10S UV–Vis) set at a wavelength of 254 nm. The determination of the calcium (Ca^{2+}) and Magnesium (Mg^{2+}) next together in water was done by titration with the sodium salt of ethylenediaminetetraethanoic acid (EDTA) at pH 8. Bicarbonate (HCO_3^-) level was measured by titration with 0.025 N H_2SO_4 with a routine detection limit of 0.1 meq/L. Dissolved oxygen level (O_2) was measured by an electrochemical analysis method (diaphragm electrode method) and the ascorbic acid method was used for measuring total orthophosphate. Absorbance was measured using a spectrophotometer (GENESIS 10S UV–Vis) set at a wavelength of 254 nm.

2.5. Feed water

The pilot plant was fed with Meuse River water, pre-treated in the full-scale plant by coagulation/sedimentation, micro-straining, dual-layer RSF, and managed artificial recharge. Managed artificial recharge of the pre-treated river water was carried out by discharge in infiltration lakes at the dune area. After dune filtration, the water is abstracted, softened in pellet reactors, and aerated in a cascade (Fig. 1). This pre-treated water was used as feed water for the PAC-RSF pilot plant. The quality of feed water is provided in Table 2. The water was pumped from the top of the cascade aeration into a raw water stainless steel buffer vessel (650 L) serving as the feed tank of the pilot. In this buffer vessel, the stock solutions were diluted with the feed water. Mixing was achieved through the feeding pump (3.8 L/h) of the pilot plant and a static mixer in the influent pipe. The treatment scheme is shown in Fig. 1. The average dissolved organic carbon (DOC) concentration of the feed water was 2.6 ± 0.07 mg/L (n = 14). Some studies proved that the combination of pre-treatment such as coagulation-flocculation followed by sedimentation and RSF with PAC treatment greatly decreased the amount of dissolved organic matter (DOM) across all DOM fractions [31]. Since these pre-treatments were applied to the feed water in this study, variations in DOC concentration for the feed water were relatively

small and little effect of these variations on OMP removal is expected.

2.6. Activated carbon characteristics

The type of PAC used in all experiments was Norit SA-Super (Norit), a peat-based activated carbon supplied by JACOBI CARBONS (Cabot Norit Activated Carbon, Amersfoort, Netherlands). It is highly mesoporous (between 2 and 6 nm), which reduces the effect of pore-blocking from adsorption of the dissolved organic carbon (DOC) fraction. Based on literature, this PAC has a maximum microporous size (95% below 3 nm and 64% below 2 nm) which enables the adsorption of OMPs [23]. Moreover, the type of activated carbon used in this study has a hydrophobic nature [32]. The physical properties of the tested PAC type Norit are shown in Table 3. The surface functional groups of activated carbon influence ion adsorption. The functional groups of Norit SA-Super used in this study are provided in supplementary materials Section 3. The acidic sites at the surface of Norit SA-super activated carbon contains carboxyl (Ar-COOH), phenol (Ar-OH), carbonyl (Ar-C=O), anhydride (Ar-(C=O-O-O=C), ether (Ar(—O—)Ar'), quinone (O = Ar = O), and lactone groups (Ar-C=OO-Ar') [23] and the basic sites are mostly attributed to the π electron-rich regions situated on basal planes [33] and the intrinsic properties of the ash [34]. The phenol and carbonyl densities are higher than other groups such as carboxyl and anhydrides. The presence of these functional groups makes the carbon surface more polar and the affinity for the formation of hydrogen bonds (H-bonds) through the water will increase [23]. The point of zero charge (PZC) value for this activated carbon is at a pH of 6.8 [23]. The Boehm analysis shows that the concentration of acidic sites is 1.5 μmol/m^2 and the concentration of basic sites is 1.3 μmol/m^2 in this type of activated carbon [23].

2.7. Set-up pilot installation

The pilot plant used in this study had the same process set up as a full-scale plant in the Netherlands. The RSF column used for the dosing experiment had an internal diameter of 25 cm and was filled with sand and anthracite. The filter bed height of the sand filter during the experiment was 80 cm sand and 50 cm anthracite. Before starting the experiment, the filter was flushed with a flow rate of approximately 2.8 m^3/h. To achieve a filtration rate of 5 m/h, a feed flow of 0.245 m^3/h (245 l/h) has been used. The desired amount of PAC was placed as a slurry, at the top of the filter, representing a dosage of 2 mg/L over a run time of one week (in total 82 g PAC). This represents the full-scale installation (adding a PAC slurry after a weekly flushing event). A 650L stock solution was used for a one-week dosing experiment. The stock dosing flow was 3.8 L/h and was added to the feed flow. The OMPs were continuously spiked in the influent for 7 days. The effluent was measured after day 1 (24 h), day 4, and day 7. The total contact time of the PAC-RSF was approximately 15 min. All samples were taken in

Table 4
Removal and number of measurements (n) of OMPs by PAC-RSF during the one-week experiment.

Compound	n	Removal (%)		
		day 1	day 4	day 7
NMOR	2	0.1	2	1.2
MTBE	2	0.6	2	11.1
NTS	4	1.5	0.1	1.5
PFBA	4	1.6	0.4	3.3
T-butylalcohol (TBA)	2	2.2	10	2
NDMA	2	2.7	NA	2
1,4-dioxane	2	3.3	28.9	7
PFBS	4	4.1	0.1	0.2
Metformin	4	5	0.5	1.9
PFHA	4	5.5	0.3	0.7
NDS	4	13.4	0.1	0.1
Acesulfame-K	4	19.8	5.1	5.6
PFHS	4	24	0.1	0.1
ETBE	2	37.4	2	16.2
PFNA	4	50	5.5	1.5
PFOA	2	50	1.1	2
Nicosulfuron	4	57.3	15	9.9
Guanylurea	4	57.9	20.8	9.5
PFOS	2	60.3	25	15.3
Amidotrizoic acid	2	73	2	2
NTA	4	76.9	78.2	83.3
2,4-D	4	78.1	41.3	25.4
DBP	2	80	80	80
S-Metolachlor	4	80.9	55.1	39.6
Bisphenol S	2	82.5	77.4	76.8
Diglyme	2	83	2	2
Isoproturon	4	85.8	63.2	45.2
Sulfamethoxazole	2	86.1	19.7	33.6
Iopamidol	2	86.9	2	4
Diclofenac	2	87.2	69.8	53.7
Atrazine	2	88	72.3	49.4
4-Methyl-1H-benzotriazole	4	88.5	66.3	43.2
DEP	2	90.2	95.5	80
5-Methyl-1H-benzotriazole	4	91	71.1	52
Chloridazon	4	91.5	74.4	59.1
Pentoxifylline	4	91.5	74.9	61.4
Carbamazepine	2	91.9	80.9	63.4
Carbendazim	2	92	99.1	98.9
Sotalol	2	92.1	62.4	64.8
Chlortoluron	4	93.7	78.8	64.8
Diuron	4	97	87.1	77.2
Erythromycin	2	97.3	91.7	66.7
Ibuprofen	2	97.4	61.5	NA
Metoprolol	2	97.4	89.6	87.4
Dimethenamid	2	97.8	89.2	52.2
Triglyme	2	98.2	49	23
TCEP	2	98.9	84.5	19.6
Estrone	2	99	99	NA
Bisphenol A	2	99.5	99.5	NA

NA: not available.

replicate. The RSF experiment without PAC dosing is performed in a similar way as the RSF experiment with PAC dosing and sampling took place one day after the start of the spiking.

2.8. Assessment of solute removal

OMPs removals were calculated according to Eq. (1) where R (%) is OMP removal (%), C_{in} is OMP influent concentration (μg/L), and C_{out} is OMP effluent concentration (μg/L).

$$R\ (\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \tag{1}$$

Moreover, since the OMPs concentrations were measured in several replicates, to determine the average OMPs removal of the measured replicates, the specific OMP removal percentages were transformed to a logit-scale through Eq. (2) in order to obtain the normal distribution of the data. After determination of the average of the logit transformed

removal, this value is transformed back to a percentage removal.

$$Logit\ (R) = ln\left(\frac{R}{1-R}\right) \tag{2}$$

where R is the value of OMPs removal.

2.9. Statistical analysis

As explained in Section 2.6, the measurements were carried out at three specific times during one week (after days 1, 4, and 7). A repeated measures ANOVA with a Greenhouse-Geisser correction was used to determine if there were statistically significant differences between OMPs removal during the one-week experiment. A Bonferroni post-hoc test was used for conducting multiple comparison tests on a repeated measures ANOVA. Afterward, one-way ANOVA was applied to categories 1, 2, and 3 explained in Section 2.2 in order to test the hypothesis that the three groups of compounds distinguished by their charge and hydrophobicity had the same removal means. The Tukey Honestly Significant Difference (HSD) test was used for conducting multiple comparison tests on a one-way ANOVA. Moreover, The Spearman correlation was applied in order to find the relationship between the physical-chemical properties of compounds and their removal efficiencies.

3. Results and discussion

3.1. Removal of compounds

The removal of compounds was calculated, and the results are shown in Table 4. The removal of the selected OMPs by PAC-RSF was determined on day 1, day 4, and day 7 (Table 4 and Fig. 2). As discussed in the introduction, activated carbon and RSF may contribute both to the removal of OMPs. For the majority of compounds, the average removal efficiency after 1 day (24 h) filtration was higher than after 4 and 7 days, because of the better adsorption onto the freshly dosed PAC in day 1. Moreover, due to the long duration of the test (7 days), the RSF was heavily loaded with the dosed substances over the time and the filter material, either by adsorption or biodegradation, or both, contributed less to the OMPs removal. Also, the competition between OMPs and NOM might cause the reduction of removal on days 4 and 7. As a result, the observed removal decreases over the time for 41 out of 49 OMPs within a test.

The exceptions were 1,4 dioxane, DEP, MTBE, NTA, PFBA, TBA for which the removal on day 4 and day 7 was slightly higher than on day 1. However, this indicates that a PAC dose of 82 g at the start (equivalent for continuous dosing of 2 mg/L for 7 days) provided after 24 h a maximum removal efficiency for 41 out of 49 OMPs in this study showing the time-dependence of the removals and obviously the adsorption capacity of PAC decreased with increasing running time. This finding is in line with robust statistical test results. A repeated measures ANOVA with a Greenhouse-Geisser correction was applied to determine the statistical differences between the removal values of OMPs measured after 1 day, 4 days, and 7 days. The result showed that the mean score for removal of OMPs at different time points was significantly different ($p < 0.001$), meaning that the OMP removal in the PAC-RSF decreased statistically in time during the one-week experiment (Table 5).

Post-hoc tests using the Bonferroni correction revealed that the OMPs dosing experiment for 7 days with a constant amount of PAC on top of the filter caused a reduction in OMPs removal efficiency from day 1 to day 7 (62% vs 33.3% respectively), which was statistically significant (Table 5). Therefore, we can conclude that a long-term OMP dosing experiment (more than 24 h) with a constant amount of PAC on top of the filter elicits a statistically significant reduction in average removal efficiency of substances from 62% to 33% after 4 days and 7 days of OMP dosing, respectively. As a result, the highest removals of OMPs were
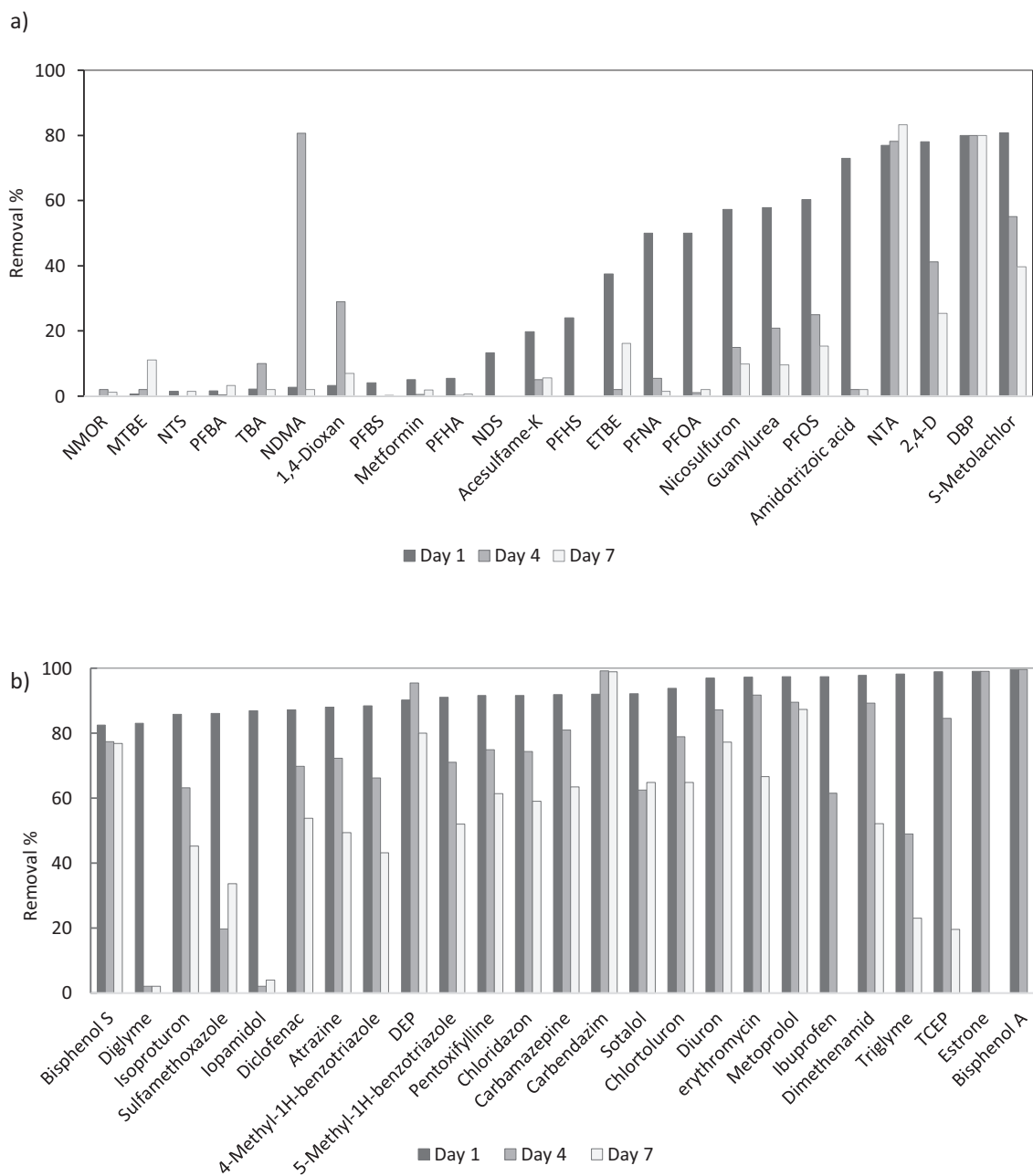
a)

b)

Fig. 2. Comparison of OMPs removal by PAC-RSF during the one-week dosing experiment.

Table 5
The results of repeated measured ANOVA test between removal of OMPs by PAC-RSF after 1 day, 4-day and 7-day.

(I) removal	(J) removal	Mean Difference (I-J)	Std. Error	Significance[a]	95% Confidence Interval for Difference[a]	
					Lower Bound	Upper Bound
Day 1	Day 4	20.3[*]	3.57	0.000	11.46	29.20
	Day 7	28.7[*]	3.84	0.000	19.18	38.31
Day 4	Day 1	−20.3	3.57	0.000	−29.20	−11.46
	Day 7	8.4	2.11	0.001	3.17	13.66
Day 7	Day 1	−28.7	3.84	0.000	−38.31	−19.18
	Day 4	−8.4	2.11	0.001	−13.66	−3.17

Based on estimated marginal means.
 [*] The mean difference is significant at the 0.05 level.
  [a] Adjustment for multiple comparisons: Bonferroni.

Table 6

Results of Tukey's HSD test between three properties category, the significant mean differences between categories are in bold.

Dependent Variable: removal %						
Tukey HSD						
(I) category	(J) category	Mean Difference (I-J)	Std. Error	Significance Level*	95% Confidence Interval	
					Lower Bound	Upper Bound
neutral HP	neutral HL	31.85*	13.49	**0.04**	−0.82	64.52
	charged	39.63*	12.72	**0.00**	8.82	70.43
neutral HL	charged	7.77	11.31	0.77	−19.63	35.19

* The mean difference is significant at the 0.05 level.
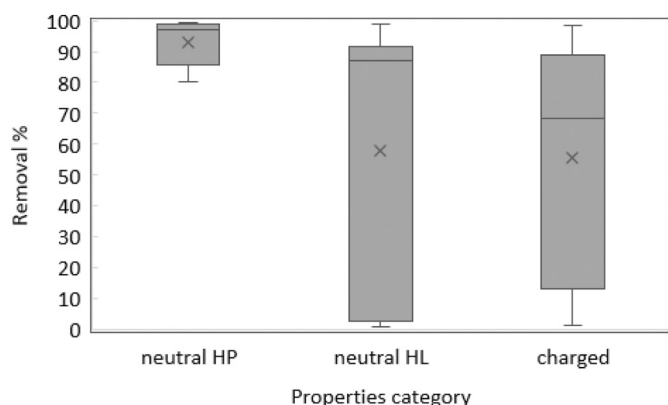
Fig. 3. Box-and-Whisker plot of OMP removal range after 1-day dosing on PAC-RSF for property categories.

achieved after 1-day dosing indicating that the OMPs removal in our study was highly dependent on a dosing time. However, other factors (e. g., compound's properties) might influence the OMPs removal in addition to the dosing time. Thus, the role of charge and hydrophobicity of OMPs in the optimal dosing time (24 h) were assessed by applying a one-way ANOVA statistical test. Therefore, this study will continue to focus on the highest removal of compounds after 1-day dosing (24 h).

Despite the dosing time, several studies reported the reduced capacity of activated carbon during OMPs adsorption due to the competitive adsorption between NOM and OMPs during treatment. However, wastewater has a higher potential for direct adsorption competition than surface water since wastewater NOM contained fractions with smaller molecular weight than surface water NOM, indicating a higher potential for adsorption competition [36]. Therefore, the lower influence of NOM on OMPs removal in surface water was expected. Although there was a

competition between OMPs and NOM in this study which affected the decrease in adsorption of OMPs on day 1, day 4, and day 7, our focus was on the different behavior of OMPs on the first-day dosing (relatively fresh PAC) rather than a competition between OMPs and NOM.

The one-way ANOVA test was run based on three compound categories explained in Section 2.2; neutral hydrophobic (HP) OMPs, neutral hydrophilic (HL) OMPs, and charged OMPs. The result indicates that there was a significant difference between the removal of compounds (after 1-day dosing) in terms of their charge and hydrophobicity (p-value = 0.01). The result of Tukey's HSD test with the significance level among three categories is presented in Table 6. These results show that there was a significant relationship between OMPs removal by PAC-RSF and charge and hydrophobicity of compounds. These physical-chemical properties might control the adsorption mechanisms of investigated compounds in this study. Tukey's multiple comparison test showed a significant difference between category 1 (neutral HP) and 2 (neutral HL) with a p-value equal to 0.04 meaning that hydrophobicity played a role in the removal of neutral compounds (Table 6). Also, there was a significant difference between category 1 and category 3 (charged OMPs).

(p-value <0.001) indicating the influence of charge on compound removal whereas the mean removal difference between categories 2 and 3 (p-value = 0.77) was found not significant.

These results illustrate that there was a significant relationship between OMPs removal by PAC-RSF and charge and hydrophobicity of compounds and these physical-chemical properties might control the adsorption mechanisms of investigated compounds in this study. With regards to the three compound categories, the box and whisker plot was generated based on OMPs removal values (Fig. 3). The results highlight the higher removal of neutral HP OMPs compared to neutral HL and charged compounds. Therefore, the influence of charge and hydrophobicity on OMPs removal is discussed in detail.
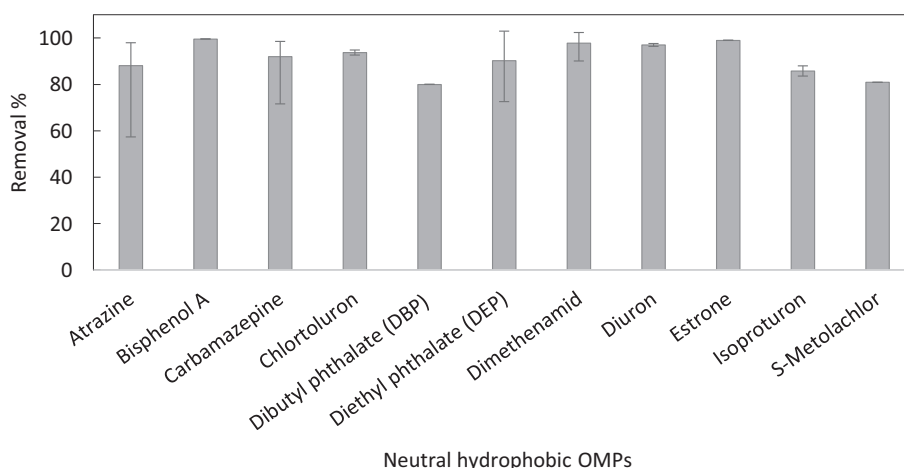
Fig. 4. Removal of neutral and hydrophobic OMPs by PAC-RSF on day 1.
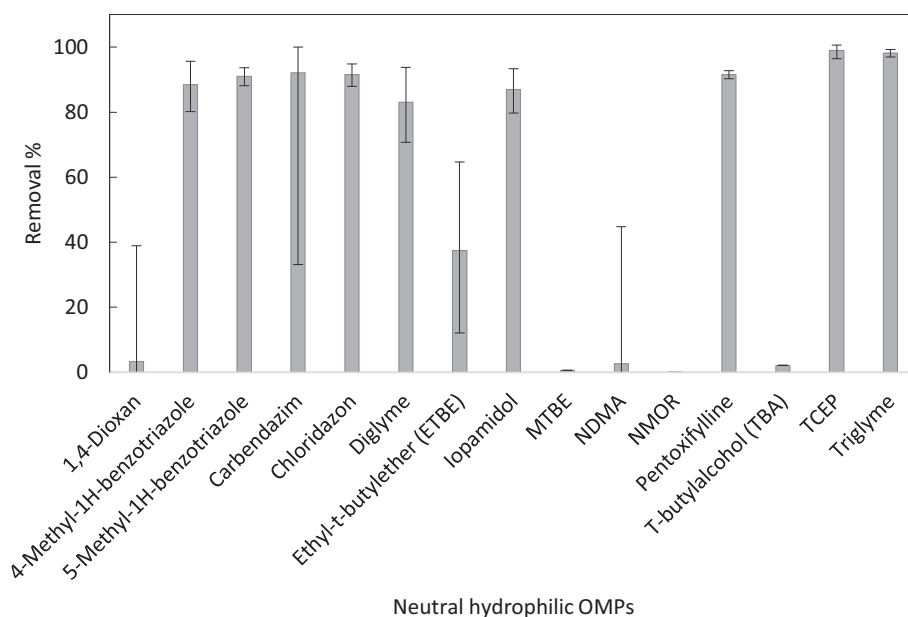
Fig. 5. Removal of neutral and hydrophilic OMPs by PAC-RSF on day 1.

3.2. Removal of neutral and hydrophobic compounds (category 1)

The neutral and hydrophobic OMPs were highly or moderately removed (> 80%; Fig. 4). Adsorption of hydrophobic OMPs onto PAC was initially assumed to be driven by hydrophobic interactions between the hydrophobic part of OMPs and activated carbon [6,8]. Moreover, competing hydrophobic adsorption interaction of DOM with hydrophobic OMPs on PAC can decline the removal of hydrophobic compounds [8]. Although DOM impacts on OMPs adsorption removals, the low impact was expected because of the low concentration of DOC in our study (2.6 mg/L). Activated carbon adsorbents are effective for non-polar neutral compounds [37], but their affinity towards very polar substances was different depending on polar functional groups. Therefore, for non-polar compounds such as estrone, S-metolachlor, DBP, DEP (see Table S1) with high removal efficiency (> 80%) the hydrophobic interactions control the mechanism of adsorption. On the other hand, for compounds that are polar and hydrophobic, both hydrophobic interactions and polar interactions contribute to the removal mechanism while the polar interactions are essentially stronger than hydrophobic interactions. For instance, diuron is insoluble and hydrophobic with a large dipole moment. Therefore, adsorption of hydrophobic parts of diuron on a hydrophobic surface of PAC as well as π-π interactions between the graphene layer of PAC and aromatic rings on diuron would increase the removal of this compound (98%). Also, atrazine was highly removed (88%). For this compound in addition to the hydrophobic interaction and π-π interaction, the amine groups in the structure of this compound (Table S1) were able to establish an H bond with H donor functional groups (O—H) of PAC. However, the side-chain in the atrazine structure might provide the steric effect which slightly decreased its removal efficiency [6]. A high removal was also observed for bisphenol A (99.5%). This could be explained by π-π electron-donor-acceptor interaction between the aromatic ring of phenol and the aromatic structure of the graphene layers in PAC. Moreover, when the adsorption process was governed by non electrostatic interactions, the pore size distribution of PAC and molecular size of the OMPs are also important factors. The minimum microporous size of activated carbon used in this study is 0.95 nm meaning that activated carbon pores are accessible for compounds having a length and width less than this value. Therefore, the microporous filling mechanism can improve the adsorption process of compounds whose dimension approaches the pore width (0.95 nm) of activated carbon. For instance, dimethenamid's length (0.91 nm) and

width (0.65 nm) are less than the microporous size of activated carbon used in this study and its removal efficiency was 97.8%. Therefore, in addition to the hydrophobic interaction, the microporous filling mechanism improved the removal efficiency of this compound.

3.3. Removal of neutral and hydrophilic compounds (category 2)

Although activated carbon is more effective for the removal of hydrophobic compounds [8], the majority of neutral and hydrophilic compounds in this study were highly or moderately removed (> 80%) with the exception of 1,4-dioxane (3.3%), MTBE (0.64%), NDMA (2.7%), NMOR (0.14%) and TBA (2.2%) (Fig. 5). Since there was no correlation between the hydrophobicity and adsorption affinity for activated carbon for hydrophilic compounds [8], the removal of neutral and hydrophilic compounds mostly included π-π interactions [12] and hydrogen bonds [38].

For instance, the π-π interactions between the electrons of the aromatic ring and the graphene layers of activated carbon caused the high removal of 4-Methyl-1H-benzotriazole and 5-Methyl-1H-benzotriazole (> 88.5%). As mentioned before, for neutral compounds with no electrostatic interactions, the molecular weight and the molecular structure of compounds as well as the pore width of activated carbon can play a role in the adsorption process. Since the dimensions of 4-Methyl-1H-benzotriazole and 5-Methyl-1H-benzotriazole (length and width < 0.62 nm) approached the pore width of the PAC (0.95 nm), the contact area between these hydrophilic compounds and the surface of activated carbon increased, leading to stronger adsorption by the microporous PAC. In previous studies, iopamidol is often reported as weakly adsorbable [39], whereas in our experiment a high affinity for activated carbon (87% removal) was shown. This disagreement with the literature can be explained by the presence of background organic matter and different activated carbon pore sizes in their experiments. In our study, a lower concentration of dissolved organic carbon (DOC = 2.6 mg/L) may have led to higher adsorption of iopamidol to activated carbon. The high removal efficiencies of the most hydrophilic compounds in this study, such as carbendazim (92%), diglyme (83%), and triglyme (98%), have been attributed to the presence of electron-donating groups attached to their structures which have a high affinity for the activated carbon surface. In contrast, Norit PAC was not effective for adsorption of highly soluble compounds with low octanol-water partition coefficient (K_{ow}) values such as 1,4 dioxane, MTBE, and TBA (removal <3%) because
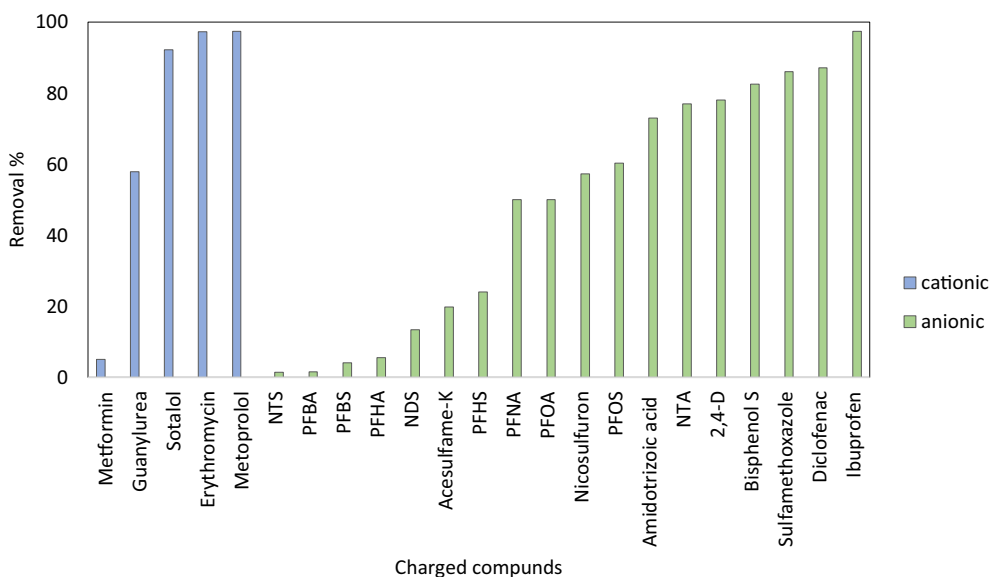
Fig. 6. Removal of charged OMPs by PAC-RSF on day 1.

these compounds tend to stay in the aqueous phase [40].

The removal of N-nitrosamines by Norit PAC was also measured and the removal efficiencies were low (removal <3%). Beita-Sandí et al. [41] found that N-nitrosamines were able to access pores less than 1 nm and the basic activated carbon ($pH_{PZC} > 8$). Moreover, hydrophilic compounds with cyclic structures can adsorb to activated carbon to a larger extent than a linear or globular structure, e.g. NDMA, NMOR, MTBE [12]. Therefore, while the pore width of Norit PAC (0.95 nm) would be accessible for NDMA, the globular structure of this molecule might restrict the available molecule surface for interaction with activated carbon leading to low adsorption. Moreover, the acidic surface chemistry ($pH_{pzc} = 6.9$) of Norit PAC was another reason for the poor removal efficiency of these OMPs.

3.4. Removal of charged compounds (category 3)

Generally, the charged compounds are subject to electrostatic attraction or repulsion with the surface of PAC, depending on the point of zero charge of the activated carbon and pH value of the aqueous solution. Activated carbon with the content of acid groups like Norit (Table S3) presents the pH_{PZC} below 7 [23] meaning that at a pH of 6.8 the surface of the Norit activated carbon is neutral. At a pH value above this value, the electric charge of the PAC is negative. Therefore, at the pH of the solution (pH = 8.6) and because of the deprotonation of phenols and carboxylic acids groups (releasing the H^+) of PAC, the surface of the Norit PAC was negatively charged (pH > pH_{PZC}) which resulted in mostly cation attraction.
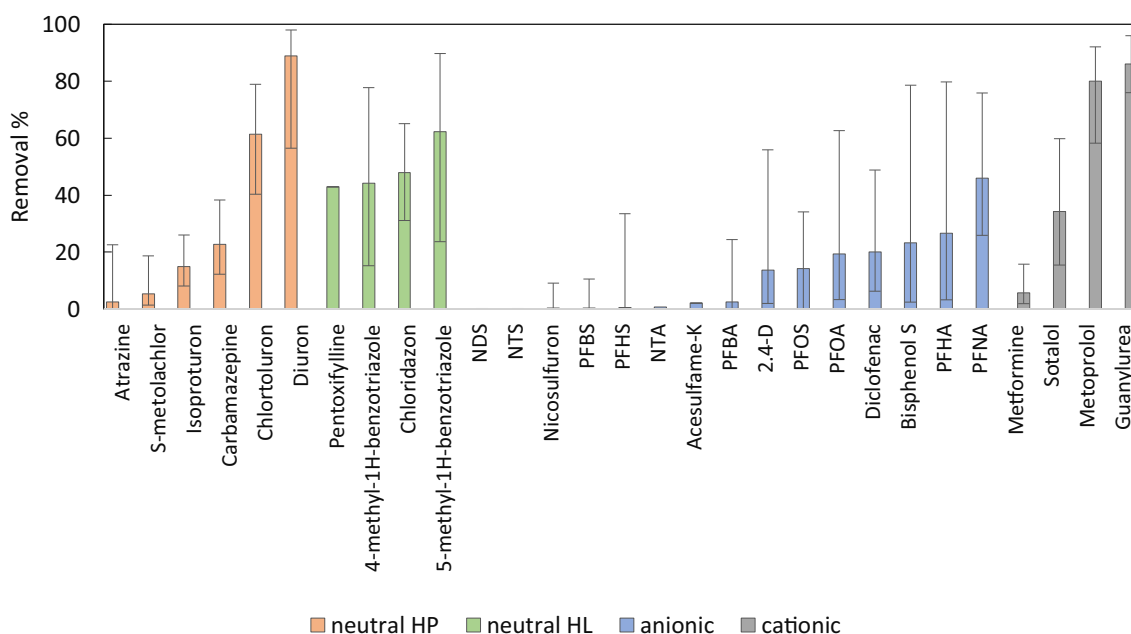

Fig. 7. Removal of selected OMPs by RSF distinguished by their charge (anionic & cationic) and hydrophobicity.

At pH 8.6, erythromycin, guanylurea, metformin, metoprolol, and sotalol are positively charged and the remaining OMPs in Fig. 6 are negatively charged. Most of the cationic compounds in our study showed a high affinity for PAC (removal >92%). This seems likely due to electrostatic interactions between cationic compounds and the negative surface of Norit PAC. However, guanylurea and metformin showed moderate and poor removal (57% and 5%, respectively) by PAC. Other studies [42,43] obtained similar results regarding the limited suitability of activated carbon for the removal of metformin and guanylurea from drinking water. This might be related to their non-cyclic structures leading to a rapid breakthrough of metformin and its metabolite guanylurea [43]. Remarkably, the removal of guanylurea by only RSF was significant (87.5%; Table S3) which will be explained in Section 3.5.

The removal of anionic OMPs varied and was highly dependent on the solute pH value which is the main controlling parameter in the adsorption process of anionic OMPs [24]. The pH of the solution affects the ionic strength as well as the surface charge of PAC which caused the specific interactions (electrostatic attraction or repulsion) between the ions and the surface of activated carbon. Since the Norit PAC in this study was negatively charged, the interactions between anionic OMPs and the surface of PAC were more repulsive. However, the presence of aromatic rings (e.g., diclofenac, ibuprofen, 2.4-D, bisphenol S) or amine groups (e.g., sulfamethoxazole) in the structure of anionic compounds could produce the electron donor-acceptor complex formation and π-π dispersion interactions with the functional groups of PAC which increase the removal (>86%). However, for the aromatic compounds containing sulphonic groups such as NDS, NTS, and nicosulfuron, the interactions with activated carbon became weaker because of the presence of oxygenated groups, e.g. carboxylic, on the surface of activated carbon. The higher removal of NDS (13.4%) compared with NTS (1.5%) can be explained by the lower number of sulphonic groups in the NDS structure (Table S1). Removal efficiencies of perfluorinated compounds (PFASs) ranged from 1.57% to 60.3%. The highest removals were observed for PFNA (50.0%), PFOA (50.0%),and PFOS (60.3%). However, these values were much lower than the reported removal in other studies [44,45]. The different removal rates could be attributed to the different particle sizes of activated carbon materials and a lower solute pH which influence the surface charge of PAC and adsorbate charge. Generally, the sorption capacity for PFOA and PFOS decreases with increasing solution pH [45], since higher pH values exceed the pKa of PFASs leading to electrostatic repulsion between the anionic compounds and negative surface of PAC. Moreover, the carbon chain length of PFASs is the most important structural feature influencing the removal of these compounds [46]. The ability of adsorption would be higher for PFASs with longer carbon chains such as PFNA, PFOA, PFOS ($C \geq 8$) compared to short chain PFASs, such as PFBA, PFBS, PFHS ($C \leq 6$) because of increasing the sorption coefficient (K_{oc}) values.

It should be mentioned that in Sections 3.2, 3.3, and 3.4 mostly the mechanisms of removal by PAC have been discussed while the influence of RSF on the removal of OMPs should not be neglected. Next, in Section 3.5, the influence of RSF on the removal of OMPs has been considered in more detail.

3.5. Influence of RSF on OMPs removal

In order to investigate the influence of RSF on the removal of OMPs in this study, 29 OMPs were directly dosed into the filter column without PAC. The removal of selected OMPs by RSF was quantified and shown in Fig. 7 and Table S4 of supplementary materials. Our results indicated that RSF has the potential to remove OMPs. This is in line with studies demonstrating the removal of some OMPs by RSF [26,29]. In this study, the removal of selected OMPs by RSF varied from 89% to 0.14%. Diuron, guanylurea, and metoprolol were highly removed (> 80%) by RSF. However, the majority of compounds were moderately (62%–19%) or poorly (less than 15%) removed (Fig. 7). The involved removal mechanisms by RSF encompass a complex mixture of physical-chemical
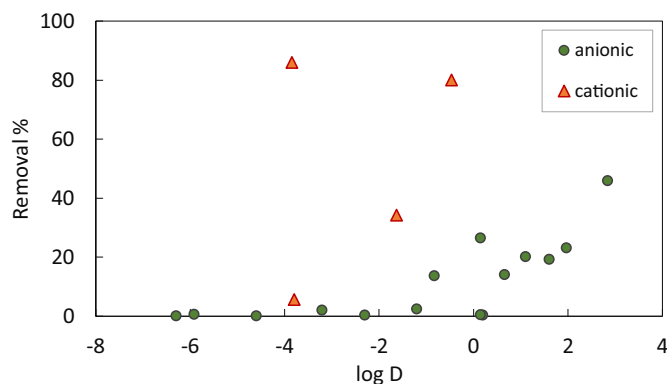
Fig. 8. Removal of charged (anionic & cationic) OMPs by RSF as a function of their log D.

processes, e.g. adsorption onto sand material, and biological processes [28]. However, since sand is not a good adsorbent material, the adsorption of OMPs onto the sand particles mainly correlated with the retention time [47]. In RSF with biological activity occurring, it is challenging to separate OMPs removal by biodegradation from adsorption onto the sand. In our study, the overall retention time in the RSF was short, 15 min, this could indicate that for most selected OMPs, biodegradation is a more dominant removal mechanism than adsorption onto the sand. This result is in agreement with other studies showing that biodegradation was the most important removal mechanism in RSF treatment [29,48].

The biodegradation rate of OMPs can be related to their charge, hydrophobicity, and functional groups in their structures while the influence of the functional group's characteristics is more dominant [29]. Therefore, to get more insight into the removal mechanism by RSF, OMPs were classified into three groups based on their charge and hydrophobicity (neutral HP, neutral HL, and charged compounds) as explained in Section 2.2 (Fig. 7). Regarding the neutral OMPs in this study, no clear trend between hydrophobicity of compounds expressed as log D and their removal efficacies by RSF was observed. Also, the spearman correlation between log D and removal values was not significant ($r = 0.2$, p-value $= 0.65$). This result is in line with several studies that reported the low removal of neutral compounds in biological processes [26,29]. For instance, atrazine was not or very poorly biodegraded in other sand filtration studies [49,50] and showed very poor removal (2.5%) in this study. Also, the persistent behavior (removal 22.7%) of carbamazepine shown in this study is in line with previous studies [49,51].

However, the removal of neutral compounds with hydrophilic characteristics (between 43% and 62%) was higher than that of neutral hydrophobic compounds (between 2.5% and 22%). The only exceptions were chlortoluron (61%) and diuron (88%) which were well removed despite their hydrophobic characteristics. This might be because of their functional groups present within the chemical structure [29]. Regarding the charged compounds, There was a correlation between log D and removal of anionic OMPs which was strongly and positively significant ($r = 0.72$, p-value = 0.002). Charged anionic compounds with higher log D represented a higher removal efficiency by RSF than the OMPs with a lower log D (Fig. 8).

For instance, perfluorinated compounds (PFBS, PFHS, PFBA, PFOS) with low log D (<0.15) showed a poor removal in RSF (Fig. 7) compared to PFNA with higher log D (=2.84) with 46% removal efficiency. Other studies also reported very poor or no removal efficiencies of PFASs by sand filters as a result of hydrophilic characteristics [44,52]. The relationship between cationic compounds and their log D, although limited to four compounds only, suggests an increasing removal trend with increasing log D for most of the compounds (Fig. 8).

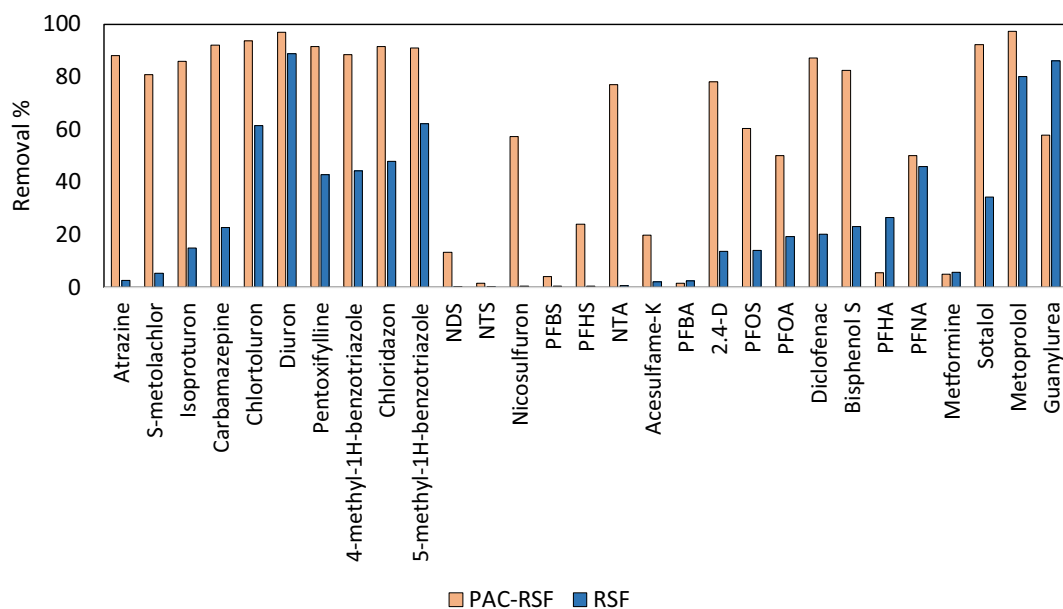Despite the hydrophobicity, characteristics of the OMP functional

Fig. 9. The comparison between OMPs removal by PAC-RSF and RSF.

groups may be strongly linked to their biodegradability. Carbonyl and ether groups contribute positively to the biodegradability of compounds while amine groups, ring structures, aliphatic ethers, and sulfur will decrease the biodegradability [29]. In this study, this was clearly shown by chlortoluron (61%), diuron (89%), metoprolol (80%), and guanylurea (86%) which displayed the highest removal efficiencies by RSF. These OMPs all have carbonyl and ether groups present in their structures (Table S1). This is also a reason for the lower removal of metformin (5.6%) than guanylurea which is the main metabolite of metformin. The presence of the carbonyl group in the guanylurea structure increased its biodegradability. Also, the presence of sulfur groups and aromatic rings in the structure of NTS, NDS, and nicosulfuron (Table S1) may be responsible for very poor removal values (< 0.4%) of these compounds. In addition, perfluorinated compounds (PFASs) which contain sulfonic acid in their structure (PFBS, PFHS, PFOS) showed a lower removal (< 4%) compared to the PFASs with carbonyl groups (PFNA, PFHA, PFOA), which were removed around 46%. In addition to the aromatic rings, compounds containing amine groups such as atrazine (2.5%) and diclofenac (20%) were removed poorly by RSF. More than the charge and hydrophobicity of OMPs, as discussed earlier in this subsection, the functional groups of both neutral and charged compounds influenced significantly the removal values.

In order to determine whether the RSF collaborated in the removal of OMPs by PAC-RSF, Fig. 9 was prepared. As expected, for the majority of compounds the removal efficiency by PAC-RSF treatment was higher than the RSF individually except for PFHA, PFBA, and guanylurea. This result is in accordance with previous studies [43] in which the removal efficiency of guanylurea was most likely be achieved in the sand filtration unit rather than in activated carbon treatments. Thus, in this study, the high removal of guanylurea by PAC-RSF (57%) was achieved by the biodegradation and sorption onto sand filter more likely than adsorption onto PAC. Furthermore, PFHA and PFBA were removed better by RSF than by PAC-RSF. As it was pointed out before, activated carbon was not a good absorbent for these compounds and biodegradation might be a dominant removal mechanism of this compound as a result of the presence of carbonyl group in their structures. Consequently, since

activated carbon alone was ineffective in removing guanylurea, PFHA, and PFBA, the RSF can significantly improve their removal efficiency. Although the removal of OMPs by RSF was associated with their charge, hydrophobicity, and functional groups, some OMPs can be biologically removed from drinking water in RSF either individually or in combination with other treatments such as PAC.

4. Conclusions

In the studied PAC-RSF pilot installations at Dunea drinking water company, during one-week continuous OMP dosing experiments, most OMPs (27 out of 49) were removed to a large extent (> 80%) in the first 24 h, and afterward, the removal significantly decreased. Statistical analysis revealed that OMP removal by PAC-RSF not only highly depends on the dosing time but also the charge and hydrophobicity of compounds influenced significantly the OMPs removal. Neutral and hydrophobic compounds showed the highest removal between 80 and 99.5% (91.2% on average) followed by the neutral and hydrophilic compounds which were removed for 59.4% on average. The charged compounds displayed 0.14% as the lowest removal and 97.4% as the highest removal (51.6% on average). The removal of OMPs by only RSF revealed that while some OMPs were removed in the sand filters, the efficiency of treatment would be higher in the presence of PAC. Also, the combination of PAC and PSF treatments improved the removal efficiency of some compounds (e.g., metoprolol and guanylurea). However, none of the investigated pilot installations in this study is capable of removing all dosed OMPs to a large extent which implies that always a combination of processes is required for the removal of all OMPs in full-scale treatment. Removal of some OMPs in RSF (e.g. naphthalene-1,3,6-trisulfonic acid and naphthalene-1,5-disulfonic acid) was described for the first time in this study. However, these compounds showed poor removal with RSF. Consequently, for OMPs that show no or moderate removal in the investigated processes in the different pilots of the current study, removal efficiency in the remaining processes of the full-scale drinking water treatment plant should be assessed more to prevent their presence in drinking water.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2022.102792.

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