Biodegradation and adsorption of micropollutants by biological activated carbon from a drinking water production plant

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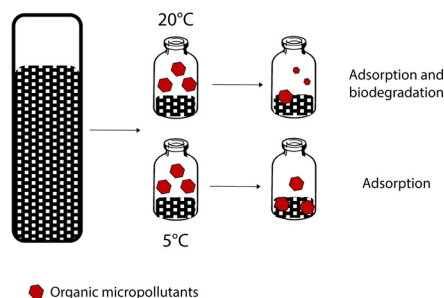[b] Wageningen Food Safety Research – Wageningen University & Research, P.O. Box 230, 6708 WB, Wageningen, the Netherlands
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GRAPHICAL ABSTRACT

ABSTRACT

The presence of micropollutants in surface water is a potential threat for the production of high quality and safe drinking water. Adsorption of micropollutants onto granular activated carbon (GAC) in fixed-bed filters is often applied as a polishing step in the production of drinking water. Activated carbon can act as a carrier material for biofilm, hence biodegradation can be an additional removal mechanism for micropollutants in GAC filters. To assess the potential of biofilm to biodegrade micropollutants, it is necessary to distinguish adsorption from biodegradation as a removal mechanism. We performed experiments at 5 °C and 20 °C with biologically active and autoclaved GAC to assess the biodegradation of micropollutants by the biofilm grown on the GAC surface. Ten micropollutants were selected as model compounds. Three of them, iopromide, iopamidol and metformin, were biodegraded by the GAC biofilm. Additionally, we observed that temperature can increase or decrease adsorption, depending on the micropollutant studied. Finally, we compared the adsorption capacity of GAC used for more than 100,000 bed volumes and fresh GAC. We demonstrated that used GAC shows a higher adsorption capacity for guanylurea, metformin and hexamethylenetetramine and only a limited reduction in adsorption capacity for diclofenac and benzotriazole compared to fresh GAC.

1. Introduction

Anthropogenic organic micropollutants have been detected in surface water worldwide (Christoffels et al., 2016; Reungoat et al., 2010; Starling et al., 2019), threatening production of safe drinking water. Micropollutants consist of a wide range of compounds, such as pharmaceuticals, industrial chemicals, pesticides, as well as their transformation products. These compounds often enter into the environment via the effluent of a wastewater treatment plant (WWTP) and diffuse sources, such as stormwater runoff, sewer leakage and sewer overflow (Han et al., 2019). An unknown fraction of micropollutants in the environment is adsorbed to sediments or organic matter, or transformed via biotic and abiotic reactions. The fraction that is not removed, can end up in the feed water used for drinking water production (Mompelat et al., 2009).

Micropollutants are partially removed in a drinking water treatment plant (DWTP) from surface water sources by adsorption onto granular activated carbon (GAC) in fixed-bed filters (Stackelberg et al., 2007; Ternes, 2007; Ternes et al., 2002). GAC has also been applied at pilot scale in filters and fluidized bed reactors for removing micropollutants from wastewater (Altmann et al., 2016; Guillossou et al., 2018; Mailler et al., 2016). Apart from adsorbing the micropollutants, GAC also functions as a carrier material for biofilm. As a result, micropollutants are concentrated on the GAC surface, which results in an increased contact time between the compounds and microorganisms (Çeçen and Aktaş, 2012), and higher likelihood of biodegradation. Biodegradation is therefore an alternative pathway for removing micropollutants in GAC applications. The extent to which a micropollutant will be adsorbed to GAC and eventually be biodegraded depends on the reversibility of adsorption and on the potential of the biofilm to biodegrade the micropollutant (Abromaitis et al., 2016).

Distinguishing between adsorption and biodegradation as removal mechanisms in GAC filters is required in order to assess the potential of the biofilm in these filters to biodegrade micropollutants. Furthermore, this knowledge contributes in determining limiting factors for micropollutants biodegradation in the current GAC filters. In adsorption studies with fresh GAC, the adsorbed amount of a certain adsorbate is calculated based on the change in concentration in the liquid phase, assuming that adsorption is the only removal mechanism (Worch, 2012). When experimenting with biologically active GAC (bGAC), the adsorbate can also be biodegraded, apart from adsorbed. However, inhibiting biodegradation by applying GAC treatments, such as autoclaving, or adding chemicals to the solution can also affect adsorption to an unknown extent. For instance, sodium azide, is commonly used as biodegradation inhibitor in adsorption experiments (Shimabuku et al., 2017; Ye et al., 2019). However, sodium azide affects adsorption, as demonstrated by Klimenko et al. (2010) who studied the influence of this chemical on the removal of fulvic acids by AC. The authors concluded that the sodium azide did not fully inhibit biological activity and also that it interacted with the AC surface thus changing its adsorption properties. In addition to chemically affected AC, autoclaved used AC might have different adsorption properties compared with non-autoclaved AC, because autoclaving can potentially alter the biofilm formed on the AC surface and the organic matter previously adsorbed to it, thus affecting adsorption of micropollutants.

Experiments with bGAC at relatively low and high temperatures are an alternative control strategy to distinguish between adsorption and biodegradation for micropollutants removal. Increasing temperatures up to 42 °C increases microbial activity (Lengeler et al., 1999). The effect of temperature on adsorption, however, is less predictable. Temperature can have an effect on adsorption rate and on the overall adsorption at equilibrium conditions. Increasing temperatures increase adsorption rate due to a faster adsorbate diffusion (Taghdiri and Zamani, 2013) but the overall adsorption capacity can be either increased or reduced (Moreno-Castilla, 2004), depending on whether the adsorption is endothermic or exothermic (Al-Degs et al., 2008; Gupta

et al., 2011; Wang and Li, 2013).

Given the difficulty of distinguishing adsorption and biodegradation as removal processes, few studies have assessed the micropollutants biodegradation capacity of biomass growing in GAC filters used in DWTP (Altmann et al., 2016; Zhang et al., 2017). In contrast, biodegradation of micropollutants by activated sludge from WWTP is well documented in literature (Besha et al., 2017; Grandclément et al., 2017). Our goal is to investigate if the biomass growing in GAC filters is capable of degrading a selection of micropollutants relevant for drinking water. We studied the removal of micropollutants with activated carbon that originates from a drinking water production location. Experiments with biologically active or autoclaved GAC at two different temperatures were performed to distinguish removal due to adsorption and biodegradation or adsorption only.

2. Materials and methods

2.1. Organic micropollutants

A mixture of 10 organic micropollutants was used in this study: benzotriazole, desphenyl-chloridazon, diclofenac, guanylurea, hexamethylenetetramine, iopamidol, iopromide, melamine, metformin and pyrazole. These selected micropollutants have been found in surface water in Europe in concentrations ranging from 0.1–6 μg/L, and are considered relevant in drinking water treatment (Buttiglieri et al., 2009; Kiss and Fries, 2009; RIWA-Maas, 2016; Ruff et al., 2015). Desphenyl-chloridazon and iopamidol were purchased from AKOS, iopromide was purchased from Bayer, pyrazole was purchased from Merck and all other micropollutants were purchased from Sigma Aldrich. All micropollutants have a neutral charge at pH 7.5, except for guanylurea and metformin which are positively charged (Markiewicz et al., 2017a) and diclofenac which is negatively charged (De Ridder et al., 2011). This mixture consists of hydrophilic micropollutants of different molecular weights (Table 1).

2.2. Micropollutants biodegradation by biologically active GAC

To assess the potential of biofilm growing in GAC filters to degrade the selected micropollutants, a batch experiment with used GAC, from a DWTP, was performed. The filter where the used GAC (Filtrasorb TL-830, Chemviron®) was collected had been in operation for more than 100,000 bed volumes by Evides Water Company (location Kralingen, the Netherlands). This material will be referred to as bGAC. The bGAC worked both as adsorbent and inoculum. To supply microorganisms with additional carbon source similar to what is available in the GAC filters, the culture media was prepared using GAC filter influent, obtained from the same DWTP as the bGAC, and demineralized water, in a 1:1 ratio. Concentrated nutrient solutions were diluted in this matrix. Demineralized water was used together with GAC filter influent to

Table 1
Micropollutants used in this study, their Log D_{OW} and molecular weight.

Micropollutant	Log D_{OW} at pH 7.0[1]	Molecular weight (g/mol)
Benzotriazole	1.23[2]	119
Desphenyl-chloridazon	− 0.78[3]	146
Diclofenac	1.37[4] to 3[5]	296
Guanylurea	− 2.06[3]	102
Hexamethylenetetramine	0.36[3]	140
Iopamidol	− 2.4[5]	777
Iopromide	− 2.1[5]	791
Melamine	− 2.0[3]	126
Metformin	− 4 to -3.2[6]	129
Pyrazole	0.02	68

1: for benzotriazole and pyrazole, values reported in literature refer to Log K_{ow}; 2: (Hart et al., 2004); 3: Marvin Scketch (v.16.9.12.0, ChemAxon Ltd.); 4: (Huntscha et al., 2012); 5: Margot et al. (2013); 6: ACD/Labs (V11.02).

avoid high salt concentration in the culture media, which could inhibit microbiological activity. The composition of the concentrated nutrient solutions is given in Table S1 and GAC filter influent quality parameters are given in Table S2. Additional inoculum was prepared as follows: 15 g of used GAC was mixed with 20 mL of culture media and vortexed for 5 s. This procedure was repeated several times to obtain biomass in the liquid phase, which was used as additional inoculum.

A mass of 0.26 g of bGAC wet weight, corresponding to approx. 0.1 g dry weight, was used to inoculate 250 mL serum bottles. The bottles contained 10 mL of additional inoculum, micropollutants and culture media in a total liquid volume of 100 mL. All micropollutants were added in similar molar concentrations and three different initial concentrations were used, approximately 25 μM, 45 μM and 69 μM (ranging from 1.7–54.6 mg/L depending on the micropollutant). Initial micropollutants concentrations were measured after spiking the bottles. Therefore, in case these micropollutants were already present in the GAC filter influent used to prepare the media, the initial concentration was the sum of the spiked and the already present micropollutants. The bottles were closed with butyl rubber stoppers and aluminium crimp caps, wrapped in aluminium foil to prevent micropollutants photodegradation and cultivated at either 5 °C or 20 °C, mixed at 120 rpm. Triplicates were run for each condition (Fig. 1). Samples were taken on days 0, 9, 21, 33, 44 and 54. Samples were centrifuged for 10 min at 10,000 rpm, the supernatant was transferred to a clean tube and centrifuged again. After that, the supernatant was diluted and frozen until analysis. Results up to the 54th day were sufficient to test our hypothesis and draw conclusions and the experiment was stopped.

2.3. Micropollutants adsorption onto autoclaved used GAC

The effect of temperature on micropollutants adsorption to GAC was assessed in a test with autoclaved used GAC. This experiment was similar to the one described in 2.2 with the following differences: used GAC and media were autoclaved before being used and no additional inoculum was added to the bottles. Since no biodegradation was expected in experiments with autoclaved GAC, we expected little variation between replicates, which indeed was observed in our data. Therefore, only duplicates were run. This experiment was done with one initial concentration of micropollutants, approximately 69 μM (Fig. 1). Bottles were cultivated in the same conditions as in the experiment described in 2.2 and samples were taken on days 0, 9, 21, 32, 44 and 53.

2.4. Micropollutants adsorption onto fresh GAC

To compare the adsorption capacity of used GAC and fresh GAC, an additional adsorption experiment was performed. Experimental conditions were similar as described in 2.2 and 2.3, except that: 1) fresh GAC (Filtrasorb TL-830, Chemviron®) was used instead of used GAC; 2) only demi-water was used in the preparation of the media instead of a mixture of demi-water and GAC filter influent; 3) one initial concentration of micropollutants was used (62 μM) instead of 3 initial concentrations. Bottles were kept at 5 °C and mixed at 120 rpm. Samples were taken on days 0 and 9. Previous studies showed this time interval to be sufficient for fresh GAC to reach near equilibrium conditions for adsorption of the selected micropollutants (Piai et al., 2019).

2.5. Chemical analyses

Micropollutants were measured using liquid chromatography coupled to high-resolution accurate-mass mass spectrometry, according to the method described in Piai et al. (2019). In short, compounds were separated using an Atlantis T3 column and a gradient based on water/ammonium formate 2 mM/formic acid 0.016 % (v/v) and methanol/ammonium formate 2 mM/formic acid 0.016 % (v/v). Mass spectrometric analysis was performed in positive electrospray ionisation mode on a Thermo QExactive MS in full-scan mode (resolution = 70,000).

3. Results and discussion

3.1. Distinguishing micropollutants biodegradation and adsorption

We assessed whether biofilm from GAC filters can biodegrade a selection of micropollutants by performing experiments with bGAC and autoclaved GAC at different temperatures. We assumed that at low temperature, the removal of the micropollutant was mainly due to adsorption, thus serving as control. Since temperature can also affect adsorption, experiments with autoclaved GAC were performed in order to assess the extent of the effect of temperature on adsorption.

Until day 9, the removal of iopromide with bGAC was similar at 5 °C and 20 °C (Figs. 2a and S1). After this period, different removal trends at the different temperatures were observed. In 54 days, more than 99 % of iopromide was removed at 20 °C regardless of the initial concentration (Figs. 2a and S1) and the remaining iopromide concentration was below 0.46 μM. At 5 °C, the removal varied between 50 and 92 % depending on the iopromide initial concentration (Figs. 2a and S1), and

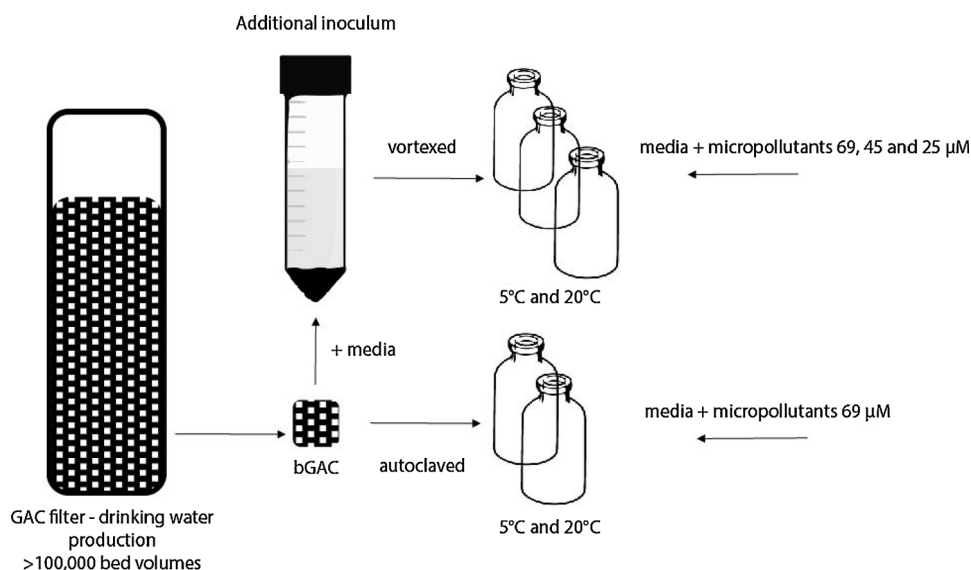**Fig. 1.** Schematic representation of experiments with used GAC.

Additional inoculum

vortexed

media + micropollutants 69, 45 and 25 μM

5°C and 20°C

+ media

bGAC   autoclaved

media + micropollutants 69 μM

5°C and 20°C

GAC filter - drinking water production
>100,000 bed volumes
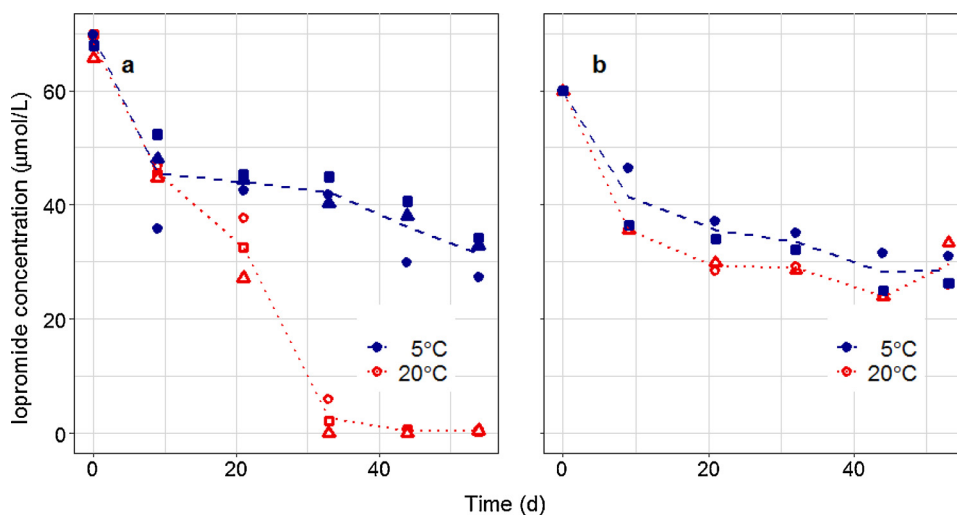
Fig. 2. Iopromide concentration in time at 5 °C and 20 °C with bGAC (a) and autoclaved GAC (b). Different symbols represent different replicates of the same treatment. Lines connect the mean value of replicates in each time point.

a similar removal was observed with both bGAC and autoclaved GAC (Fig. 2).

Our results with autoclaved GAC show that iopromide adsorption increased with increasing temperature (Fig. 2b). It is known that increased temperatures increase diffusion rates, and diffusion can limit adsorption (Taghdiri and Zamani, 2013). However, this is not the reason for the higher iopromide adsorption at 20 °C given that the adsorption rate at both temperatures was similar. Alternatively, these results might indicate that iopromide adsorption is an endothermic process. Endothermic adsorption of compounds such as ibuprofen and rhodamine B has been reported and attributed to the creation of adsorption sites at higher temperatures (da Silva Lacerda et al., 2015; Dubey et al., 2010). The comparison of iopromide removal at both temperatures by bGAC and autoclaved GAC supports the hypothesis that biodegradation is a relevant removal mechanism with bGAC.

Iopromide removal in bGAC filters has been reported in literature. Altmann et al. (2016) observed more than 50 % iopromide removal in a bGAC filter treating secondary effluent from a WWTP. Removal remained stable even after prolonged operation (25,000 bed volumes) and was attributed to iopromide adsorption and biodegradation. Zhang et al. (2017) reported up to 60 % iopromide removal for micropollutants in bGAC filters. The authors hypothesize that biodegradation was the main removal mechanism based on the age of the bGAC (2 years) and on the amount of organic matter (around 2 mg/L) present in the influent. In this paper we present additional evidence that iopromide can be degraded by biomass growing in bGAC filters.

Iopromide biodegradation results in recalcitrant transformation products and full mineralization has not yet been reported (Müller et al., 2019). Peaks with the same exact mass (within 5 ppm) and isotope pattern corresponding to 3 iopromide biodegradation products described by Schulz et al. (2008) were detected in our experiments with bGAC (Figure S2). The detection of iopromide degradation products is additional evidence of iopromide biodegradation.

Similarly to iopromide, metformin was biodegraded at 20 °C with bGAC (Fig. 3a and Figure S3a, c). Initially, metformin removal was higher in experiments at 5 °C than at 20 °C (32 % and 20 % average removal on day 9 at 5 °C and 20 °C respectively), indicating that metformin adsorption is an exothermic process. This period lasted 9 days for the lowest initial concentration (25 μM) and 21 days for the intermediate and highest initial concentrations (respectively 45 μM and 69 μM). After that, metformin biodegradation was observed in 6 out of 9 bottles at 20 °C and its removal was more than 99 % by day 33, regardless of the initial concentration. A further evidence for metformin biodegradation at 20 °C is the production of its first degradation

product guanylurea (Fig. 3a and Figure S3a, c). Guanylurea concentration increased in all cases where metformin was biodegraded, and correlated strongly in time with the biodegradation of metformin. The experiments with autoclaved GAC show that both metformin and guanylurea were removed to a larger extent at 5 °C than at 20 °C (24 % and 15 % metformin removal at 5 °C and 20 °C respectively, 87 % and 79 % guanylurea removal at 5 °C and 20 °C respectively), similarly to what was observed in the first days with bGAC (Figure S3). This shows that the adsorption of metformin and guanylurea is exothermic.

After guanylurea was produced, it was further removed due to either adsorption or biodegradation. Guanylurea removal between day 33 and 54 cannot be explained by adsorption alone (Fig. 3a and Figure S3a, c). Adsorption happens initially at a fast rate and slows down in time (Piai et al., 2019). However, our results show the opposite trend: guanylurea removal rate is initially lower (between days 33 and 44) and becomes higher between days 44 and 54. This trend is more consistent with removal due to biodegradation then removal due to adsorption. Initially, guanylurea has been described as the dead-end metformin biodegradation product (Trautwein and Kümmerer, 2011). However, recent studies have reported guanylurea biodegradation by activated sludge or cultures enriched from activated sludge (Briones et al., 2018; Tisler and Zwiener, 2019), indicating that guanylurea can be biodegraded, as also observed in our experiments.

Metformin biodegradation and guanylurea production were not observed in all replicates. Metformin biodegradation was observed in the 3 replicates with initial concentration of 25 μM (Figure S3a), but in only 2 out of 3 replicates with initial concentration of 45 μM (Fig. 3a) and in only 1 out of 3 replicates with initial concentration of 69 μM (Figure S3c). Therefore, replicates at 20 °C in which metformin was not degraded were not included in the mean calculation in those figures. We also observed variability between replicates in an independent experiment performed in similar conditions as described in 2.2 and 2.3. In this experiment, metformin was biodegraded in 2 out of 3 replicates (Figure S4).

Several authors have reported a similar variability between replicates in metformin biodegradation studies (Markiewicz et al., 2017a, 2017b; Poursat et al., 2019; Trautwein and Kümmerer, 2011). Poursat et al. (2019) reported 99 %, 28 % and 7 % metformin biodegradation for 3 replicates in experiments with sludge pre-exposed for 9 months to 1.5 mg/L metformin as initial concentration. Markiewicz et al. (2017a) studied metformin biodegradation by activated sludge following the protocol of OECD 301 F. In their experiments, replicate bottles removed metformin to different extents (0 vs. 30 % and 50 % vs. 100 % in two independent experiments). The authors hypothesize that the large
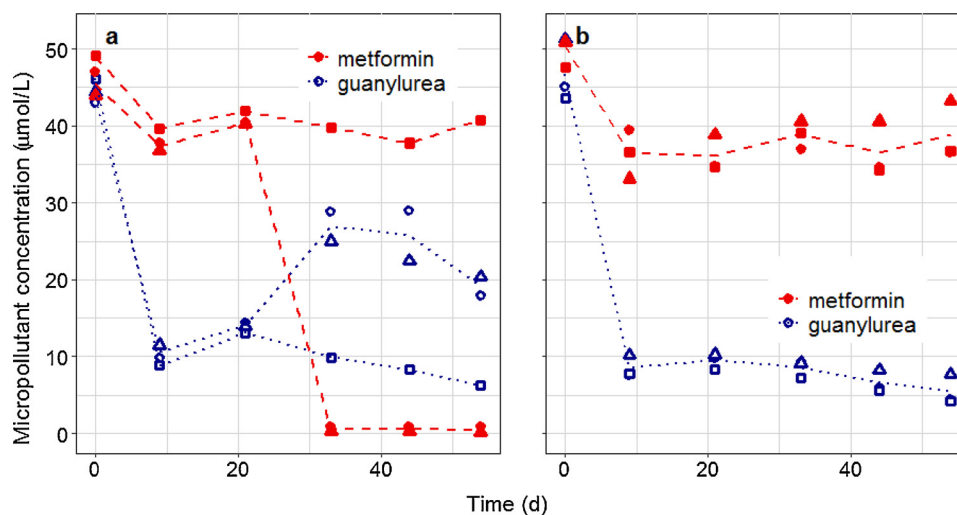
Fig. 3. Metformin and guanylurea concentration in time at 20 °C (a) and 5 °C (b) in experiment with bGAC. Different symbols represent different replicates of the same treatment. Lines connect the mean value of replicates in each time point.

variation in the results was due to the diversity of the microbial community in the inoculum and concluded that metformin biodegradation might occur only if specific degraders are present. Since part of the inoculum used in our experiments consisted of bGAC and collecting a homogeneous sample of this material is difficult, inoculum heterogeneity is likely the reason for the different behaviour of our replicates.

Given the different effects of temperature on micropollutants adsorption, two scenarios can be distinguished in our study. In the first one, adsorption of a micropollutant decreases with increasing temperature (exothermic process). In this case, temperature is negatively correlated to adsorption but positively correlated to biodegradation. Therefore a higher removal at 20 °C is a strong indication for micropollutant biodegradation, which is the case for metformin. In the second situation, adsorption of a micropollutant increases with increasing temperature (endothermic process). In this case temperature is positively correlated to both adsorption and biodegradation and a higher removal at 20 °C does not necessarily imply that the compound is biodegraded. Therefore, the removal trends at both temperatures, combined with the removal with autoclaved GAC, can indicate whether the compound was biodegraded or not. This is what we have shown for iopromide removal.

In our experiments, a positive correlation between temperature and

adsorption was also observed for iopamidol (Fig. 4). Iopamidol removal at 20 °C with bGAC was higher than with autoclaved GAC, whereas at 5 °C iopamidol was removed to a similar extent in both experiments (Fig. 4). At the end of the experiments at 20 °C, 45 % of iopamidol was removed with autoclaved GAC, whereas 68 % was removed with bGAC. This indicates that iopamidol was biodegraded in the later. A peak with exact mass (within 5 ppm) and isotope pattern corresponding to an iopamidol biodegradation product described by Kormos et al. (2010) was detected in experiments with bGAC cultivated at 20 °C (Figure S5), but not when cultivated at 5 °C. This supports the hypothesis of iopamidol biodegradation. An alternative explanation for the higher iopamidol removal with bGAC at 20 °C is related to iopromide and metformin biodegradation. Biodegradation of the dissolved fraction of iopromide and metformin creates a driving force for the desorption of these compounds from the bGAC. This releases adsorption sites on the GAC surface, which might have contributed to increasing iopamidol removal due to adsorption.

Different from iopromide and iopamidol, diclofenac removal was higher with bGAC than with autoclaved GAC at both temperatures (Fig. 5). As a result, it is difficult to assess whether diclofenac was biodegraded or only adsorbed onto bGAC. A possible explanation is that diclofenac was biodegraded in bottles cultivated at both 5 °C and 20 °C
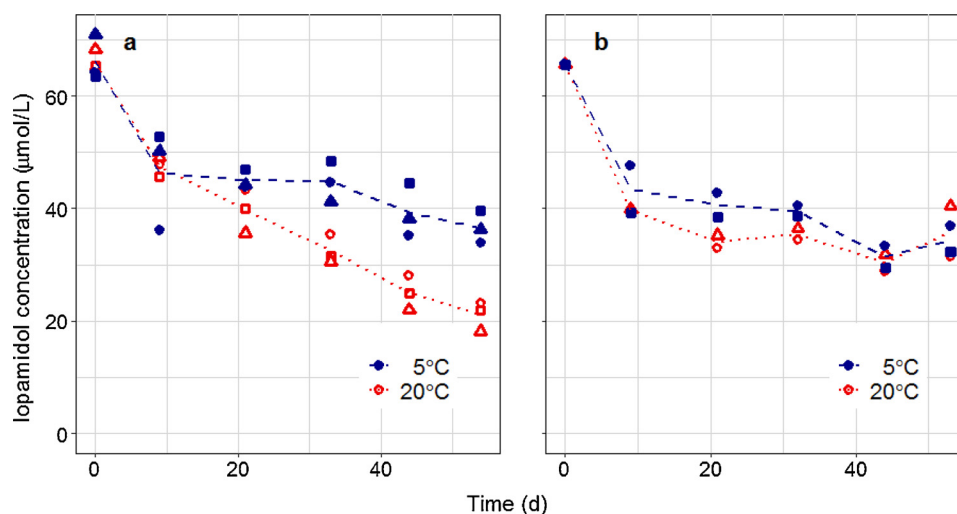
Fig. 4. Iopamidol concentration in time at 5 °C and 20 °C with bGAC (a) and autoclaved GAC (b). Different symbols represent different replicates of the same treatment. Lines connect the mean value of replicates in each time point.
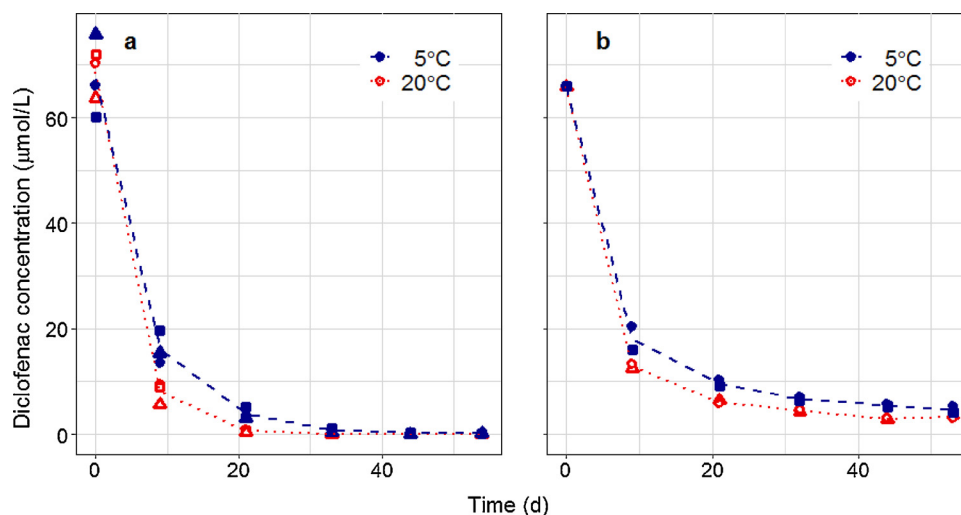
Fig. 5. Diclofenac concentration in time at 5 °C and 20 °C with bGAC (a) and autoclaved GAC (b). Different symbols represent different replicates of the same treatment. Lines connect the mean value of replicates in each time point.

with bGAC. However, we expect that the biodegradation rate at 5 °C would not be significant enough to explain the removal observed. Furthermore, peaks corresponding to diclofenac transformation products described by Kosjek et al. (2009) were not found in any of the samples from day 54 in either temperature. Therefore, we could not elucidate if biodegradation was an additional removal mechanism for diclofenac with bGAC.

3.2. Temperature effect on adsorption of non-biodegraded micropollutants

We observed no trends indicating biodegradation of the following micropollutants with bGAC: benzotriazole, desphenyl-chloridazon, hexamethylenetetramine, melamine and pyrazole. For these compounds, we found that adsorption was the only removal mechanism, both with bGAC as well as with autoclaved GAC. Therefore, results from both experiments were used to evaluate the effect of temperature on adsorption of these micropollutants in different concentrations.

Melamine and desphenyl-chloridazon were removed to a larger extent at 5 °C than at 20 °C, both with bGAC and autoclaved GAC (Fig. 6 and Figure S6). This indicates that adsorption of melamine and de-sphenyl-chloridazon is exothermic, similarly to metformin and guany-lurea. Interestingly, the difference between melamine and desphenyl-chloridazon removal at 5 °C and 20 °C reduced with increasing micropollutant initial concentration. This can be explained based on the increased coverage of the GAC surface at increasing micropollutant initial concentrations. Studies show that at higher GAC coverage, the temperature dependence of adsorption is reduced (Hindarso et al., 2001; Pikaar et al., 2006; Sander and Pignatello, 2005), which is related to the presence of sites with different adsorption affinities on the AC surface. High affinity adsorption sites are the first to be occupied by the adsorbate and the temperature dependence of adsorption is higher in those sites. Low affinity adsorption sites are occupied only at higher AC surface coverage and the temperature dependence of these sites is smaller or negligible (Pikaar et al., 2006).

At an initial concentration of 69 μM, desphenyl-chloridazon was removed to a larger extent at 5 °C than at 20 °C with autoclaved GAC (figure S5d), but it was removed to the same extent at both temperatures with bGAC (Figure S5c). This difference can be related to a different AC coverage in each experiment. As previously mentioned, the temperature dependence of adsorption can reduce at higher AC coverage. Autoclaving the AC might have affected the biofilm and/or organic matter previously adsorbed to the AC, reducing its coverage.

Hexamethylenetetramine was removed to a larger extent at 20 °C both with bGAC and autoclaved GAC (Fig. 7). Different from our

results, a negative correlation between hexamethylenetetramine adsorption and temperature was found by Taghdiri and Zamani (2013). Differences between their work and ours include use of column experiments instead of batch, a different type of AC, powder AC instead of GAC and a shorter contact time (200 min instead of 54 days). However, we could not explain the difference between our results and theirs based on the difference in experimental setup.

No difference in pyrazole and benzotriazole removal between temperatures was observed, neither with bGAC, nor with autoclaved GAC (data not shown). This indicates that these compounds were not biodegraded and that adsorption is not strongly affected by temperature. To the best of our knowledge, the effect of temperature on the adsorption of these compounds onto GAC has not been reported in literature.

Benzotriazole, iopamidol and melamine were not biodegraded in our experiments with bGAC, even though their biodegradation has been reported in literature (El-Sayed et al., 2006; Herzog et al., 2014; Kormos et al., 2010; Wagner et al., 2020). These studies applied constructed wetlands or used activated sludge, WWTP effluent or soil impacted by WWTP effluent as inoculum. We hypothesize that the biodegradation potential for micropollutants is smaller in GAC filters used in drinking water production than in those systems, for various reasons. One possible reason is the fact that micropollutants concentrations are expected to be higher in constructed wetlands and WWTP than in DWTP. Another reason is the higher concentration of dissolved organic carbon in wastewater, compared to drinking water (Zietzschmann et al., 2016), which creates favourable conditions for biodegradation of micropollutants via cometabolic routes (Tran et al., 2013). Still, GAC filters harbour a diverse microbial community with high metabolic versatility (Oh et al., 2018). We have demonstrated that biofilm growing on used GAC from a DWTP can biodegrade at least 3 out of the 10 micropollutants tested. Moreover, we propose that experiments involving micropollutants removal at different temperatures can be used to assess their biodegradability by bGAC.

3.3. Adsorption capacity of used and fresh GAC

We compared the adsorption capacity of used and fresh GAC to gain insight in the possible loss of adsorption capacity due to GAC use. For this purpose, we compared the micropollutant removal of fresh GAC (see 2.4) with MP removal by bGAC (initial concentration 69 μM) on day 9. Despite the hydrophilic character of these micropollutants, as indicated by their Log D_{OW} (Table 1), more than 90 % removal was achieved for 5 out of 10 compounds (Table 2). A more detailed
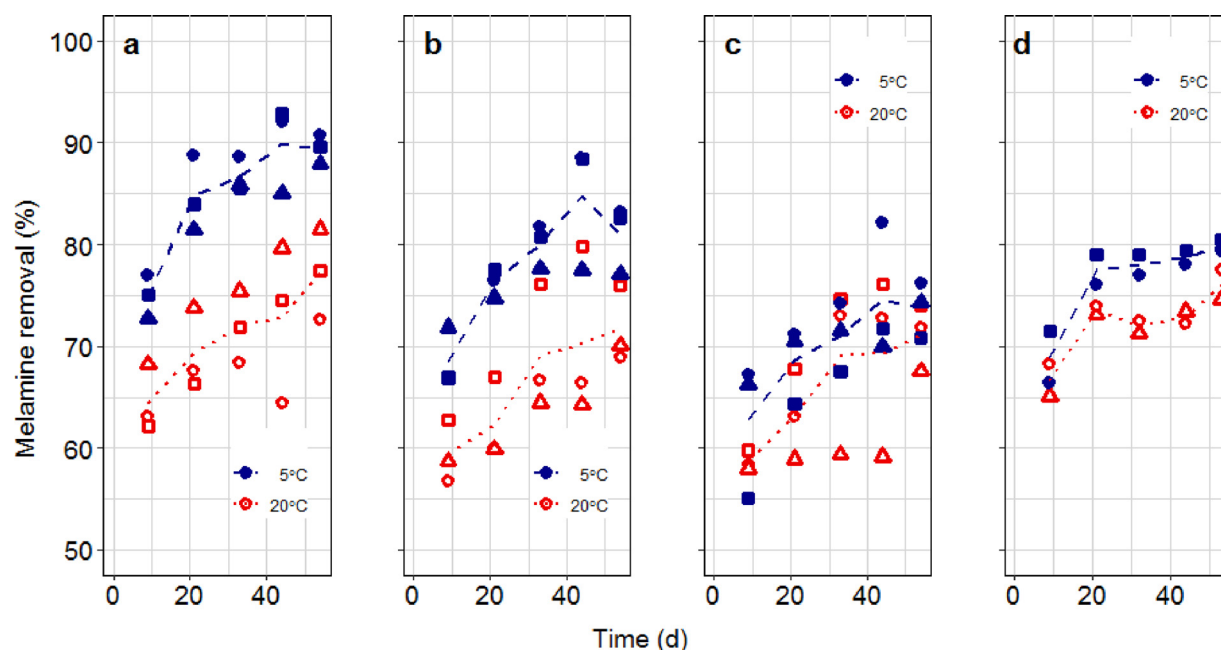
Fig. 6. Melamine removal with bGAC at 3 different initial concentrations - a) 25 µM, b) 45 µM, c) 69 µM - and autoclaved GAC - d) 69 µM - at 5 °C and 20 °C. Different symbols represent different replicates of the same treatment. Lines connect the mean value of replicates in each time point. Y-axis scale runs from 50 %–100 % for better visualization of the data.

discussion regarding affinity of these micropollutants towards GAC, including adsorption isotherms, is presented in Piai et al. (2019).

The loss of adsorption capacity due to GAC use differs considerably per compound (Table 2). The adsorption capacity of benzotriazole and diclofenac by used GAC is respectively only 16 % and 23 % lower than of fresh GAC. This shows that even though GAC was used for more than 100,000 bed volumes, the adsorption capacity for these micropollutants was still high. Guanylurea, metformin and hexamethylenetetramine adsorbed to a larger extent onto used GAC than onto fresh GAC. The higher removal of guanylurea and metformin with used GAC can be related to the increased electrostatic attraction between the negatively charged biofilm on the used GAC surface and these positively charged micropollutants (Briones and Sarmah, 2018). Increased removal of cationic compounds due to biofilm growth on GAC surface has already been reported (Yin et al., 2007). The higher removal of hexamethylenetetramine with used GAC compared to fresh GAC cannot be explained

Table 2

Micropollutant removal by used and fresh GAC at 5 °C and relative removal of used and fresh GAC. Values correspond to mean of triplicates for used GAC and duplicates for fresh GAC.

Micropollutants	Removal (%)		
	Fresh GAC	Used GAC	Used/fresh GAC
Benzotriazole	99	83	84
Desphenyl-chloridazon	99	66	67
Diclofenac	97	75	77
Guanylurea	52	77	148
Hexamethylenetetramine	14	23	161
Iopamidol	90	30	33
Iopromide	93	35	38
Melamine	94	63	67
Metformin	12	30	250
Pyrazole	51	28	55
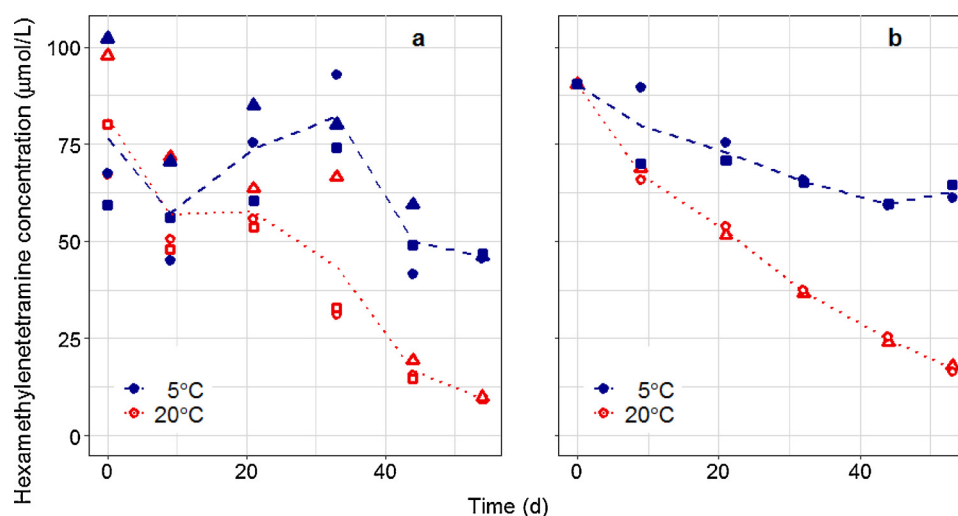
Fig. 7. Hexamethylenetetramine concentration in time at 5 °C and 20 °C with bGAC (a) and autoclaved GAC (b). Different symbols represent different replicates of the same treatment. Lines connect the mean value of replicates in each time point.

based on charge interactions, given that this compound is neutral at the pH of the experiment. This result might be related to the unexpectedly high initial concentration of hexamethylenetetramine in one of the replicates in the experiment with bGAC (Fig. 7a).

The loss of adsorption capacity due to GAC use was the highest for iopamidol, iopromide and pyrazole. Iopamidol and iopromide are the largest molecules in the experiment, which means that they are most affected by pre-adsorbed organic matter onto used GAC, due to pore blockage and competition for adsorption sites (Zietzschmann et al., 2015). The difference between adsorption capacity of used and fresh GAC for the different micropollutants can also be partially explained by the previous exposure of the used GAC to some micropollutants. It is expected that less adsorption sites will remain available for the compounds to which the GAC has been more exposed (Greenstein et al., 2018). However, with the available data, it is not possible to conclude if that is the reason why the loss of adsorption capacity was high for pyrazole.

4. Conclusions

In this study, we have shown that biofilm growing in GAC filters at a DWTP can biodegrade iopromide, metformin and iopamidol. In addition, we have shown that temperature is positively correlated to adsorption of iopromide, iopamidol, diclofenac and hexamethylenetetramine, but negatively correlated to adsorption of desphenyl-chloridazon, guanylurea, melamine and metformin. We could also demonstrate that the adsorption capacity of GAC used for more than 100,000 bed volumes is comparable to adsorption of fresh GAC for diclofenac and benzotriazole and higher for guanylurea, metformin and hexamethylenetetramine.

Our experimental set-up of comparing micropollutants removal at different temperatures can be used to distinguish biodegradation from adsorption in used GAC. The distinction between these two processes allows to assess the potential of biofilm growing in GAC filters to biodegrade micropollutants and to elucidate the contribution of biodegradation as a removal process for micropollutants in these filters during drinking water production. This study contributes to more insights related to bioregeneration of loaded GAC. Demonstrating that sorption and biodegradation occur simultaneously and sufficiently, and leads to an efficient bioregeneration of the GAC, can aid in reducing the thermal regeneration that is currently used for GAC filters at DWTP.

CRediT authorship contribution statement

Laura Piai: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Visualization, Project administration. **Marco Blokland:** Resources, Writing - review & editing, Supervision. **Albert van der Wal:** Conceptualization, Resources, Writing - review & editing, Supervision, Funding acquisition. **Alette Langenhoff:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Funding acquisition.

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

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