Testing monolithic activated carbon adsorbers for in-line removal of organic micropollutants

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ABSTRACT

Anthropogenic organic micropollutants (OMP) occur along the whole urban water cycle including drinking water. Various OMP can be efficiently adsorbed onto activated carbon. In the present study a commercial monolithic adsorber (MA), originally developed for gas treatment, was examined for the removal of OMP from drinking water. As a promising advantage, the adsorber can be introduced into existing pipes without causing substantial pressure losses. The MA was first characterized with scanning electron microscopy and energy dispersive X-ray spectroscopy. Weight loss during incineration at 550 °C indicated an activated carbon content of around 25%. Adsorption isotherms were recorded with milled material of the MA to estimate the capacity of the embedded adsorbent. Long-term flow-through experiments with two different flow rates were conducted to estimate the in-line removal efficiency. At low flow rates removals of 60% benzotriazole, 40% carbamazepine and 30% diclofenac were observed initially followed by a linear increase of effluent concentrations. Calculated loadings after 60 days of operation were e.g. 30 μg benzotriazole per g adsorber or 110 μg benzotriazole per g activated carbon as constituent of the adsorber. For specific applications, MA might be useful for the in-line elimination of OMP within drinking water distribution systems.

Key words | adsorption, emergency treatment, honeycomb, pharmaceuticals, trace organic pollutants

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INTRODUCTION

The widespread occurrence of organic micropollutants (OMP) such as pharmaceuticals and contrast agents in wastewater treatment plant effluents, surface waters (Ternes 1998; Reemtsma et al. 2006; Kasprzyk-Hordern et al. 2008; Loos et al. 2009; Loos et al. 2013) and in ground water (Reddersen et al. 2002; Loos et al. 2010; Wiese et al. 2011) has been confirmed by manifold investigations. Therefore the occurrence of OMP in drinking water cannot be excluded in partially closed urban water cycles. Granular activated carbon is successfully applied in fixed bed adsorption filters for the adsorptive elimination of OMP in waterworks (Moore et al. 2001; Yu et al. 2008; Scheurer et al. 2010). Recent investigations revealed that powdered activated carbon can also be applied in fixed beds (Ruhl et al. 2014a, 2014b; Altmann et al. 2015). However,

another type of activated carbon fixed bed adsorber referred to as a monolithic adsorber (MA) or activated carbon monolith or activated carbon honeycomb has not been tested for the removal of widespread OMP from drinking water yet, to our knowledge.

Different types of MA have been developed for the adsorption of gas phase contaminants such as volatile organic compounds (Yates et al. 2002; Moreno-Castilla & Perez-Cadenas 2010). One type of MA is produced by activating a monolith consisting of phenolic resin (Gadkaree & Jaroniec 2000) while another type of MA is obtained by coating ceramic monoliths with polymers and subsequent activation (Vergunst et al. 1998). Liu et al. (2006) developed a method to extrude an MA on the basis of milled coal. Powdered activated carbon in combination with a mineral

binder such as silicate clay can also be extruded to MA (Yates et al. 2002).

The different types of MA have been tested for the adsorptive removal of different contaminants, mainly from the gas phase. Agueda et al. (2011) studied the adsorption of volatile organic compounds onto MA with different degrees of activation. Through a high degree of activation an increase in the average pore size and a wider pore size distribution could be attained, which led to an increase in the adsorption capacity for dichloromethane. A mesoporous carbon monolith has also been used as a catalyst support and for the treatment of effluent gas purification Yates et al. (2000).

An advantage of MA is the convenient handling, as they are quick to replace in cases of saturation. Due to their open channel structure lower pressure drops occur at high flow rates in comparison to granular materials (Crittenden et al. 2005). However, Yates et al. (2000) reported that the dynamic adsorption capacity is limited by the width of the open channels and that a decrease of 20% of the channel width led to a fourfold amount of adsorbed toluene while an increase of the wall thickness did not lead to a significant increase. Gatica et al. (2010) examined the influence of the activation process on the adsorption capacity of coal-based MA for the removal of methylene blue and p-nitrophenol from liquid streams. The pore structures of the adsorber and thus the removal efficiencies of certain pollutants differed depending on the activation process (Gatica et al. 2013). Cheah et al. (2013) investigated acid modified carbon coated monoliths for methyl orange adsorption.

The main objectives of this work were: (1) to characterize the monolithic activated carbon adsorber, (2) to determine the adsorption capacity of milled MA material in batch tests in order to estimate the capacity loss of the activated carbon due to embedding, and (3) to evaluate how efficiently OMP can be removed from aqueous solutions in continuous in-line applications.

METHODS

MA

A set of MA (Aktiwa-w 100, Hydrotec, Germany) was received in cylindrical shape with a diameter of 8 mm and 60 mm length. According to the supplier the MA consisted of powdered activated carbon made of coconut shell and a binder. The outer surface area of the MA was calculated to be ca. 60 cm^2 by considering the number of channels (ca. 24), each with an approximate width of 1.0 mm and the length of the MA. The adsorber volume (corresponding to the bed volume of a filter) was 3.0 cm^3 and the total weight was 2.43 g. The weight loss after drying at 105 °C for 24 h revealed an initial water content of 6%. An additional weight loss of 28% was determined after combustion at 550 °C for 6 h. The residue, consisting of the inorganic binder material, was still in the shape of the MA.

Test solution

A test solution was prepared by adding benzotriazole (BTA), carbamazepine (CBZ) and diclofenac (DCF) as representative indicator OMP (Jekel et al. 2015) to tap water. Stock solutions of each compound with concentrations of 20 mg/L were added to Berlin tap water (ca. 4.5 mg/L dissolved organic carbon, DOC) to achieve target concentrations of 1 μg/L. All compounds were supplied by Sigma-Aldrich.

Experiments

The MA was milled for batch experiments in order to estimate equilibrium loadings of the activated carbon and to compare it with loadings obtained on the embedded activated carbon. A stock suspension of 1 g/L pulverized MA was prepared. Defined volumes were then pipetted to volumes of 100 mL of the test solution to achieve doses of 1, 2, 4 and 8 mg/L of the pulverized MA. The flasks were then shaken for 72 h to obtain equilibrium.

The MA was placed in a customized holder with minimal space between the outer adsorber wall and the inner holder wall. The adsorber was fed in up-flow with contaminated tap water from a 500 L tank using a peristaltic pump. The effluent was collected and weighed to adjust flow rates of 100 or 500 mL per hour, corresponding with ca. 1.8 or 0.4 minutes residence times. The tests were operated over 60 and 26 days, respectively. Samples for chemical analyses were collected at the effluent and references were taken from the tank.

Analyses

The surface morphology of the MA was investigated by scanning electron microscopy (SEM) with cold field emission cathode and detectors for secondary electrons (SE) and back-scattered electrons (BSE). The SEM was equipped with energy dispersive X-ray spectroscopy (EDX) that was used to determine the chemical composition of the MA. Prior to analyses, the monolith was fractured to analyze the inner composition of the adsorber material.
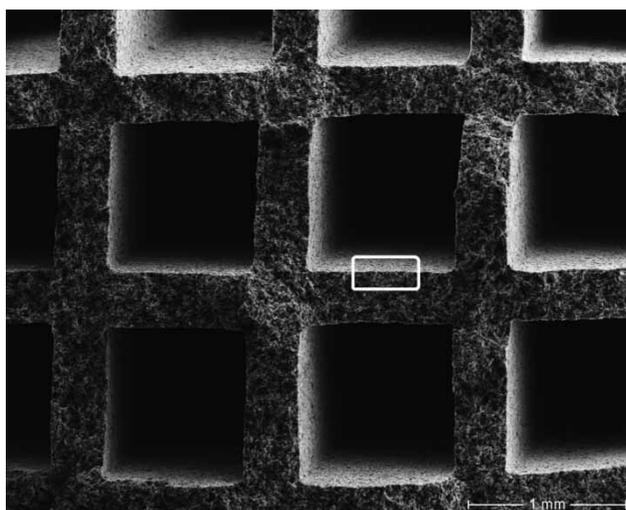
A dual beam spectrophotometer (type Smartline UV Detector 200, Knauer, Germany) was used to measure the UV absorption at a wavelength of 254 nm (UVA_{254}). OMP were quantified by high-performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS) with a method described elsewhere in detail (Zietzschmann *et al.* 2014a).

RESULTS AND DISCUSSION

Characterization of the monolith

The geometric shape of the rectangular channels within the cylindrical adsorber is shown in Figure 1. The width (edge length) of the channels was approximately 1.00 mm and the wall thickness 0.30–0.35 mm.

A greater magnification of the fracture area of the monolith is shown in Figure 2 where different constituents can be differentiated. The brighter structures in the BSE image indicate the presence of heavier elements compared to the darker constituents. EDX analyses for two different points are indicated in the SEM image and corresponding EDX spectra are provided in Figure 2. The composite is a net-like binder structure mainly consisting of silicon and oxygen with smaller fractions of sodium, aluminum, potassium and barium and traces of calcium and iron (point 1), with carbon grains (point 2 in Figure 2)
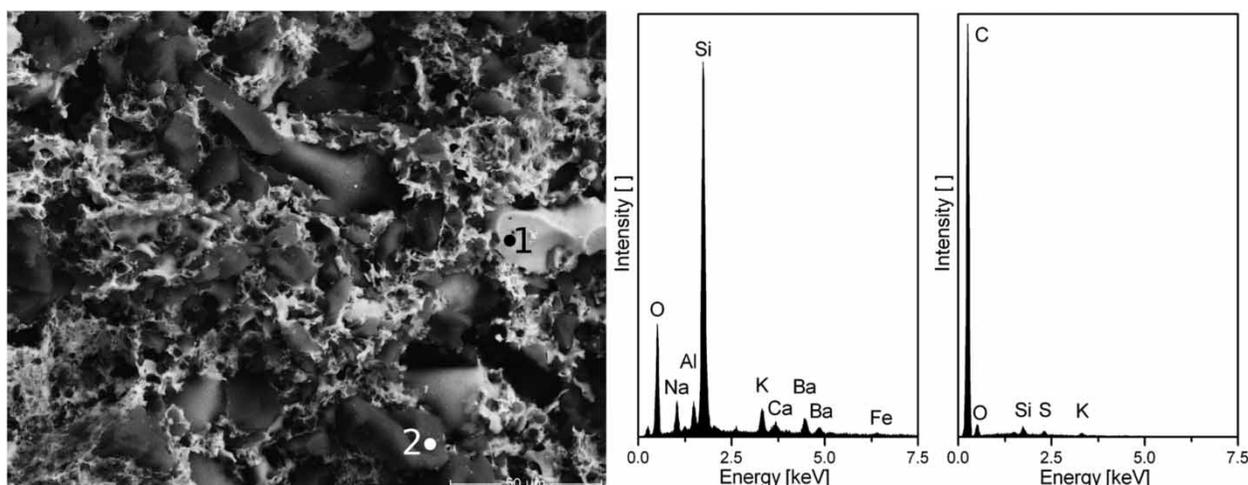

Figure 1 │ SEM image (SE detector) of the fracture area with rectangular channels in the MA (with schematic indication of the detail (not to scale) shown in Figure 3).

Figure 2 │ SEM image (BSE) of the fracture area (left) and EDX spectra of the indicated points 1 (middle) and 2 (right) with the detected elements oxygen (O), sodium (Na), aluminum (Al), silicon (Si), potassium (K), calcium (Ca), barium (Ba), iron (Fe), carbon (C) and sulfur (S).
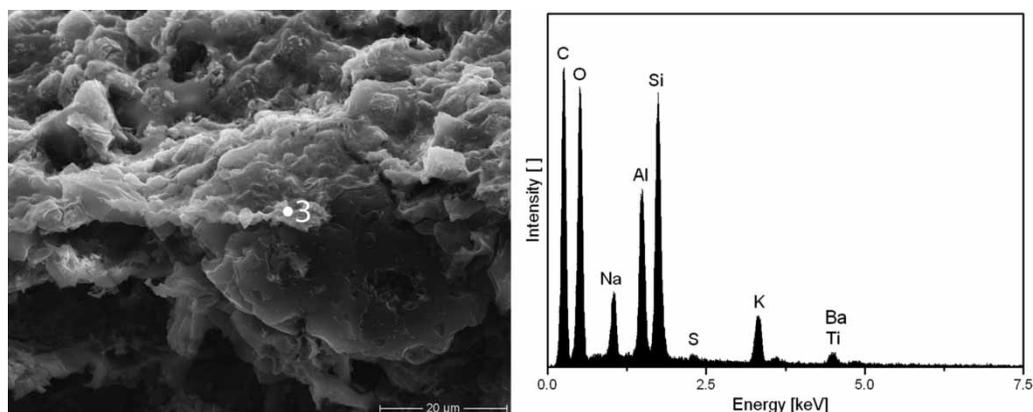
Figure 3 │ SEM image of the edge between inner surface and fracture area of the monolith (as schematically (not to scale) indicated in Figure 1, left) and EDX spectrum of the indicated point of measurement (right) with the detected elements carbon (C), oxygen (O), sodium (Na), aluminum (Al), silicon (Si), sulfur (S), potassium (K), barium (Ba) and titanium (Ti).

embedded within. The adsorber used in the present study thus belongs to the group of ceramic activated carbon monoliths.

The edge between the inner surface and the fracture area (as indicated in Figure 1) is shown in Figure 3. The inner surface is covered with a thin layer of the ceramic material that might disturb the mass transfer of OMP to the embedded activated carbon. The EDX spectrum displayed in Figure 3 includes constituents of the ceramic material and of the embedded activated carbon particle. As shown in Figure 2, the adsorber mainly consists of carbon (activated carbon), oxygen and silicon with smaller fractions of sodium, aluminum and potassium (ceramic material).

Batch experiments

Results of the batch experiment with pulverized MA are shown in Figure 4. The removal of BTA was above 80% with the lowest adsorber concentration of 1 mg/L. Higher adsorber doses led to BTA concentrations below the level of quantification. CBZ removals above 90% were achieved with 4 mg/L pulverized MA. Almost no removal of DCF was achieved with 1 mg/L pulverized MA but removal increased to above 70% with a dose of 4 mg/L. When the amount of activated carbon was then doubled, it only led to an insignificant increase in removal of DCF.

Continuous experiments

Relative effluent concentrations of BTA, CBZ and DCF in the continuous experiment with a flow rate of 500 mL/h are
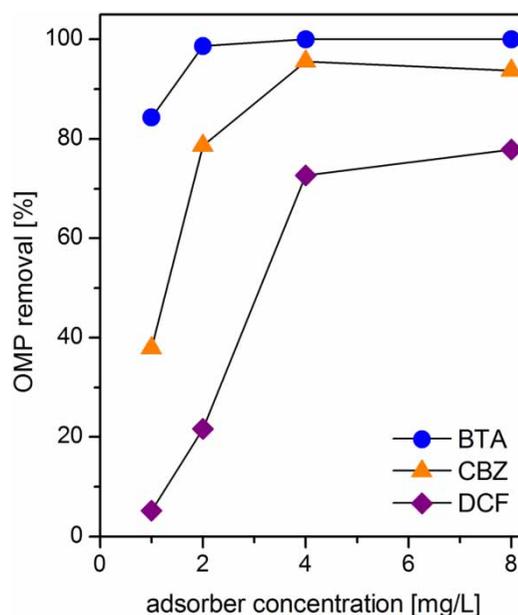

Figure 4 │ Percentage removals of BTA, CBZ and DCF obtained with 1, 2, 4 and 8 mg/L pulverized MA in batch experiments with tap water and 72 h contact time.

shown in Figure 5. Directly after start-up, 70% of the influent BTA concentrations were quantified at the effluent. Even lower removals of only 20% were obtained for CBZ and DCF due to mass transfer limitation at short residence times. The effluent concentrations further increased until an almost complete break-through after a cumulative effluent volume of 200 L. Residence times of 0.4 min are therefore not sufficient to achieve acceptable OMP removals.

The UVA_{254} as bulk parameter was measured to estimate the breakthrough of competing bulk organic constituents and as a surrogate parameter that has been
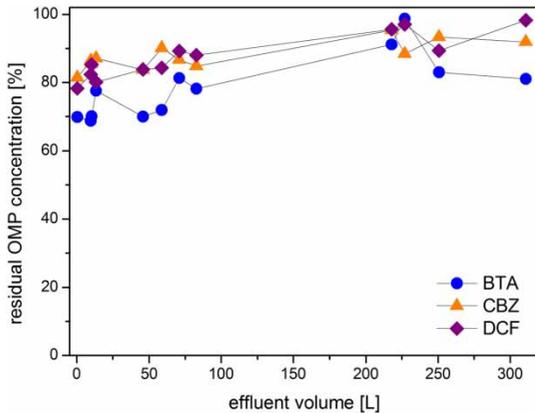
Figure 5 │ Relative effluent concentrations of BTA, CBZ and DCF in the long-term experiment with a flow rate of 500 mL/h.
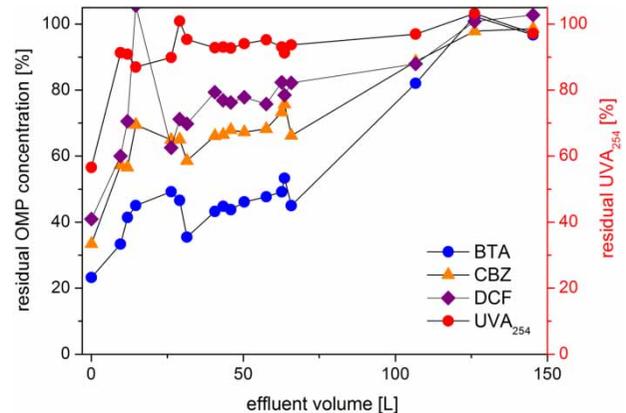

Figure 6 │ Relative concentrations of the selected OMP and the surrogate parameter UVA_{254} obtained in the experiment with a lower flow rate of 100 mL/h.

reported to correlate with OMP removals (Zietzschmann *et al.* 2014a; Anumol *et al.* 2015). At the beginning the UVA_{254} was reduced to around 60% but quickly increased to almost the influent UVA_{254}. The early breakthrough of UVA_{254} indicates that the adsorption capacity for bulk organic constituents is largely exhausted after a throughput of 100 L or 30,000 bed volumes, respectively. However, as long as 5–10% UVA_{254} abatement was observed, OMP removals were still significant. A much earlier breakthrough of UVA_{254} compared to OMP was also reported for granulated activated carbon (Corwin & Summers 2012; Zietzschmann *et al.* 2014b; Frank *et al.* 2015). The target OMP show a greater affinity towards the activated carbon surface compared to the bulk water constituents that cause the UVA_{254} (otherwise adsorption onto activated carbon would not be an efficient method for OMP removal). Due to the low concentration of 1 µg/L compared to a DOC concentration of 4.5 mg/L in the Berlin tap water, the UVA_{254} caused by the OMP does not significantly contribute to the overall UVA_{254}. However, UV light absorption of OMP at higher concentrations (above 1 mg/L) has been reported to enable targeted activated carbon testing (Ruhl *et al.* 2014a, 2014b).

OMP removals in the experiment with fivefold empty bed contact time compared to the results shown in Figure 5 were much higher as shown in Figure 6. At the beginning of the experiment the elimination of all OMP was between 50 and 80%. BTA removals were above 50% for approximately 50 L or ca. 16,500 bed volumes. Almost complete break-through was observed after 130 L or 40,000 bed volumes for all OMP.

A comparison of Figures 5 and 6 underlines the importance of sufficient contact time. Thus for efficient OMP removals either a greater adsorber length or low flow rates in the MA is decisive for high removals.

Comparison between batch and continuous experiments

The solid phase concentration on the embedded MA after continuous treatment of 145 L at a flow rate of 100 mL/h was estimated by integrating linear regressions of the breakthrough curves shown in Figure 6. For comparison, the OMP solid phase concentrations on milled MA material obtained in batch tests were also calculated. The results shown in Figure 7 reflect the order of adsorbability as discussed by Jekel *et al.* (2015) with the greatest removal for BTA and CBZ.

The OMP load on the pulverized MA with its liberated activated carbon is several times greater than on the MA after the long-term experiment. A BTA solid phase concentration of almost 600 µg/g was obtained in the batch experiment with a dose of 1 mg/L pulverized MA while the solid phase concentration in the long-term experiment was below 30 µg/g. The difference can be attributed to the higher specific surface area of the pulverized MA and the better contact between the adsorber and the OMP. A large fraction of the activated carbon in the MA is probably shielded by the binding material and therefore not available for OMP adsorption. CBZ loadings were lower but the
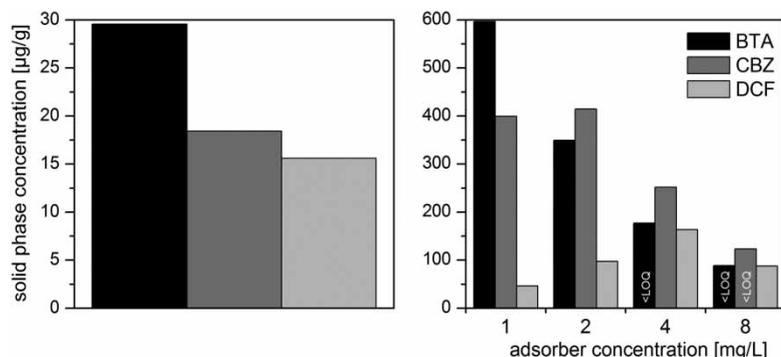
Figure 7 | Solid phase concentrations of BTA, CBZ and DCF obtained on the MA in the continuous long-term experiment (left) and with various concentrations of pulverized MA in 72 h batch tests (right) with indication of concentrations below the limit of quantification.

difference by a factor of 20 was almost identical. DCF revealed an unexpected behavior as loadings were low for doses of 1 and 2 mg/L pulverized MA. Competition for adsorption sites might have caused the comparably low DCF removal or solid phase concentration, respectively. The embedding of activated carbon in a binder material therefore leads to a loss of adsorption capacity.

CONCLUSIONS

Analysis of a MA by electron microscopy and X-ray spectroscopy revealed the presence of activated carbon particles surrounded by a mineral binder mainly consisting of silicon. Batch tests with milled MA material (and liberated activated carbon) achieved BTA loadings of 0.2 to 0.6 mg/g for doses of 4 to 1 mg/L. The two long-term tests were carried out with different flow rates and thus retention times. As expected, a longer retention time within the adsorber led to a greater OMP removal. A residence time of only 0.4 min was too short to obtain great OMP removals. The minimum contact time (depending on the flow rate within the drinking water pipe) can be easily increased by additional MA. Although lower OMP loadings were obtained with the embedded activated carbon in the MA compared to the pulverized MA, notable removals were obtained for more than 10,000 bed volumes. As the MA can be easily integrated into existing pipes and replaced after breakthrough, MA might be an interesting option for e.g. short-term application in the case of emergency. The pressure loss is expected to be negligible due to the geometry

shown in the SEM images and according to Crittenden *et al.* (2005) but needs some further investigation with larger MA.

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