



Influence of dissolved organic matter and activated carbon pore characteristics on organic micropollutant desorption

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ABSTRACT

By simulating decreasing inflow concentrations, the extent of desorption of organic micropollutants (OMP) from three activated carbons (AC) was examined in laboratory batch tests. The tested AC showed strong differences in pore size distribution and could therefore be characterized as typical micro-, meso- and macroporous AC, respectively. Adsorption and desorption conditions were varied by using drinking water (containing dissolved organic matter (DOM)) and DOM-free pure water as background solutions to examine the influence of DOM on OMP desorption for the different AC. Under ideal conditions (adsorption and desorption in pure water) adsorption of the tested OMP was found to be highly up to completely reversible for all tested AC. Under real conditions (adsorption and desorption in drinking water) additional DOM adsorption affects desorption in different ways depending on the AC pore structure. For the micro- and mesoporous AC, an increased irreversibility of OMP adsorption was found, which shows that DOM adsorption prevents OMP desorption. This could be referred to pore blockage effects that occur during the parallel adsorption of DOM and OMP. For the macroporous AC, DOM adsorption led to an enhanced OMP desorption which could be attributed to displacement processes. These results show that smaller pores tend to be blocked by DOM which hinders OMP from desorption. The overall larger pores of the macroporous AC do not get blocked which could allow (i) OMP to desorb and (ii) DOM to enter and displace OMP.

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1. Introduction

Despite their trace-level concentrations, organic micropollutants (OMP), such as pharmaceuticals and household chemicals, are suspected to be a potential risk for aquatic ecosystems as well as for human health. A promising technique for the removal of OMP in water treatment processes is the application of activated carbon (AC).

Adsorption in water treatment is generally supposed to be dominated by physical adsorption (Crittenden et al., 2005; Worch, 2012). Due to the comparatively low binding energies involved in physisorption, adsorption processes are considered reversible. It is therefore assumed that previously adsorbed compounds can desorb and reach the aqueous solution again. Thus, desorption could lead to an undesired increase of OMP concentrations in the effluent of AC stages during the regular treatment process.

Essentially, the occurrence of desorption requires (i) a loading of

the adsorbent surface with adsorbates and (ii) a change in solute concentration and/or composition in the inflow of the system. Thus, desorption can occur in processes where the AC retention time is much higher than the hydraulic retention time. This is especially the case, when AC is applied as granular media in filters. But desorption might also occur in systems where powdered AC is separated by sand filters and remains there until backwashing (typically after several hours) (Altmann et al., 2015a), or where powdered AC is recirculated within the treatment system (Meinel et al., 2016).

The mechanisms which can lead to desorption in water treatment are (a) a displacement of an adsorbate from an adsorption site by subsequent adsorption of a competitive adsorbate and (b) a reversion of the reaction pathway due to high OMP loadings on the AC surface and low OMP concentration in the bulk aqueous phase. Scenario (a) can be interpreted as competitive adsorption, which is the object of a high number of studies (Pelekani and Snoeyink, 1999; Quinlivan et al., 2005; Zietzschmann et al., 2014b). However, competition effects in terms of OMP adsorption are mainly examined concerning simultaneous adsorption of target and

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competitive compounds. The effects of a subsequent occurrence or a subsequent increase of concentration of competitive substances on already adsorbed OMP are only rarely studied. Scenario (b) can occur due to a sudden decrease of the inflow concentration, e.g. after a stoppage of a long-lasting contamination. If the liquid phase concentration is below the equilibrium concentration that corresponds to the solid phase concentration on the AC, a reversion of the sorption pathway and a transition of already adsorbed OMP from the adsorbent into the liquid phase might be the result.

Such gradient reversal-induced desorption from AC has been rarely examined to date, especially with respect to OMP. Several authors studied the reversibility of adsorption of other compounds like phenol, dyes (Tanthapanichakoon et al., 2005), pentachlorophenol (Mollah and Robinson, 1996), toluene (Chatzopoulos et al., 1993) or BTEX (Yakout and Daifullah, 2014). There are no consistent findings concerning the reversibility of adsorption onto AC in these studies. Whereas in some cases hysteresis was found, other studies see completely reversible adsorption of the respective adsorbent onto AC.

Desorption studies with respect to OMP focused on the kinetics of desorption (Corwin and Summers, 2011; To et al., 2008a, b). The results by To et al. (2008a, b) indicate that dissolved organic matter (DOM) of real waters can have different effects on the kinetics of atrazine desorption. Pore blocking compounds could decrease desorption kinetics whereas directly competing compounds could increase kinetics. However, no clear conclusions concerning the potential extent of OMP desorption under equilibrium conditions could be drawn from these results.

With respect to OMP adsorption it is known that DOM affects not only the kinetics of adsorption, but also the extent/capacity of adsorption (de Ridder et al., 2011; Pelekani and Snoeyink, 1999; Zietzschmann et al., 2016a). These competitive effects of DOM are referred to two causes: (i) direct competition of OMP and DOM on adsorption sites (Zietzschmann et al., 2014b) and (ii) pore blockage by DOM adsorption and, as a result, decreased availability of adsorption sites (Quinlivan et al., 2005). Both effects have the same consequence: a lower extent of OMP adsorption under equilibrium conditions. However, the cause and extent of competition effects was shown to be influenced by the AC pore size distribution (Quinlivan et al., 2005). With respect to desorption, it can be assumed that pore blocking DOM and directly competing DOM do not have the same, but opposite effects on the extent of desorption under equilibrium conditions: Direct competition on adsorption sites would potentially lead to (enhanced) desorption by displacement, whereas pore blockages could lead to steric hindrance and decreased desorption.

These mechanisms were examined in the current study, by elucidating

- the extent of OMP desorption under ideal, DOM-free conditions,
- the extent of OMP desorption under real conditions and the effects of DOM on desorption,
- the influence of AC pore characteristics on desorption, under ideal as well as under real conditions.

2. Material & methods

2.1. Activated carbons

Three commercial granular activated carbons (AC) were used for experiments: Hydriffin CC (raw material (as given by the manufacturer): coconut husk, Donau Carbon, Germany), Epibon A (raw material: lignite, Donau Carbon, Germany) and HC HK 1200 (raw material: renewable material, CSC, Germany). They were

pulverized on a Pulverisette mill (Fritsch, Germany) and sieved (Retsch, Germany) to obtain powdered AC with particle sizes below 63 μm . Before usage the AC materials were dried at 105 °C overnight and stored in a desiccator until experimental usage.

2.2. Organic micropollutants

Five substances, which can typically be found in ng/L to $\mu\text{g/L}$ concentrations in waste water treatment plant effluents (Margot et al., 2013; Zietzschmann et al., 2014a), were used as representative OMP for experiments: carbamazepine, diclofenac, 4-formylaminoantipyrine, sulfamethoxazole (all Sigma Aldrich, Germany) and iomeprol (Dr. Ehrenstorfer, Germany). From initial single stock solutions with a concentration of 20 mg/L a mixed stock solution with concentrations of 2 mg/L of each OMP was prepared. From this mixed stock solution certain amounts were taken to spike the particular experimental solutions for the adsorption experiments.

2.3. Experimental procedure

2.3.1. Standard batch experiments

Batch experiments were conducted with the three AC products in parallel. The adsorbents were prepared as stock suspensions in ultra pure water, with concentrations of 0.2 and 1.5 g/L (for adsorption in pure water) and 0.8 and 5 g/L respectively (for adsorption in drinking water). Prior to the experiments the suspensions were degassed under partial vacuum in an ultrasonic sound bath for 10 min and subsequently homogenized with a magnetic stirrer.

The experimental procedure is shown in Fig. 1. It was adapted from multi-stage adsorption tests, carried out by Zietzschmann et al. (2015a). All experiments consisted of an adsorption and a desorption phase, respectively. For the adsorption phase, centrifuge flasks (175 mL, Falcon, USA) were filled with 100 mL of an adsorption solution. This solution was previously spiked with OMP to a concentration level of $\sim 50 \mu\text{g/L}$ each. Per batch series seven different doses of the respective AC were added from stock suspensions using lab pipettes (Eppendorf, Germany). Added volumes were between 250 and 1000 μL so that dilution due to dosing is negligible. After an equilibrium contact time of 48 h on a horizontal shaker (Certomat R, Braun Biotech, Germany; 220 rpm) the AC and the aqueous phase were separated by centrifugation (Hettich Rotanta, Germany; 3000 rpm for 10 min). 95 mL of the supernatant were removed using a modified bulb pipette with an electric pipetting aid (Easy Pet, Eppendorf, Germany). A residue of 5 mL remained in the centrifuge flask to assure that no AC was withdrawn. The extracted 95 mL were filtered with 0.45 μm regenerated cellulose membrane filters (Chromafil Xtra, Macherey-Nagel, Germany).

Subsequently, 100 mL of an unspiked desorption solution were added to the loaded AC in the centrifuge flask to initialize the desorption phase. The suspension was put again on the horizontal shaker for thorough mixing for another 48 h before the AC was removed by membrane filtration as mentioned above. 48 h were chosen based on previous tests with the AC Epibon A, where this time was identified as sufficient also for reaching the desorption equilibrium (see Figure S 8 and Figure S 9 in the Supporting Information). All samples were stored at 4 °C prior to analyses.

The experiments were conducted under different background conditions by using different experimental solutions: (i) ultra pure water (provided by a Maxima UF device (ELGA LabWater, Germany)) and (ii) Berlin drinking water (taken from laboratory tap after adequate flushing). The concentration of dissolved organic carbon (DOC), the UV absorbance at 254 nm ($\text{UV}_{254\text{nm}}$), and the

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