Removal of antibiotics in sand, GAC, GAC sandwich and anthracite/sand biofiltration systems

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Abstract

Drinking water biofiltration offers the possibility of the removal of trace level micropollutants from source water. Sand, granular activated carbon (GAC), GAC sandwich (a layer of GAC loaded in the middle of sand bed), and anthracite-sand dual biofilters were set-up in duplicate at bench-scale to mimic the filtration process in real drinking water treatment works. During the 3-month system operation, removal of five antibiotics (amoxicillin, clarithromycin, oxytetracycline, sulfamethoxazole, and trimethoprim) and overall biofilter performance were evaluated. Natural surface water spiked with a mixture of the target antibiotics was used as feedwater to the biofilters. Results showed that the target antibiotics were substantially removed (> 90%) by GAC-associated biofilters and partially removed (≤ 20%) by sand alone and anthracite-sand biofilters. In particular, the GAC sandwich biofilter exhibited superior performance compared to sand/anthracite biofilter, and the comparisons among all biofilters indicated that both adsorption and biodegradation contributed to the removal of the target antibiotics in the GAC-associated biofilters. Adsorption kinetics showed that sulfamethoxazole fitted with pseudo-first-order adsorption model, while trimethoprim,
amoxicillin, oxytetracycline and clarithromycin fitted the pseudo-second-order model. All antibiotics fitted the Langmuir model according to the isotherm experiment. To date, this is the first study evaluating the removal of antibiotics by GAC sandwich biofilters. Overall, this research will provide useful information which can be used for optimising or updating existing biofiltration processes in industry to reduce antibiotic residues from source water.

Keywords: Drinking water biofiltration; antibiotics; sand; granular activated carbon; anthracite; adsorption
1. Introduction

Antibiotic residues are being detected at increasing concentrations in aquatic environments, including water bodies used as drinking water sources (Luo et al., 2014; Simazaki et al., 2015). Few studies have reported the presence of antibiotics in drinking waters in different countries and regions. In Spain, four antibiotics (azithromycin, clarithromycin, erythromycin and sulfamethoxazole) were detected at measurable levels in finished drinking water (Boleda et al., 2014). Nineteen water utilities in the U.S. have detected sulfamethoxazole and trimethoprim (< 3.0 ng/L) in both finished drinking water and tap water (Benotti et al., 2009). Thiamphenicol has been reported at a maximum of 104.3 ng/L among 32 pharmaceuticals in tap waters collected from 13 cities in China, followed by sulfamethazine (89.6 ng/L) and sulfathiazole (27.4 ng/L) (Leung et al., 2013). In general, the lack of comprehensive and systematic studies on the occurrence of antibiotics in drinking water may limit the assessment of the potential human health risks from exposure to a mixture of very low concentration antibiotic residues via drinking water throughout a lifetime (WHO, 2012). The effect of chronic, low-level exposure to antibiotics on the human body is still unknown.

Biofiltration is a natural and cost-effective drinking water treatment technology which is widely used in Europe (Zearley and Summers, 2012). Media commonly used for drinking water treatment are adsorptive media such as granular activated carbon (GAC) and non-adsorptive media such as sand and anthracite. Sand biofiltration is one of the earliest water treatment process and often regarded as an efficient and stable technology in drinking water treatment plants (DWTPs). The major component of the treatment process in sand biofilters occurs at the surface layer (known as the *schmutzdecke*) of the sand bed in which biological activities are highest (Zhu and Bates, 2013). As an energy-efficient drinking water treatment technology, sand biofiltration offers an opportunity to remove trace level micropollutants from the source water. For instance, Zearley *et al.* reported removal efficiencies of 4.2% for sulfamethoxazole and 92% for trimethoprim by lab-scale sand filtration (Zearley and Summers, 2012). Pompei *et al.* observed removals ranging from 70 – 99% of 2 µg/L of paracetamol,
Diclofenac, naproxen, ibuprofen, benzophenone-3 and methylparaben in a sand biofiltration pilot plant in Brazil (Pompei et al., 2019). GAC biofilter has also been widely used in DWTPs (Suffet, 1980). Adsorption and biodegradation are main mechanisms contributing to the removal of organic compounds during the GAC biofiltration process. The unique porous surface structure and high surface area of GAC enable its capacity for the adsorption of organic compounds and other non-polar contaminants; while the biofilm formed on the surface of GAC can remove organics via biodegradation. It has been proven that GAC biofiltration can effectively remove a number of organic micropollutants (including antibiotics) in drinking water and wastewater treatment processes (Gerrity et al., 2011; Reungoat et al., 2011; Kennedy et al., 2015). Gerrity et al. reported that 90 – 95% of sulfamethoxazole and trimethoprim were removed by pilot-scale biological GAC filter (Gerrity et al., 2011). Major drawbacks of the GAC biofiltration include the formation of biofilm and the continuous loading of natural organic matter may block the adsorbable area and cause a reduction in the GAC media lifespan.

In addition to single medium biofilters, combination of different filter materials is also common practice in DWTPs. The mostly commonly used dual-media configurations are anthracite/sand and GAC/sand (Shirey et al., 2012). Introducing a layer of GAC to the slow sand filter (GAC sandwich biofilter) to form ‘super-filters’ make an advanced treatment being used in DWTPs worldwide. The GAC sandwich biofilter was first studied in the UK by Bauer et al. in 1996 for the removal of pesticides (Bauer et al., 1996). As well as increasing the adsorption capacity of the carbon, it enhances the already excellent biological performance of the slow sand filter. Recent studies based on lab-scale GAC sandwich biofilters have shown capacity to remove DEET (N,N-diethyl-m-toluamide), paracetamol, caffeine and triclosan from synthetic waste water (Li et al., 2018; Li et al., 2019). To date, no research has been conducted for the removal of antibiotics by bench or pilot-scale GAC sandwich biofiltration in the context of drinking water treatment. Moreover, previous bench-scale biofiltration experiments often use synthetic tap water as the feed (Zearley and Summers, 2012; Paredes et al., 2016), which cannot represent the complexity of real environmental conditions. Considering the persistence of antibiotic residues in natural water environments, it is of great importance to
find an economical and effective way to reduce the risk of antibiotic resistance dissemination in drinking water.

Four types of commonly used biofilters, including Sand, GAC, GAC sandwich, and anthracite-sand, were set-up at bench-scale. Over the course of three months, this study focused on the following: (1) the effectiveness in removing five antibiotics (amoxicillin, clarithromycin, oxytetracycline, sulfamethoxazole and trimethoprim) by different types of biofilters; and (2) the overall biofiltration process robustness. The adsorption kinetics of the target antibiotics onto GAC under the experimental conditions were determined to further explore the adsorption removal mechanism by GAC.
2. Materials and methods

2.1 Chemicals

Five antibiotics amoxicillin (AMOX), clarithromycin (CTM), oxytetracycline (OTC), sulfamethoxazole (SMX) and trimethoprim (TMP) were selected, representing different commonly used classes. The major physical-chemical properties of the selected antibiotics are summarised in Table S1. All standards (purity ≥99.0%) were purchased from Sigma-Aldrich, UK. HPLC grade acetonitrile and methanol were obtained from Fisher Scientific, UK. Individual stock standards were prepared in methanol at 1 mg/mL, except for amoxicillin, which was dissolved in acetonitrile/water (50:50, v/v) at 1 mg/mL. A working solution was prepared by diluting the stock solutions in ultrapure water into 1 mg/L. All the stock solutions were stored at -20 °C and working solutions were preserved at 4 °C.

2.2 Biofilter design and operation

A total of 25 L of lake water was collected twice a week from Regent’s Park, London (latitude 51.525187, longitude -0.158017) from October 2017 to January 2018. Fresh feedwater was added to the system every day, while the remaining of raw water was kept at 4 °C. Biofilter feedwater was spiked with the target antibiotics at 2 μg/L, except for amoxicillin which was spiked at 5 μg/L due to the analytical method constraints. The concentration selected in this study was according to their reported removal in the literatures and the analytical method limitations (Zearley and Summers, 2012; Paredes et al., 2016; Zhang et al., 2017).

Sand, GAC, GAC sandwich, and anthracite-sand biofilters were set-up in duplicate at bench scale. Silica sand was purchased from Mineral Marketing, UK with an effective size of 0.20 mm (size range 0.16 - 0.50 mm) and a uniform coefficient of 1.82; GAC was purchased from Chemviron Carbon, UK with an effective size of 0.72 mm (size range 0.62 - 1.60 mm) and a uniform coefficient of 1.68; anthracite was purchased from EGL Puracite, UK with an effective size of 0.90 mm (size range 0.85 - 1.46 mm) and a uniform coefficient of 1.32. Surface characteristics of the filter media are shown in Fig. S1. The media was uniformly placed into
62 cm-length laboratory acrylic (Plastic Shop, UK) columns with a 36-mm inner diameter (ID) and 2-mm wall thickness. In this study, depending on the effective size of sand, GAC and anthracite, the ratio of the column diameter to the filter media diameter ranged from 40-180, which are sufficiently large to prevent wall effects of media packing (Jiang et al., 2017). The composition of biofilters is shown in Fig. 1, each column was loaded with 36 cm of filter media and 5 cm of support media (0.6–3.0 mm gravel) to allow free drainage of filter effluent.

The biofiltration system was operated continuously at room temperature (20.3 ± 2.0 °C) for 12 weeks. A filtration rate of 0.06 m/h was used for all filters (D’Alessio et al., 2015). The run was divided into three phases; phase I (maturation), when ≥ 99% reduction was achieved for total coliforms and *Escherichia coli* (*E. coli*) after 4 weeks’ operation; phase II (antibiotics spike), from which the target antibiotics were added to the feed for 8 weeks; and phase III (backwashing/cleaning) at the end of system run. Specifically, for phase II, the spike of the five antibiotics started at the same time and continued for the remainder of the study. Fresh feedwater spiked with antibiotics were refilled to the system every day. For the cleaning of GAC sandwich, the *schmutzdecke* layer was stirred by glass rod and water above the filter was then withdrawn using a syringe at the same time (Reungoat et al., 2011). The remaining biofilters were backwashed for 10 min using biofilter effluents to achieve a 20 - 30% bed expansion (Liu et al., 2012).

### 2.3 Biofilter sampling strategy

During the course of system run, duplicate influent and effluent samples were taken weekly (one-time sampling) for the determination of general water quality parameters, including pH, conductivity, turbidity, dissolved organic carbon (DOC), ultraviolet absorbency (UV$_{254}$), dissolved oxygen (DO), phosphate (PO$_4^{3-}$), nitrite (NO$_2^-$) and nitrate (NO$_3^-$), total coliforms and *E. coli*. Duplicate influents and effluents were also collected weekly (one-time sampling) for antibiotic removal determination after the spike of antibiotics to the system. Details on the analytical methods are provided in Section 2.5. In particular, as a slow filtration rate (0.06 m/h) was used throughout this study, effluents for antibiotic analysis were collected.
continuously until enough volume (500 - 550 mL) was achieved, while influents were collected five times and mixed as one during the collection of the effluents. Prior to sampling, the flow was rechecked and adjusted as needed.

2.4 GAC adsorption kinetics

In addition to the biofiltration experiment, isotherms and adsorption kinetics of the five antibiotics on GAC were determined to further explore the removal mechanisms of the target antibiotics. GAC used in the adsorption experiment was the same type of media used in the biofiltration experiment (see Section 2.2 for details). The initial concentration of the five antibiotics were set at 5 μg/L by adding stock solution to aqueous samples. For the contact time test, 0.5 g GAC was added into glass bottles filled with 1 L lake water spiked with antibiotics. Bottles were placed in a rotary mixer at a speed of 30 rpm. Reaction time was set at 1 h, 3 h, 6 h, 9 h, 12 h, 24 h, and 48 h, respectively. For the GAC dosage test, 0.025 g, 0.05 g, 0.1 g, 0.25 g, 0.5 g, and 1 g GAC were added into 1 L lake water. Bottles were placed in a rotary mixer at the speed of 30 rpm for 24 h. All bottles were prepared in triplicate and samples process followed the analytical procedures described in Section 2.5.2. In addition, for each test, lake water spiked with 5 μg/L of antibiotics without GAC addition was used as a control to check the biodegradation of the target antibiotics during the experimental period. No measureable biodegradation of the target antibiotics was observed in the control bottles, hence, only adsorption mechanism was considered in the test.

2.5 Analytical techniques

2.5.1 General water quality parameters

Determination of general water quality parameters followed standard methods (APHA) (Baird et al., 2012). Table S2 lists the methods and instruments used in this study. Influent and effluents were filtered through a 0.45 μm mixed cellulose esters membrane (Millipore, UK) for the analysis of DOC, phosphate, nitrite and nitrate. DOC was determined by a Shimadzu TOC-L machine (UK) following manufacturer’s procedures; while phosphate, nitrite and nitrate
were analysed by ion chromatography (IC, Dionex ICS 1100, US). A standard membrane filtration method was used for the enumeration of *E. coli* and coliform bacteria following ISO 9308-1:2014.

2.5.2 Quantification of Antibiotics

Solid phase extraction (SPE) was used to extract target antibiotics from aqueous samples. Prior to extraction, samples were filtered through a 0.45 µm membrane filter (Millipore, UK) and acidified to pH 3.0 with hydrochloric acid. Na₂EDTA was added to samples at 0.5 g/L. Then, all samples were subjected to SPE using 500 mg Oasis HLB (hydrophilic lipophilic balance) cartridges (Waters, UK). Lake water spiked with 2 µg/L of antibiotic mixture was used to control for SPE recovery. Details of SPE protocol are summarised in Fig. S2. Samples were reconstituted to a final volume of 500 µL with 0.1% formic acid in acetonitrile-water (50:50, v/v). A matrix-matched calibration method was used throughout this study (Ben et al., 2008; Grujic et al., 2009). The lake water was free of the selected antibiotics and thus was used to prepare the matrix-matched standards in order to minimise the influence of interfering substances from the environmental sample. An Accela 1100 HPLC system coupled to a LTQ ion-trap mass spectrometer (Thermo Finnigan LTQ) was used for the detection of target antibiotics. The optimised mass spectrometer parameters are summarised in Table S3. Mean recoveries and limit of detection (LOD) for the antibiotics are reported in Table S4.

2.6 Data analysis

Removals of DOC, turbidity, UV₂₅₄, total coliforms, *E. coli* and antibiotics were calculated based on influent and effluent concentrations. Mean and standard deviation were calculated in Microsoft Excel 2016. One-way analysis of variation (ANOVA) and Pearson correlation analysis were performed using OriginPro 2018. All figures were generated by OriginPro 2018.
3. Results and discussion

3.1 Biofilter performance

The main physico-chemical characteristics of the lake water is summarised in Table S5. The lake water is slightly alkaline, with pH ranging from 7.85 - 8.35. The average turbidity, DO and DOC in the lake water during this study were 0.54 ± 0.07 NTU, 7.32 ± 1.49 mg/L and 3.82 ± 0.31 mg/L, respectively. The biofiltration system was operated continuously for 12 weeks, which generated a total of 12 batch samples. The overall performances of the sand biofilter (SB1 and SB2), GAC biofilter (GB1 and GB2), GAC sandwich biofilter (GSB1 and GSB2) and anthracite-sand biofilter (ASB1 and ASB2) are discussed in this section.

Generally, microbiological activities were more dynamic in phase I by the evidence of greater oxygen consumption/pH drop (Fig. S3), and DOC removal (Fig. S4). The levels of DO present in the effluent were above the recommend value of 3 mg/L for slow sand filtration (Fig. S3-c), suggesting an aerobic environment in the aqueous phase throughout the biofilter columns (Huisman and Wood, 1974). The GSB was found to be the most effective in removing turbidity-causing particles (Fig. S3-d). By contrast, ASB exhibited the worst performance in terms of turbidity reduction. Nitrate concentration increased in the effluent of SB and ASB during phase I and II (Fig. S3-e), while decreased in the effluent of GB and GSB. As no chemical oxidant was included in the filtration process, biological nitrification was the main causative agent for the increase of nitrate concentration in the effluents. The involvement of GAC in GB and GSB may contribute to the removal of nitrate through adsorption (Zhang et al., 2015). Bacterial communities attached to the filter media may affect the extent of nitrification during biofiltration (White et al., 2012), resulting in the differences in nitrate concentration in the effluents. After biofiltration, phosphate remained stable (ranged between 0.31 mg/L and 0.35 mg/L) in phase I and increased moderately to 0.41 mg/L (on average) in phase II (Fig. S3-f), with no statistical difference (p > 0.05). The increased phosphates in the effluents may be due to algal respiration which converts algal phosphorus to inorganic phosphorus (Pompei et al., 2017). No phosphate was found in the lake water samples in
January, which may be due to the seasonal variation and result in the absence of phosphate in the influent and SB in phase III. Removal profiles of total coliforms and *E. coli* are presented in Fig. S5. After four weeks’ operation, both total coliforms and *E. coli* achieved 2-log removal by all of the biofilters, indicating that a matured biofilm has been established. The removal slightly fluctuated between week 5 to 11, probably due to the detachment of biofilm from the media surface. The removals of total coliforms and *E. coli* were consistently above 90%, which was within the typical removal range of between 90% and 99.9% required by conventional slow sand filters (NDWCH, 2000).

A general trend of a decreasing removal of DOC from phase I to II was observed across all types of biofilters (Fig. 2A). The finding is in agreement with Gibert's research, where the DOC removal progressively declined over time (Gibert et al., 2013). GAC-associated filters revealed significantly greater DOC removal efficiencies (*p* < 0.001) than SB and ASB during the operational period of 3 months, attributed to the adsorption of organic matter by the porous GAC structure. The introduction of a GAC layer to the sand filter showed a similar initial DOC removal compared to the whole GAC-bed filter, although a reduced removal percentage (by 11%) was observed by the sandwich filter at the later stage of the system run. This is somewhat expected, as the dosage of GAC in GSB was lower than in the whole GAC bed and the sorption capacity of GAC gradually declines over time (Gibert et al., 2013). Mean removals of DOC were 21 ± 8% and 14 ± 9% by SB and ASB, respectively. Previous research has also reported that by using anthracite-sand dual media (similar grain size with this study), partial DOC removal (< 27%) was observed and after 6-months of operation, the removal plateaued at 7.6% (Zhang et al., 2017). Campos *et al.* found an average of 23% DOC removal by full-scale drinking water slow sand filters (Campos et al., 2002). The trends for the reduction of UV\textsubscript{254} absorbance in biofilters were consistent with DOC removal (Fig. 2B).

In DWTPs, biofilters are backwashed, which involves pumping water backwards through the filter media, periodically to restore the hydraulic capacity as the filters are usually used to remove both DOC and particles (Basu et al., 2016). In this study, biofilter backwashing/cleaning had a significant impact on pH, conductivity, DO, turbidity, nitrate, total...
coli forms and *E. coli* (Fig. S3 and S5), while DOC was not sensitive to backwashing/cleaning (Fig. S6). These observations are similar to those reported by Emelko *et al.*, in full-scale biofilters, allowing conventional performance parameters to be optimised without compromising DOC removal (Emelko *et al.*, 2006).

### 3.2 Overview of target antibiotics removal

The overall mean removal of the five antibiotics over the entire course of the experiment were 20 ± 19% by SB, 97 ± 2% by GB, 97 ± 3% by GSB, and 18 ± 9% by ASB. Fig. S7 shows the average removal of antibiotics by the duplicate biofilters. GB and GSB exhibited considerably superior performance in eliminating all five antibiotics compared to sand or anthracite media biofilters. TMP and OTC were removed significantly more effectively by SB (55 ± 24%, *p* < 0.01) and ASB (33 ± 12% on average, *p* < 0.05), respectively. The remaining three antibiotics showed comparable removal rates by the SB and ASB. The dynamic concentration changes of the five antibiotics over time are shown in Fig. 3. No obvious trend of increasing or decreasing removal was found for antibiotics over the two-month study period. Details of individual antibiotic are discussed below.

### 3.3 Removal of antibiotics by sand and anthracite-sand dual biofilters

Over the antibiotic-spiking operational period, similar SMX effluent concentrations were found in SB and ASB, with a mean value of 1.88 ± 0.11 μg/L for SB and 1.76 ± 0.15 μg/L for ASB, respectively (Fig. 3). In general, SMX showed very limited removal (< 15%) in the system, which was similar to the removal of 4.1% reported in previous laboratory sand biofiltration study (Zearley and Summers, 2012). The removal of TMP in SB ranged from 39% to 75% at the earlier stage (5-8 weeks) after antibiotics spike and from 60% to 87% at the later stage (9-11 weeks), with the lowest effluent concentration of 0.27 μg/L found in week 10 samples. TMP was reported to be readily biodegradable (removal ranged from 50% to 92%) in a previous sand biofilter study (Zearley and Summers, 2012). These results suggest that conventional sand biofilter is effective for the elimination of TMP during drinking water
Removal of TMP in the SB was significantly higher \( (p < 0.01) \) than that in the ASB (Fig. 3). For comparisons, mean effluent concentration of TMP was 0.89 ± 0.48 μg/L and 1.74 ± 0.18 μg/L for SB and ASB, respectively. A much higher (> 75%) TMP removal in anthracite-sand dual media biofilters was observed by Zhang \textit{et al.}, when 2-year-old media from a drinking water treatment facility were used (Zhang \textit{et al.}, 2017). As TMP was found to be readily biodegradable in sand biofilters under the identical operational conditions, it is likely that 3 months were not sufficient to develop an effective biofilm on the surface of anthracite for biodegrading TMP. ASB showed slightly better removal of AMOX than the SB. The mean value of AMOX effluent concentration was 4.32 ± 0.25 μg/L for SB and 4.05 ± 0.32 μg/L for ASB, respectively (Fig. 3). OTC was removed more effectively by the ASB than other antibiotics, ranging from 19% to 58%. The highest and lowest OTC effluent concentrations were found in SB (1.87 μg/L in week 10 sample) and ASB (0.85 μg/L in week 5 sample), respectively. Similar to SMX, both the SB and ASB showed limited removal for CTM, with the effluent concentrations ranging from 1.51 μg/L (25% removal) in ASB to 2.00 μg/L (no removal) in SB. This observation is in agreement with the results reported by Nakada \textit{et al.}, where no removal was observed for CTM during sand filtration in a pilot-scale plant (Nakada \textit{et al.}, 2007). The removal of TMP was considerably reduced \( (p < 0.01) \) from 69% to 7% after backwashing of SB. By contrast, removals of the remaining antibiotics were not affected \( (p > 0.05) \), which is possibly due to the already low removal rates before backwashing occurred. Fig. S8 shows the percentage removal of the target antibiotics by SB and ASB.

For the non-adsorptive media, biodegradation is the only significant removal mechanism for the antibiotics from the feedwater (Reungoat \textit{et al.}, 2011; Zearley and Summers, 2012). The antibiotics exhibited different levels of biodegradability in this study. Based on the mean removal by SB and ASB, the antibiotics were classified as follows (Zearley and Summers, 2012): SMX and CTM had removals of less than 15% and were classified as recalcitrant to biodegradation, AMOX and OTC had removals between 15% and 50% and were classified as having slow biodegradation rates (moderately biodegradable), and TMP
had removals between 50 and 85% (only in SB) and was classified as being readily biodegradable.

Sand biofiltration works through a slime layer that accumulates above the sand surface (known as the *schmutzdecke*) and within the upper layers of the sand bed (Huisman and Wood, 1974; Campos et al., 2002; Unger and Collins, 2008). The *schmutzdecke* layer is highly biologically active and has been shown to have the ability to biodegrade many trace level micropollutants (Wang et al., 2007; Maeng et al., 2011; Zearley and Summers, 2012; Dalahmeh et al., 2018). The biodegradation rate of antibiotics is possibly affected by their initial concentration in the raw water. It was hypothesised that SMX degradation would only occur if a threshold concentration of 0.3 μg/L was exceeded (Gruenheid et al., 2008). This was further confirmed by a laboratory column experiment, where a higher concentration of SMX (4 μg/L) in the feed water can be removed more effectively than at 0.25 μg/L (Baumgarten et al., 2011). This is due to the adaptation of biomass for degradation proceeded faster at elevated concentration of SMX. Furthermore, the sorption of antibiotics onto the *schmutzdecke*, or within the filter column might also contribute to their removal (Rooklidge et al., 2005). For hydrophilic antibiotics (AMOX, OTC, SMX and TMP), their removal through sand filtration might also attribute to the removal of the fine suspended particles adsorbing to these compounds (Huisman and Wood, 1974; Nakada et al., 2007). The filter substrate plays an important role in determining bacterial community composition. Although seeded from the same source water, compared to anthracite, microorganisms are prone to colonise on the surface of sand due to its smaller particle size and larger surface area (Wang et al., 2007). Furthermore, the different elemental compositions of sand and anthracite surfaces may also have influenced bacterial attachment (Wang et al., 2007). These factors could explain to a certain extent the variations of removal efficiencies for individual antibiotic throughout this study.
3.4 Removal of antibiotics by GAC and GAC sandwich biofilters

The GB and GSB showed consistent and stable removals for all of the antibiotics over time. Fig. S9 shows the removal efficiencies of the antibiotics by the two types of biofilters. The overall mean removals of the five antibiotics during the whole operational period were 97% for both GB and GSB. Except for AMOX, the effluent concentrations of antibiotics were all below 0.07 μg/L. GSB achieved considerably higher removals (p < 0.01) than the conventional sand filter, indicating the applicability of GSB in eliminating trace organic compounds from drinking water. This observation is in agreement with the results reported by Li et al., where an average removal of 95% was observed for DEET, paracetamol, caffeine, and triclosan in sandwich biofilters with various GAC layer depths (Li et al., 2018). Comparing the results obtained from SB and GSB, it can be assumed that the removal of target antibiotics in the sandwich biofilter could be attributed to both adsorption by the GAC layers and biodegradation within the schmutzdecke layer. The contribution of biodegradation could not be elucidated in the sandwich biofilter since the overall removal of antibiotics was similar to that obtained in the pure GAC column. However, it is worth mentioning that the GAC sandwich seems a cost-effective option compared to full GAC contactors (Bauer et al., 1996). Antibiotic removal was not affected by the cleaning/backwashing of GAC and GAC sandwich biofilters in this study.

3.5 Relationship between general water quality parameters and antibiotics in effluents

Pearson correlation analysis showed that the removal of antibiotics is significantly correlated to nutrient levels, i.e. organic carbon and nitrate in the effluents (Table 1). Nitrification occurs in both sand and GAC biofilters (Nakhla and Farooq, 2003; de Vera et al., 2018). It has been reported that effluents from wastewater treatment plants (WWTPs) containing antibiotics have the potential to disrupt nitrification/denitrification processes in aquatic ecology (Costanzo et al., 2005). For instance, Costanzo found that the bacterial denitrification rates were reduced significantly after short term exposure to clarithromycin and amoxicillin at 1000 μg/L (Costanzo et al., 2005); antibiotics such as oxytetracycline have been shown to inhibit the nitrification process in surface water (Klaver and Matthews, 1994).
Significant positive correlations between the antibiotics (except for TMP) and nitrate in the effluents indicated the possible impact of antibiotics on the nitrification/denitrification processes. In agreement with this observation, Watkinson et al. identified nitrate as a potential indicator to predict total antibiotic concentration in effluent in a case study of WWTP (Watkinson et al., 2007). However, the extent of the interference exerted by antibiotics on nitrification/denitrification was not clear as low exposure level was used in the present study. A mass balance study with regards to nitrogen should be included in future study. A limitation is that the present research only investigated the non-metabolised parent form of the target antibiotics, therefore, in the context of antibiotic pollution risks, removal rates presented can be overestimated as metabolites may remain pharmaceutically active in the filtered water (Mompelat et al., 2009). Additional research is needed to identify the dominant antibiotic biodegradation by-products and clarify the relevant pathways in drinking water biofilters to understand the degradation mechanisms before substantial conclusions can be made.

3.6 Antibiotics adsorption onto GAC

3.6.1 Adsorption kinetics

Fig. 4 shows the adsorption of the five antibiotics by GAC in surface water samples. The optimal contact time was 12 h for TMP, 24 h for SMX, OTC and CTM, and 48 h for AMOX, when each antibiotic had reached an equilibrium concentration and > 90% removal was achieved. From Fig. 4, experimental adsorption capacity ($q_e$) of the five antibiotics in surface water was 0.0099, 0.0099, 0.0091, 0.0097, and 0.0096 mg/g for SMX, TMP, AMOX, OTC and CTM, respectively. Further kinetic modelling of the adsorption removal of antibiotics onto GAC was carried out using Lagergren pseudo-first-order and pseudo-second-order equations, which are two types of models that have been widely used to describe the adsorption of pollutions from water onto adsorbents (Hameed and Rahman, 2008; Simonin, 2016; Li et al., 2018). Details on the calculations of kinetic modelling are provided in the Supporting Information (page 12).
Table 2 lists the results of the rate constants for different antibiotics. The results suggest that for TMP, AMOX, OTC and CTM, the pseudo-second-order adsorption mechanism was predominant, indicating that the rate of the adsorption is controlled by the adsorption reaction at the liquid/solid interface in the GAC (chemisorption process) (Ho and McKay, 1999; Hameed and Rahman, 2008). SMX had a better fit with the pseudo-first-order model, suggesting that the adsorption is a diffusion-controlled process (Simonin, 2016).

3.6.2 Adsorption isotherms

The impact of GAC dosage on antibiotic removal is shown in Fig. S10. Data from the batch experiments were fitted to the Freundlich and Langmuir isotherm models to evaluate the adsorption characteristics of the five antibiotics on GAC. Details are provided in the Supporting Information (page 13). Isotherm parameters are summarised in Table 3. Real data fitted better with the Langmuir model ($R^2 > 0.9099$) than the Freundlich model, especially for AMOX and CTM. Based on these results, GAC has $q_m$ values (maximum/saturation adsorption capacity) ranging from 0.0072 mg/g for CTM to 0.0269 mg/g for TMP. This could be explained by the hydrophobicity of CTM as the difference in adsorption capacities is related to the hydrophobicity of a compound (Nam et al., 2014). Considering the antibiotic spike concentration (2 and 5 μg/L), the amount of GAC loaded (approximately 50 g in the sandwich filter) and the filtration rate used (0.06 m/h), theoretically, it would take approximately 1~2 years until the GAC is saturated in the sandwich filter (surface sand cleaning is required regularly). This is consistent with practice in DWTPs, as it typically requires years of operation until GAC sorption capacity becomes exhausted.
4. Conclusion

Biofiltration has the potential to be an effective process for controlling trace level antibiotic contaminations in drinking water. During 3-months of system operation, GAC-associated biofilters exhibited a considerably superior performance in eliminating all of the five antibiotics and the mean removal was 97 ± 2%. In contrast, much lower removals were observed for the sand and anthracite-sand dual biofilters, where an average of 20 ± 19% and 18 ± 9% of antibiotics were removed from the feedwater, respectively. Considering costs and maintenance of GAC contactors, the GAC sandwich biofilter represents a more promising process for drinking water treatment. Biofilter backwashing/cleaning showed no effect on DOC removal. GAC adsorption kinetics showed that sulfamethoxazole fitted with pseudo-first-order adsorption model, suggesting that the adsorption is a diffusion-controlled process. Trimethoprim, amoxicillin, oxytetracycline and clarithromycin fitted the pseudo-second-order model, indicating that the adsorption is controlled by the surface reaction. The applicability of the Langmuir model suggests a uniform adsorption of the antibiotics on the GAC surface. Overall, this research will provide useful information which can be used for optimising or updating existing biofiltration processes in industry to reduce antibiotic residues from drinking water.

Declaration of Competing Interests

No conflict of interest declared.

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References


NDWCH, National Drinking Water Clearing house (U.S.), June 2000. Slow Sand Filtration, Tech Brief Fourteen, Morgantown, WV.


