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Prolonged lifetime of biological activated carbon filters through enhanced biodegradation of melamine

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ABSTRACT

Micropollutants can be removed in Biological Activated Carbon (BAC) filters through biodegradation, besides adsorption, when the conditions are favorable. In the present study, we build upon previous work on melamine biodegradation and activated carbon regeneration in batch experiments and assess the efficiency of this process in continuous flow lab-scale BAC filters. Melamine is frequently detected at low concentrations in surface water and is used here as a model micropollutant. BAC filters were inoculated with melamine degrading biomass and the contribution of biodegradation to melamine removal was assessed. Furthermore, we tested the effect of an additional carbon source (methanol) and the effect of contact time on melamine removal efficiency. We demonstrate that inoculation of activated carbon filters with melamine degrading biomass increases melamine removal efficiency by at least 25%. When an additional carbon source (methanol) is supplied, melamine removal is almost complete (up to 99%). Finally, through a nitrogen mass balance, we demonstrate that around 60% of the previously adsorbed melamine desorbs from the BAC surface when biodegradation rates in the liquid phase increase. Melamine desorption resulted in a partial recovery of the adsorption capacity.

1. Introduction

Micropollutants that are present in drinking water sources can be fully or partly removed by the use of Granular Activated Carbon (GAC) filters. GAC filters have been used for decades in drinking water production plants and their application for wastewater treatment is increasing (Benstoem et al., 2017; Reungoat et al., 2010). Micropollutants removal in GAC filters occurs not only through adsorption to the activated carbon, but also through biodegradation by the microorganisms that grow in the filters (Zhang et al., 2017; Zhiteneva et al., 2020). Due to the relevance of biodegradation as an additional removal process, these filters are also referred to as Biological Activated Carbon (BAC) filters. Increasing the role of biodegradation in the overall micropollutants removal in BAC filters can delay the saturation of the activated carbon and extend the filter lifetime, both due to a reduced loading to the BAC and due to bioregeneration. Bioregeneration is the process in which microorganisms restore at least part of the adsorption capacity of the BAC by biodegrading micropollutants, in a way that occupied adsorption sites become available for readsorption. This effect also contributes to increasing the removal efficiency of non-biodegradable micropollutants (Putz et al., 2005) in these filters.

Biodegradation of micropollutants in GAC filters requires the presence of microorganisms capable of degrading the contaminants under the filter conditions. In the present study, we used a micropollutant frequently detected in surface water, melamine, as a model compound. Previous research has shown that melamine is not sufficiently removed in pilot-scale GAC filters and is not biodegraded by indigenous biomass grown in GAC filters used for drinking water production (Brunner et al., 2020; Piai et al., 2020). Yet, melamine can be biodegraded by specific microorganisms isolated from soil and industrial wastewater treatment plants (El-Sayed et al., 2006; Takagi et al., 2012; Wang et al., 2014). In a previous study we demonstrated in batch systems that melamine degrading microorganisms can be used to restore at least 28% of the GAC adsorption capacity through bioregeneration (Piai et al., 2021).

In this paper, we build upon previous work and investigate the contribution of biodegradation to the removal of melamine in continuous flow lab-scale GAC filters. We assessed the biodegradation capacity of the Biological Activated Carbon (BAC) filters in the absence and presence of an additional carbon source (methanol). In addition, we studied the effect of Empty Bed Contact Time (EBCT) on melamine removal efficiency, as well as the effectiveness of two different inoculation methods. Melamine desorption from the filter bed in the lab-scale

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filters was studied by feeding the filter with melamine free influent. Finally, we were able to quantify the amount of melamine desorbed due to increased biodegradation rates and assess the remaining adsorption capacity of the regenerated BAC. By stimulating micropollutants biodegradation, the lifetime of activated carbon filters can be extended.

2. Materials and methods

2.1. Experimental setup

Melamine removal was tested in lab-scale filters with and without inoculation of melamine degrading biomass. The filters were made of glass cylinders with 2.6 cm internal diameter and 20 cm length. Each filter had 2 sampling points located at 6.0–8.0 cm (A) and 2.5–4.5 cm (B) from the bed bottom (Fig. 1). The dead volume of the sampling points was filled with clean glass wool before each experiment. The GAC used was AcquaSorbTM K- CS (Jacobi®), previously sieved to obtain particle sizes between 0.5 and 0.85 mm diameter. Before being used in the filters, the GAC was boiled in demineralized water for 10 min to remove entrapped air. Once inside the filters and before starting experiments, GAC was flushed with tap water until the effluent pH stabilized (pH ~ 8).

Nylon meshes at the top and bottom of the filters prevented GAC wash out. Initial bed height was 10 cm, and changed to 12–16 cm at the end of the experiments due to biomass growth and bed expansion. The remaining volume of the column was permanently filled with influent. Despite the variation in bed height, a fixed Bed Volume (BV) of 0.053 L was used for calculations, corresponding to the BV at the beginning of the experiments. This approach is justified as the GAC mass in the filter bed did not change during the experiment and the increased volume in the filter bed corresponded either to void space or biomass volume.

Influent consisted of a phosphate buffer and nitrogen-free nutrients solutions (adapted from Tros et al., 1996) spiked with melamine (8.0 ± 0.8 mg melamine/L). This concentration was chosen in order to obtain meaningful results, which allow us to distinguish adsorption from biodegradation, in an acceptable time frame. The detailed influent composition is described in the Supplementary Information (Table S1). Influent was pumped through the filters in a downwards direction by a peristaltic pump (Ismatec Reglo ICC). Actual flow was checked periodically by weighing the effluent of each filter at a determined time interval. The flow rate was adjusted when needed to obtain a desired EBCT. In those cases where a carbon source was added, a solution of 0.1% methanol stored at 10ºC was mixed with the influent by a second peristaltic pump. The flow of influent:methanol was approximately 100:1, which resulted in approximately 40% of the total organic carbon in the influent being originated from methanol.

The pressure at the top of the filters was monitored using DMP 331Pi pressure sensors (BD sensors). If overpressure exceeded 200 mbar, automatic backflushing was initiated. In addition, regular backflush with tap water was performed weekly for 5 min at a flow rate of 3–6 L/h. This flow rate was enough to wash out the excess biomass from the top of the bed, but low enough not to disturb the GAC layers. Backflush flow was controlled using a flow controller (ES-FLOW™ Bronkhorst®). Temperature in the filters was monitored with Teflon® coated temperature sensors (ProSense Pt-100) and remained between 27 and 30 °C. LabVIEW 2018 was used to monitor filter pressure, effluent temperature and pH and to control valves for backflush.

2.2. Melamine removal

Melamine removal due to adsorption alone or in combination with biodegradation was assessed in 6 experiments. We tested the effect of an additional carbon source (methanol), the method of inoculation (direct or indirect) of melamine degrading biomass and EBCT on melamine removal in lab-scale GAC filters (Table 1). BAC 1 – 5 were inoculated with activated sludge containing melamine degrading biomass, which

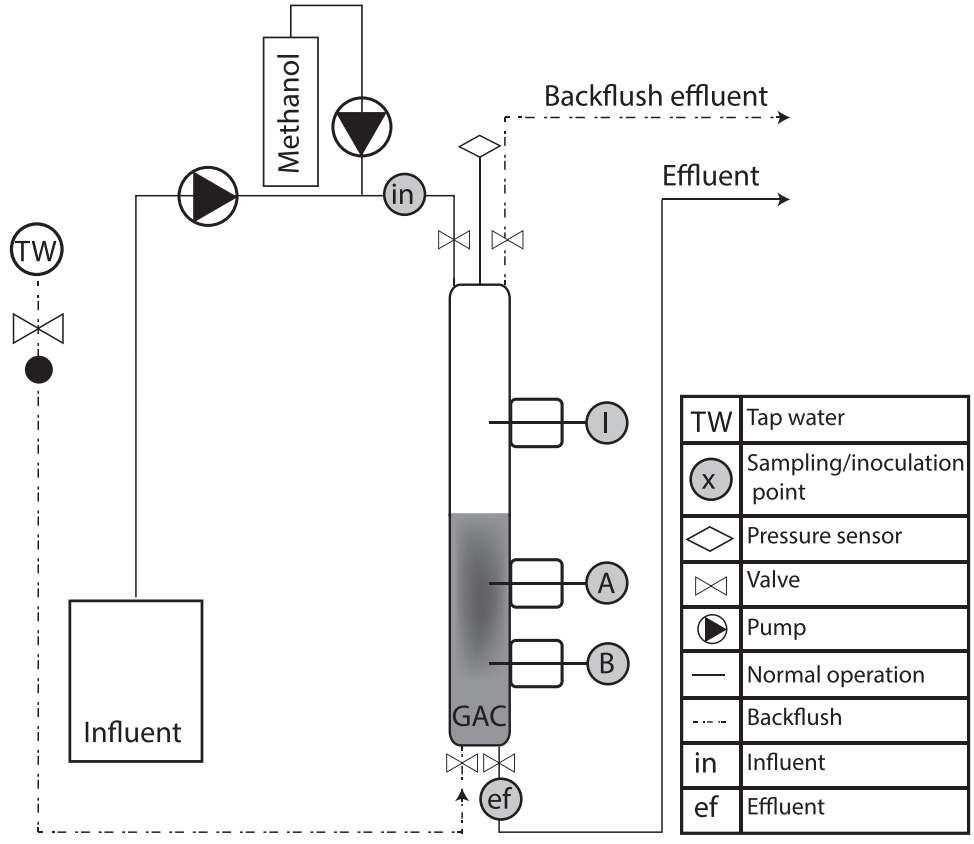

Fig. 1. Schematic representation of experimental set-up. Column dimensions and sampling points positions are to scale.

Table 1
Melamine removal experiments performed in lab-scale GAC filters.

Filter	EBCT at effluent point (min)	Flow rate (mL/min)	Filter inoculation	Methanol in influent	Duration (BVs)	Desorption (BVs)
GAC 1	18 ± 2	2.90 ± 0.27	No	No	6067	NA
BAC 1	32 ± 3	1.63 ± 0.13	Direct	No/Yes	14000	>8300
BAC 2	32 ± 3	1.63 ± 0.13	Direct	Yes	4923	NA
BAC 3	32 ± 3	1.63 ± 0.13	Indirect	Yes	5829	NA
BAC 4	18 ± 2	2.90 ± 0.27	Direct	Yes	8724	>6000
BAC 5	18 ± 2	2.90 ± 0.27	Indirect	Yes	6990	NA

NA: not applicable.

originated from a wastewater treatment plant (Azomures, Romania) treating industrial wastewater containing melamine (Piai et al., 2021). A non-inoculated filter (GAC 1) was used as control for assessing melamine removal due to adsorption only.

Melamine desorption was assessed in BAC 1 and 4 by feeding the filters with influent without melamine after approximately 8300 and 6000 BVs respectively. During this stage, the filters were no longer backflushed.

Experiment BAC 1 consisted of 3 phases. In phase I, the influent did not contain methanol. In phase II, which started after approximately 6200 BVs, methanol was added to the influent in the same way as in BAC 1–4. In phase III, which started after approximately 8300 BVs, the filter was still fed with influent containing methanol, but without melamine.

Melamine removal (r, in mg melamine/g GAC) was calculated based on the amount of melamine (m, in mg) removed in the filter in a specific time interval normalized by the GAC mass. GAC mass was calculated based on the bed volume (BV, in L) and the bed density (ρ_b, in g/L):

$$r = \frac{m}{BV\rho_b} \quad (1)$$

The value of m was obtained from the area between the influent and effluent concentration curves using the spline interpolation method (example in Fig. S2). The value of bed density used was 450 g/L, based on the material fact sheet from the GAC supplier.

2.3. Inoculation of BAC filters

2.3.1. Direct

In experiments BAC 1, 2 and 4, filters were directly inoculated with melamine degrading biomass on days 0, 7 and 14. A volume of 1.6 mL sludge was added at both points I and A (Fig. 1). In experiment BAC 1, the filter was reinoculated 5 times between days 81 and 103 (3500–4500 BVs).

2.3.2. Indirect

In experiments BAC 3 and 5, the GAC was inoculated with melamine degrading biomass in batches, before being used in the filters. The batches contained 7.5 g fresh GAC, 10 mL melamine degrading biomass (9.4 mg VSS/L), 3 g/L methanol and mineral media (composition in Table S1) containing 1000 mg/L melamine and a total liquid volume of 550 mL. After 21 days, the liquid medium was removed from each batch, the BAC was washed 3 times with fresh mineral media to remove suspended biomass, after which the BAC was stored wet at 4 °C for 48 h. After this period, the BAC was transferred to the filter containing fresh GAC, in a ratio of 1:3 (BAC:GAC). The BAC and GAC were mixed by inverting the filter several times. The filters were stored at 4 °C for approximately 16 h before starting the experiments.

2.4. BAC regeneration

For BAC 1 we calculated the amount of melamine desorbed due to biodegradation from the liquid phase and the remaining adsorption capacity of the regenerated BAC (in relation to fresh GAC) by going through the following steps (Fig. 2):

2.4.1. BAC load (phase I)

The amount of adsorbed melamine at the end of phase I (BAC load, q_I, in mg melamine/g BAC) was calculated, assuming equilibrium between the filter bed and influent concentration at the end of that phase (6200 BVs). BAC load q_I was calculated from the average influent concentration (c_0 in mg/L) during phase I and by applying the Freundlich isotherm using the values for the parameters (K_f in (mg/g)/(mg/L) and n (dimensionless)) as described in our previous study (Piai et al., 2021) and by correcting these values for the temperature of the filters.

2.4.2. Desorbed melamine (phases II and III)

The amount of desorbed melamine (mel_{des}, in mg melamine/g BAC)

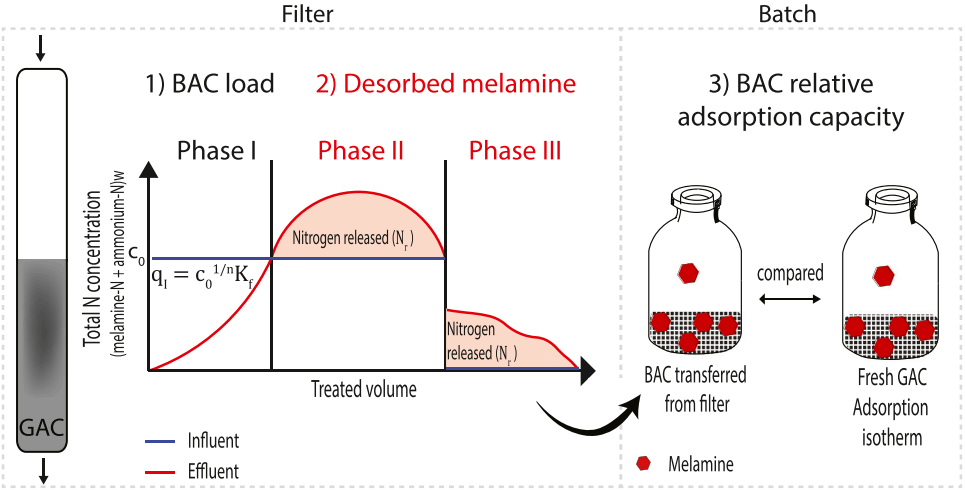

Fig. 2. Schematic representation of steps to assess GAC regeneration.

from BAC 1 in phases II and III was calculated from the amount of nitrogen released (N_r, in mg N/g BAC), assuming full melamine mineralization in the column. The value of N_r was obtained from the area between the effluent and influent total nitrogen concentration curves. The total measured amount of nitrogen originates from both ammonium and melamine, therefore the total amount of nitrogen is the sum of the nitrogen present in these two compounds. We calculated the percentage of melamine desorbed by dividing mel_{des} by the BAC load q_I for the phases II and III.

2.4.3. BAC relative adsorption capacity

The relative adsorption capacity of the BAC was calculated as the adsorption capacity of regenerated BAC compared to the adsorption capacity of fresh GAC. The adsorption capacity of regenerated BAC after melamine desorption and biodegradation at 14,000 BVs (end of phase III) was determined by removing the material from the filter BAC 1 and readsorbing melamine to the BAC in batch experiments. We ensured that melamine biodegradation did not take place by using two approaches: i) BAC was autoclaved and adsorption capacity was measured at 20 °C, and ii) BAC was not autoclaved and adsorption capacity was measured at 5 °C. Due to the low temperature in the second approach, only adsorption would take place and no melamine biodegradation. We verified this assumption of inhibited biodegradation by measuring ammonium, nitrite and nitrate in the liquid at the end of the readsorption test. In both approaches, 0.26 g wet GAC (corresponding to 0.1 g in dry weight) was mixed with 100 mL of media with the same composition as the filter influent, spiked with melamine at 3 initial concentrations: 50, 74 and 96 mg/L. Bottles were mixed at 120 rpm for 21 days. Adsorption capacity of fresh GAC was determined in experiments performed in the same conditions as BAC. To compare the adsorption capacity of BAC and fresh GAC at the same equilibrium concentration, a Freundlich isotherm was fitted to the adsorption data of fresh GAC, and the melamine load on fresh GAC at the same equilibrium concentrations as obtained for BAC was calculated. The adsorption capacity of BAC in both cases was compared to the adsorption capacity of fresh GAC at the same temperature.

2.5. Modeling melamine adsorption in fixed-bed filters

Melamine adsorption in fixed-bed filters was modeled using the Homogeneous Surface Diffusion Model (HSDM) (Worch, 2012) implemented in MATLAB®. For the equilibrium conditions we used the Freundlich isotherm. The values used for each model parameter are presented in Table S2. Surface and film diffusion coefficients were obtained from a previous study where we fitted batch kinetic experiments and breakthrough curves for a comparable micropollutant (pyrazole) and are comparable to typical values reported in literature (Lee and Mckay, 2004; Worch, 2012). Experimental data from the non-inoculated filter (GAC 1) was fitted to the HSDM to validate the model output.

2.6. Analysis

Samples for melamine and methanol analysis were filtered with 0.2 μM polyethersulfone membrane filters and stored at −20 °C until analysis. Samples for methanol analysis were spiked with 10% (v/v) of 4 M formic acid before being stored.

Dissolved oxygen concentrations were measured using non-invasive oxygen sensors (Spot SP-PSt3, PreSens) and an oxygen meter (Fibox 4). Ammonium was measured using Hach Lange colorimetric kits (LCK 303 and LCK 305) and a spectrophotometer (Hach Lange DR 3900). Methanol was measured with gas chromatography as described in Jourdin et al. (2018). Concentrations of melamine and its transformation product ammeline were measured by liquid chromatography coupled to UV-detection, using a Luna CN analytical column (Phenomenex®) and an isocratic flow of 1 mL/min phosphate buffer (5 mM, pH 6.7), as described in Piai et al. (2021). Retention times were: melamine, 5.6 min; ammeline: 3.8 min. The limit of quantification was 0.05 mg/L for ammeline and 0.09 mg/L for melamine. In the same system, the other transformation products ammelide and cyanuric acid were detected, but could not be quantified due to incomplete peak separation.

3. Results and discussion

3.1. Melamine adsorption – modeled and experimental breakthrough curves

The experimental breakthrough curve of the non-inoculated filter (GAC 1) was fitted to the adsorption model (HSDM) (Fig. 3). First, the experimental breakthrough was compared to the model output, using the Freundlich coefficients as calculated in Piai et al. (2021). We observed that the model predicted a later breakthrough than obtained experimentally, which is most likely related to the higher temperature at which we operated the filters (27–30 °C), compared to the temperature at which the Freundlich coefficients have been determined (20 °C). Previous experiments have shown that melamine adsorption decreases with increasing temperatures (Piai et al., 2020). We observed that the best fitting of the experimental results was obtained by assuming 4% reduced adsorption at the higher temperature (Fig. 3). Details on how the Freundlich coefficients were calculated are provided in the Supplementary Information. The Freundlich coefficients corrected for the higher temperature (K_f=24 (mg/g)/(mg/L)^n and n = 0.43) were used to calculate the breakthrough curves under the assumption that only adsorption would take place.

3.2. Melamine adsorption and biodegradation

Next, we used an inoculated filter without addition of methanol as a carbon source and compared the breakthrough curve of our inoculated filter (phase 1 of BAC 1) with the modeled breakthrough curve calculated under the condition that only adsorption takes place (Fig. 4). For the inoculated filter, melamine breakthrough occurred at a higher throughput (increased BV), compared to the modeled breakthrough curve.

Melamine removal (r) was calculated for the modeled results (adsorption only) which shows full breakthrough and for the inoculated filter which shows partial breakthrough for a throughput up to 6000 BV. We observed that the r of the inoculated filter (80 mg/g) was 25% higher than the calculated removal for the modeled curve for adsorption only (60 mg/g) (Fig. 4). We therefore conclude that in the presence of biomass, biodegradation is an important melamine removal mechanism in addition to adsorption.

Reinoculating the filter between 3500 and 4500 BVs had only a temporary and local effect on melamine biodegradation, as indicated by

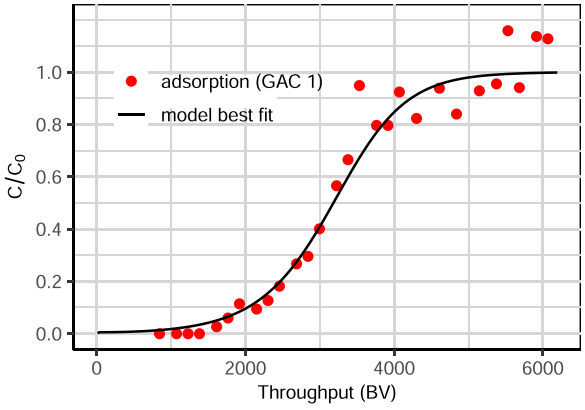

Fig. 3. Experimental and fitted (HSDM model) breakthrough curve of non-inoculated filter, assuming no biodegradation takes place.

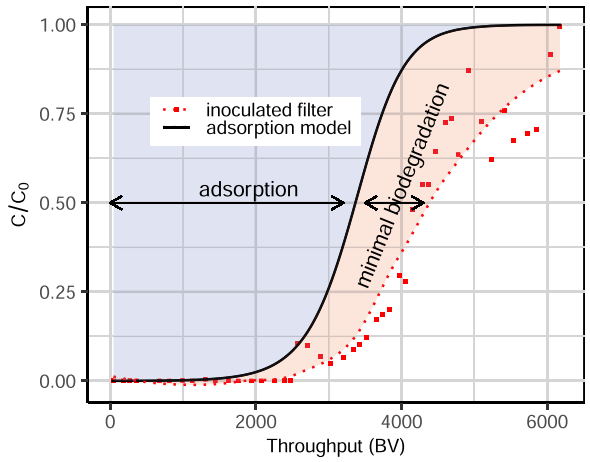

Fig. 4. Relative melamine concentration in effluent of an inoculated filter without methanol (BAC 1) and modeled breakthrough curve. Dotted line represents regression line fitted with the local estimated scatterplot smoothing method, calculated using the R package ggplot2.

the ammonium concentrations at the different filter positions for these BVs (Fig. S3). Ammonium is produced during melamine biodegradation and accumulates under anoxic conditions (Piai et al., 2021), which was the prevailing redox condition in the BAC 1 filter. An increase in ammonium concentration was measured temporarily at the top of the filter (position A), where biomass was introduced during reinoculation of the filter (Fig. S3). However, this effect was not observed further down the filter (position B) nor in the effluent, and ammonium concentrations decreased soon after reinoculation stopped (>4500 BVs). These results indicate that filter reinoculation did not significantly contribute to an increased melamine removal.

3.3. Melamine adsorption and biodegradation with methanol as additional carbon source

Fig. 5 shows complete melamine removal for inoculated BAC in the presence of methanol as an additional carbon source (both direct and indirect inoculation). For comparison, the modeled breakthrough curve for adsorption shows complete breakthrough within the time-frame of the experiments (6000 BVs). These results clearly demonstrate that melamine biodegradation is significantly enhanced due to the presence of an additional carbon source (methanol), which in turn contributes to extending the BAC filter lifetime.

The comparison between inoculated filters with (Fig. 5) and without (Fig. 4) methanol shows that an additional carbon source (methanol) is

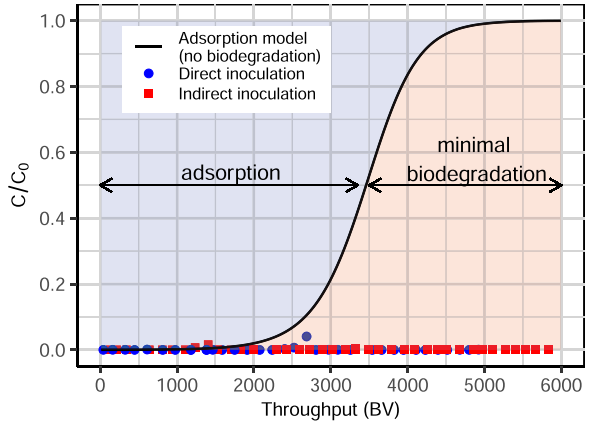

Fig. 5. Relative melamine concentration in effluent of directly and indirectly inoculated filters receiving methanol, operated at 32 min EBCT (BAC 2 and 3).

essential to prevent melamine breakthrough. The enhanced biodegradation of melamine and its transformation products in the presence of an additional carbon source has been previously been demonstrated in batch and column experiments (Galíndez-Nájera et al., 2009; Piai et al., 2021; Shelton et al., 1997; Takagi et al., 2012). Methanol is needed to compensate for the low C:N ratio of melamine (0.5 mol C/mol N). The C:N ratio in our filter's influent was 0.6–0.7 (molar basis). It has been shown that a C:N ratio of 1 or higher is required for complete biodegradation of melamine and its transformation products (Galíndez-Nájera et al., 2009; Takagi et al., 2012). Our experiments show that even at C:N ratios lower than 1 we can still obtain relatively high (>99%) melamine removal efficiency in BAC filters. Average methanol concentration in the filters influent ranged between 1.4 and 2.9 mg/L depending on the filter. In the filter bed (positions A and B), the methanol concentration was always below the limit of detection (1 mg/L). Even though methanol was already biodegraded at the top of the filter bed, its presence in the influent was enough to stimulate melamine biodegradation and prevent melamine breakthrough from these filters. In this study, we demonstrate that the addition of a carbon source can prolong the lifetime of a BAC filter by stimulating biological activity and, more specifically, melamine biodegradation. In practice biological activity can be stimulated using different strategies (e.g. aeration of influent, addition of nutrients), depending on the factors limiting micropollutants biodegradation.

Two inoculation methods were tested, each one with its advantages and disadvantages. Inoculating the GAC by directly adding biomass to a running filter is simpler, but depending on operational conditions and growth rates, biomass might not be retained in the filter and can washout. By inoculating the GAC indirectly, i.e., in a batch setup before introducing the GAC to the filter, the biomass can colonize the GAC surface without washing out. Additionally, this method is equivalent to transferring material from one BAC filter to another, which is a suitable strategy to inoculate new filters using BAC from filters where a diverse microbial community has already been developed. Our results show that both methods can be used successfully.

We also investigated if melamine could be removed efficiently at shorter contact times (EBCT of 18 min instead of 32 min) and observed that melamine removal at shorter contact times was comparable to the removal in the filters with longer contact times (Fig. 6). Only the upper layers of the filter bed (position A) showed higher melamine concentrations. Further down the column (position B), melamine concentrations are comparable, although slightly higher than those in the filters operated at longer contact times (EBCT 32 min) - 5% of the influent concentration compared to < 1%. Taking into account that position B of the filters, operated at shorter contact times, corresponds to an EBCT of 10–15 min, we conclude that an EBCT of around 15 min is the minimum time required to obtain more than 95% melamine removal. Moreover, regardless of the inoculation method, 19 min is enough to obtain more than 99% melamine removal, as long as an additional carbon source is supplied. EBCTs between 18 and 32 min are within the practical range applied in full-scale GAC filters e.g. as used in drinking water production plants (Kennedy et al., 2015).

3.3.1. Melamine desorption

A decrease in influent concentration can cause desorption of previously adsorbed melamine, as melamine adsorption is reversible (Piai et al., 2021). We assessed melamine desorption in the directly inoculated filter in the presence of methanol (EBCT 18 min, BAC 4) by feeding the filter with influent without melamine after 6000 BVs. During this phase the melamine concentration in the effluent remained rather low (<LOQ). Interestingly, higher melamine concentrations were detected in lower layers of the filter (position B) compared to the upper layers (position A) (Fig. 7). Possibly, melamine biodegradation rates are higher in the upper layers of the filter. This is in agreement with previous studies, which showed a vertical gradient of biomass activity in fixed-bed filters, with higher activity closer to the influent position, (Chen et al., 2016; Gibert et al., 2013).

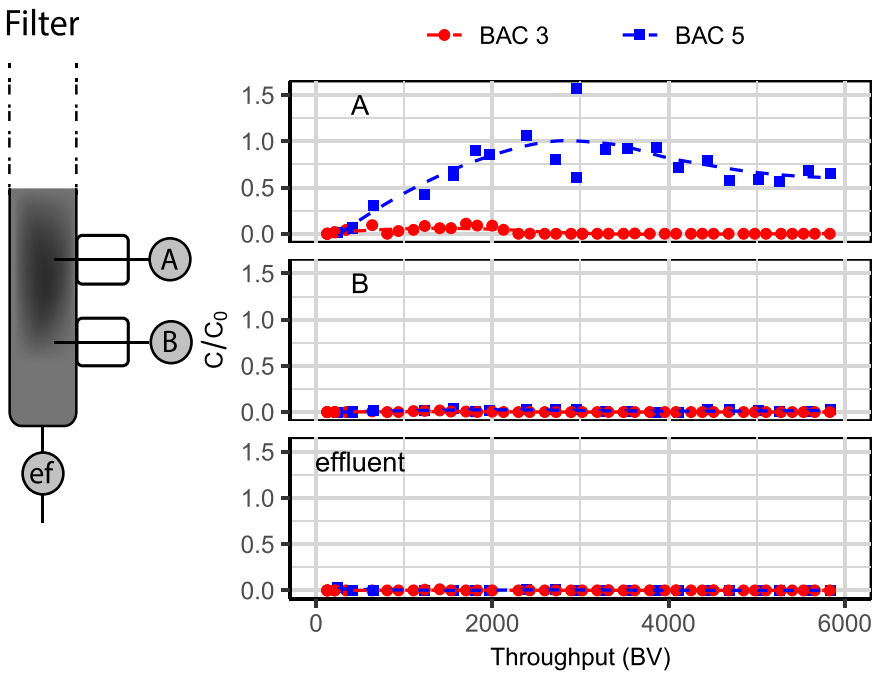

Fig. 6. Relative melamine concentration in intermediate positions (A and B) and effluent of indirectly inoculated filters with methanol, run at different EBCTs (BAC 3: 32 min at effluent point; BAC 4: 18 min at effluent point). Dotted lines represent regression line fitted with the local estimated scatterplot smoothing method, calculated using the R package ggplot2.

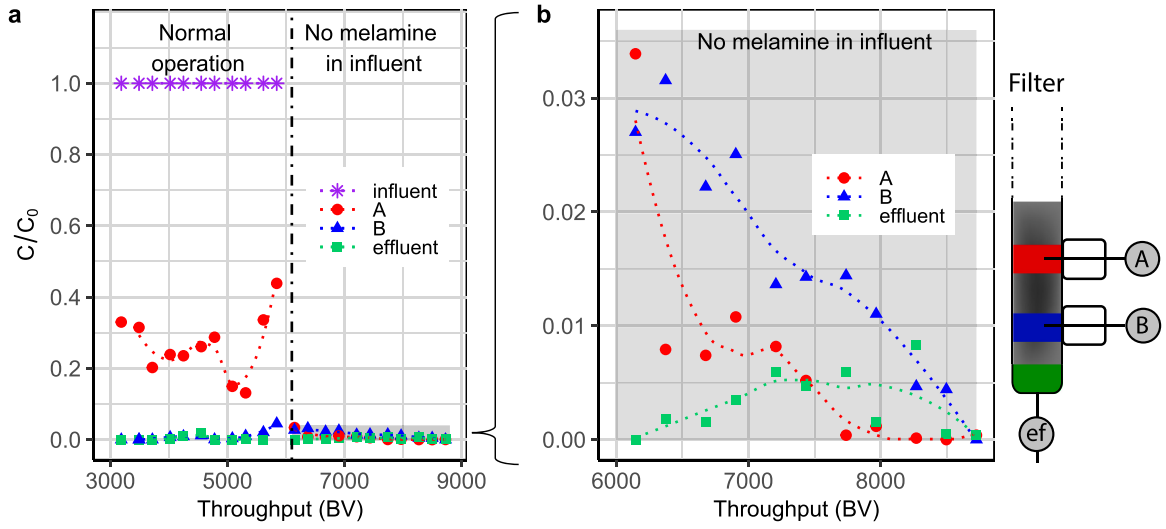

Fig. 7. Melamine in intermediate sampling points (A and B) and effluent of BAC directly inoculated, EBCT 18 min, with methanol (BAC 4). Filter was fed with influent without melamine between 6000 and 8700 BVs. a) 3000–8700 BVs; b) 6000–8700 BVs. Dotted lines represent regression line fitted with the local estimated scatterplot smoothing method, calculated using the R package ggplot2.

3.4. BAC regeneration

We divided the operation of the directly inoculated filter (BAC 1) into three phases: i) phase I, influent without methanol, ii) phase II (>6200 BVs), influent with methanol and iii) phase III (>8300 BVs), influent without melamine and with methanol.

We observed that melamine biodegradation rate increased significantly in phase II after methanol was added to the influent. The increased biodegradation rate is evident from the decreasing melamine concentrations in the column at positions A and B as well as in the effluent (Fig. 8a). We also observed a concomitant increase in ammonium concentrations in phase II (Fig. 8b). During this phase, the total nitrogen concentration in the effluent (as melamine-N and ammonium-N) exceeded the influent concentration as shown in Fig. 9. This excess nitrogen must originate from biodegradation of desorbed melamine and/or its transformation products (ammeline, ammelide and cyanuric acid) (Cook and Huetter, 1981). Based on the nitrogen mass balance in the filter in phase II and on the BAC load (q_I) at the end of phase I (before methanol addition to the filter), we calculated that 60% of the melamine that adsorbed during phase I desorbed and biodegraded during phase II when methanol was added. We hypothesize that the desorption of melamine from the BAC is the result of a concentration gradient from the surface of the activated carbon to the surrounding liquid, as a consequence of a lowering of the melamine concentration in the liquid due to biodegradation (phase II).

In phase III, when the filter did not receive melamine, melamine and

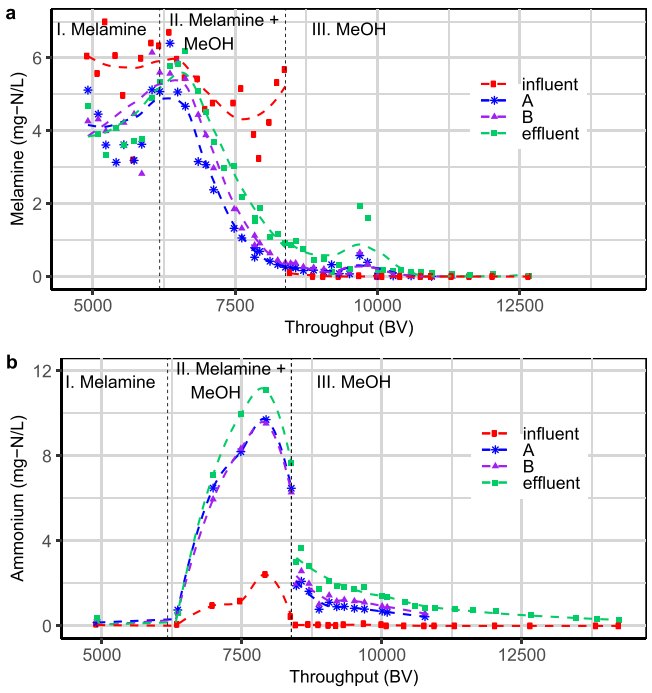

Fig. 8. Melamine (a) and ammonium (b) concentration (in mg-N/L) in influent, intermediate positions (A and B) and effluent of BAC directly inoculated, EBCT 32 min (BAC 1) before and after methanol addition to the influent. Dotted lines represent regression line fitted with the local estimated scatterplot smoothing method, calculated using the R package ggplot2.

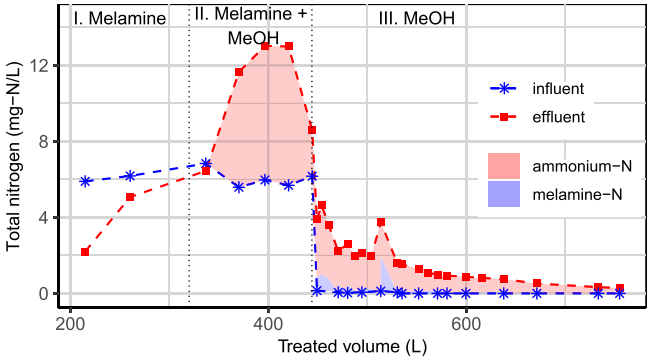

Fig. 9. Total nitrogen concentration (from melamine and ammonium) in influent and effluent of BAC directly inoculated (BAC 1) during the 3 different phases. Colored area corresponds to the amount of N originating from melamine desorption, measured as melamine-N (blue) or ammonium-N (red).

ammonium were still detected in the columns at positions A, B and the effluent (Fig. 8), indicating that melamine desorbed from the BAC and partially biodegraded. In total, an additional 38% of melamine desorbed during this phase, and most of it (81%) was biodegraded. The non-biodegraded melamine in the effluent most likely originated from the lower layers of the filter bed, where biomass activity will be lower (Gibert et al., 2013). The reason for the sudden peak and decrease in melamine concentration around 520 L of treated volume could not be elucidated. This is in agreement with the consistently higher melamine concentrations in the effluent compared to those in the column (positions A and B) once desorption occurs (phases II and III, Fig. 8a).

3.4.1. Sources of uncertainty

By the end of phase III, 98% of melamine adsorbed in phase I had been desorbed. The melamine adsorbed at the end of phase I, i.e., the BAC load (q_I) was calculated assuming equilibrium between the influent concentration and the activated carbon. There is a possibility that the actual q_I could be lower than the calculated load, given the fact that melamine effluent concentration reached only 80% of the influent concentration, due to biodegradation. However, it is not possible to assess the actual q_I, as both melamine adsorption and biodegradation occurred simultaneously and no nitrogen mass balance was calculated for phase I due to insufficient ammonium measurements. Given that the relative amount of melamine desorbed is calculated by dividing the mass of desorbed melamine by the BAC load in phase I, an overestimation of q_I would result in an underestimation of desorption. The results obtained based on this assumption (98% melamine desorbed) indicate that melamine desorption was not underestimated.

Regarding the nitrogen species, we assumed that: 1) Nitrogen uptake due to biomass growth is neglectable, given that biomass growth in the filter is limited by the low methanol concentration (<3 mg/L, C:N ratio 0.5–0.6 mol C/mol N in phase II); 2) Biodegraded melamine is fully mineralized and no transformation products (ammeline, ammelide, cyanuric acid) accumulate neither in the liquid nor in the GAC particles. This assumption is justified as ammeline was only present at (very) low concentrations (<0.6 mg/L) in all samples and at different position in the filter, and also neither ammelide nor cyanuric acid were detected. Additionally, previous experiments with melamine biodegradation using the same inoculum showed no accumulation of melamine transformation products at anoxic conditions (Piai et al., 2021). Other forms of inorganic nitrogen (nitrate and nitrite) were not detected throughout the experiment. We therefore expect that the contribution of melamine transformation products or other forms of inorganic nitrogen to the mass balance is negligible.

3.4.2. BAC relative adsorption capacity

The relative adsorption capacity of regenerated BAC was calculated by comparing in batch tests the adsorption capacity of the material from the filter BAC 1 after phase III, with the adsorption capacity of fresh GAC. We assessed melamine adsorption capacity of the material from the filter BAC 1 at 5 °C and after autoclaving, to ensure no biodegradation would take place. In order to compare the adsorption capacities at the same equilibrium concentrations, we used the fitted Freundlich coefficients to calculate the expected melamine load on fresh GAC at the equilibrium concentrations measured for BAC. We observed that the adsorption capacity of BAC determined at 5 °C was on average 29% lower than the calculated adsorption capacity of fresh GAC for the same temperature (Fig. 10a). Similarly, the adsorption capacity of BAC after autoclaving was on average 31% lower than the calculated adsorption capacity of fresh GAC at 20 °C (Fig. 10b). In neither case (autoclaved BAC at 20 °C or BAC at 5 °C), melamine degradation products or inorganic nitrogen species (ammonium, nitrate and nitrite) were detected, confirming that melamine was removed only due to adsorption, and not due to biodegradation. We conclude that the two approaches to eliminate melamine biodegradation by the BAC biomass gave comparable results and that 69–71% of the adsorption capacity could be recovered, despite the fact that 98% of previously adsorbed melamine desorbed from the BAC. This is in line with previously published batch experiments, where 27% of the GAC adsorption capacity could not be regenerated (Piai et al., 2021). The lost adsorption capacity (27–31%) for melamine is likely a consequence of the adsorption of organic molecules, which are products of microbial metabolism.

Regeneration efficiencies due to biological activity (bioregeneration) in fixed-bed filters ranging from 20% to 95% for GAC loaded with 2-nitrophenol, surfactants, benzene and toluene have been reported in literature (Klimenko et al., 2003; Putz et al., 2005; Smolin et al., 2020). Our results provide additional evidence that high levels of regeneration can be obtained when favorable conditions for biodegradation are provided. Additionally, biological activity can avoid the presence of a micropollutant in the effluent in case of desorption due to fluctuations in the influent concentration. In this study, a single micropollutant was used and the concentrations applied (mg/L range) were much higher

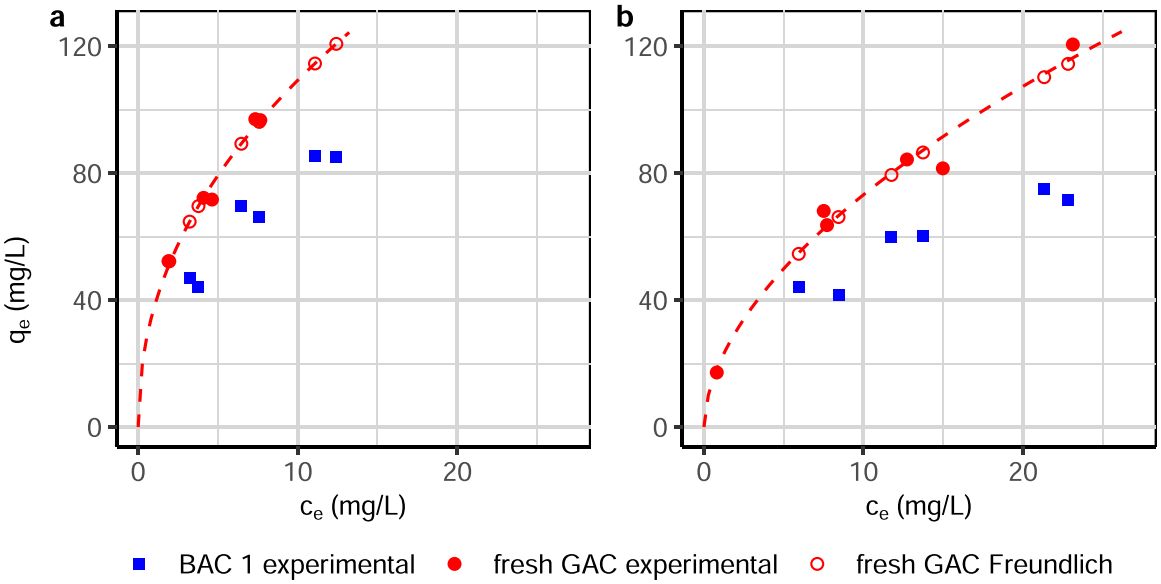

Fig. 10. Melamine adsorption by fresh GAC and regenerated BAC (material originated from filter BAC 1), using 2 different methods to avoid melamine biodegradation: a) adsorption capacity measured at 5 °C; b) autoclaved BAC (adsorption capacity measured at 20 °C). Lines represent fitted Freundlich model.

than the concentrations detected in surface water (μg/L range). In practice, micropollutants are present as complex mixtures at lower concentrations in water streams that contain also other components, such as dissolved organic matter (DOM). DOM can reduce micropollutants adsorption – by direct competition for adsorption sites or pore blockage (Hu et al., 2016; Li et al., 2003; Zietzschmann et al., 2014) – and stimulate biodegradation – e.g. by working as additional carbon source (Ma et al., 2018). Therefore DOM is expected to have both positive and negative effects on micropollutants removal with BAC and BAC regeneration. In order to prolong lifetime of full-scale BAC filters by increasing their biological activity, further studies should focus on lower concentrations of micropollutants and more complex matrix compositions.

4. Conclusions

In the current study, we have demonstrated that melamine biodegradation in continuous flow lab-scale BAC filters results in higher melamine removal and an extension of filter lifetime compared to GAC filters, where adsorption is the only removal process. Additionally, we have shown that melamine biodegradation rates in filters inoculated with melamine degrading biomass increased by adding a carbon source (methanol) to the filters influent. The increased melamine biodegradation rates resulted in desorption of melamine and consequently regeneration of a nearly saturated filter bed. However, we observed that despite that almost all adsorbed melamine desorbed, not all GAC adsorption capacity could be recovered. In the absence of a carbon source, melamine biodegradation contributed to the overall removal, but filter breakthrough did occur.

Overall, our study shows that stimulating microbial activity and hence micropollutants biodegradation is a promising strategy to making more efficient use and extend the lifetime of activated carbon filters used in water treatment. Future research should focus on investigating the effects of DOM on micropollutants biodegradation in BAC filters and how the positive effects on biodegradation can counteract the negative effects on adsorption. This knowledge will help identify opportunities to prolong lifetime of full-scale activated carbon filters and reduce the need for thermal reactivation.

CRediT authorship contribution statement

Laura Piai: Conceptualization; Methodology; Software; Formal analysis; Investigation; Writing – original draft; Visualization; Project administration. **Alette Langenhoff:** Conceptualization; Methodology; Resources; Writing – review & editing; Supervision; Funding acquisition. **Mingyi Jia:** Methodology; Software; Writing – review & editing. **Vinnie de Wilde:** Resources; Writing – review & editing. **Albert van der Wal:** Conceptualization; 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. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.126840.

References

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.

Brunner, A.M., Bertelkamp, C., Dingemans, M.M.L., Kolkman, A., Wols, B., Harmsen, D., Siegers, W., Martijn, B.J., Oorthuizen, W.A., ter Laak, T.L., 2020. Integration of target analyses, non-target screening and effect-based monitoring to assess OMP

related water quality changes in drinking water treatment. Sci. Total Environ. 705, 135779 https://doi.org/10.1016/j.scitotenv.2019.135779.
Chen, F., Peldszus, S., Elhadidy, A.M., Legge, R.L., Van Dyke, M.I., Huck, P.M., 2016. Kinetics of natural organic matter (NOM) removal during drinking water biofiltration using different NOM characterization approaches. Water Res. 104, 361–370. https://doi.org/10.1016/j.watres.2016.08.028.
Cook, A.M., Huetter, R., 1981. s-Triazines as nitrogen sources for bacteria. J. Agric. Food Chem. 29, 1135–1143. https://doi.org/10.1021/jf00108a009.
El-Sayed, W.S., El-Baz, A.F., Othman, A.M., 2006. Biodegradation of melamine formaldehyde by Micrococcus sp. strain MF-1 isolated from aminoplastic wastewater effluent. Int. Biodeterior. Biodegrad. 57, 75–81. https://doi.org/10.1016/j.ibiod.2005.11.006.
Galíndez-Nájera, S.P., Llamas-Martínez, M.A., Ruiz-Ordaz, N., Juárez-Ramírez, C., Mondragón-Parada, M.E., Ahuatzi-Chacón, D., Galíndez-Mayer, J., 2009. Cyanuric acid biodegradation by a mixed bacterial culture of Agrobacterium tumefaciens and Acinetobacter sp. in a packed bed biofilm reactor. J. Ind. Microbiol. Biotechnol. 36, 275–284. https://doi.org/10.1007/s10295-008-0496-5.
Gibert, O., Lefèvre, B., Fernández, M., Bernat, X., Paraira, M., Calderer, M., Martínez-Lladó, X., 2013. Characterising biofilm development on granular activated carbon used for drinking water production. Water Res. 47, 1101–1110. https://doi.org/10.1016/j.watres.2012.11.026.
Hu, J., Shang, R., Heijman, B., Rietveld, L., 2016. Influence of activated carbon preloading by EfOM fractions from treated wastewater on adsorption of pharmaceutically active compounds. Chemosphere 150, 49–56. https://doi.org/10.1016/j.chemosphere.2016.01.121.
Jourdin, L., Raes, S.M.T., Buisman, C.J.N., Strik, D.P.B.T.B., 2018. Critical biofilm growth throughout unmodified carbon felts allows continuous bioelectrochemical chain elongation from CO_2 up to caproate at high current density. Front. Energy Res. 6, 1–15. https://doi.org/10.3389/fenrg.2018.00007.
Kennedy, A.M., Reinert, A.M., Knappe, D.R.U., Ferrer, I., Summers, R.S., 2015. Full- and pilot-scale GAC adsorption of organic micropollutants. Water Res. 68, 238–248. https://doi.org/10.1016/j.watres.2014.10.010.
Klimenko, N., Smolin, S., Grechanyk, S., Kofanov, V., Nevynna, L., Samoylenko, L., 2003. Bioregeneration of activated carbons by bacterial degraders after adsorption of surfactants from aqueous solutions. Colloids Surf. A Physicochem. Eng. Asp. 230, 141–158. https://doi.org/10.1016/j.colsurfa.2003.09.021.
Lee, V.K.C., Mckay, G., 2004. Comparison of solutions for the homogeneous surface diffusion model applied to adsorption systems. Chem. Eng. J. 98, 255–264. https://doi.org/10.1016/j.cej.2003.08.028.
Li, Q., Snoeyink, V.L., Mariãas, B.J., Campos, C., 2003. Elucidating competitive adsorption mechanisms of atrazine and NOM using model compounds. Water Res. 37, 773–784. https://doi.org/10.1016/S0043-1354(02)00390-1.
Ma, B., Arnold, W.A., Hozalski, R.M., 2018. The relative roles of sorption and biodegradation in the removal of contaminants of emerging concern (CECs) in GAC-sand biofilters. Water Res. 146, 67–76. https://doi.org/10.1016/j.watres.2018.09.023.
Piai, L., Blokland, M., van der Wal, A., Langenhoff, A., 2020. Biodegradation and adsorption of micropollutants by biological activated carbon from a drinking water production plant. J. Hazard. Mater. 388, 122028 https://doi.org/10.1016/j.jhazmat.2020.122028.
Piai, L., van der Wal, A., Boelee, N., Langenhoff, A., 2021. Melamine degradation to bioregenerate granular activated carbon. J. Hazard. Mater. 414, 125503 https://doi.org/10.1016/j.jhazmat.2021.125503.
Putz, A.R.H., Losh, D.E., Speitel, G.E., 2005. Removal of nonbiodegradable chemicals from mixtures during granular activated carbon bioregeneration. J. Environ. Eng. 131, 196–205. https://doi.org/10.1061/(ASCE)0733-9372(2005)131:2(196).
Reungoat, J., Macova, M., Escher, B.I., Carswell, S., Mueller, J.F., Keller, J., 2010. Removal of micropollutants and reduction of biological activity in a full scale reclamation plant using ozonation and activated carbon filtration. Water Res. 44, 625–637. https://doi.org/10.1016/j.watres.2009.09.048.
Shelton, D.R., Karns, J.S., Mccarty, G.W., Durham, D.R., 1997. Metabolism of melamine by Klebsiella terragena. Appl. Environ. Microbiol. 63, 2832–2835.
Smolin, S., Kozyatnyk, I., Klymenko, N., 2020. New approach for the assessment of the contribution of adsorption, biodegradation and self-bioregeneration in the dynamic process of biologically active carbon functioning. Chemosphere 248, 126022. https://doi.org/10.1016/j.chemosphere.2020.126022.
Takagi, K., Fujii, K., Yamazaki, K.I., Harada, N., Iwasaki, A., 2012. Biodegradation of melamine and its hydroxy derivatives by a bacterial consortium containing a novel Nocardioides species. Appl. Microbiol. Biotechnol. 94, 1647–1656. https://doi.org/10.1007/s00253-011-3673-9.
Tros, M.E., Schraa, G., Zehnder, A.J.B., 1996. Transformation of low concentrations of 3-chlorobenzoate by Pseudomonas sp. strain B13: Kinetics and residual concentrations. Appl. Environ. Microbiol. 62, 437–442. https://doi.org/10.1128/aem.62.2.437-442.1996.
Wang, H., Li, J., Hu, A., Qin, D., Xu, H., Yu, C.P., 2014. Melaminivora alkalimesophila gen. nov., sp. nov., a melamine-degrading betaproteobacterium isolated from a melamine-producing factory. Int. J. Syst. Evol. Microbiol. 64, 1938–1944. https://doi.org/10.1099/ijs.0.055103-0.
Worch, E., 2012. Adsorption Technology in Water Treatment. Fundamentals, Processes and Modeling. Walter de Gruyter GmbH & Co. KG,, Berlin/Boston. https://doi.org/10.1515/9783110240238.
Zhang, S., Gitungo, S.W., Axe, L., Raczko, R.F., Dyksen, J.E., 2017. Biologically active filters – an advanced water treatment process for contaminants of emerging concern. Water Res 114, 31–41. https://doi.org/10.1016/j.watres.2017.02.014.
Zhiteneva, V., Ziemendorf, É., Sperlich, A., Drewes, J.E., Hübner, U., 2020. Differentiating between adsorption and biodegradation mechanisms while removing trace organic chemicals (TOrCs) in biological activated carbon (BAC) filters. Sci. Total Environ. 743, 140567 https://doi.org/10.1016/j.scitotenv.2020.140567.
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 micro-pollutants from treated wastewater. Water Res. 65, 297–306. https://doi.org/10.1016/j.watres.2014.07.043.