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Impact of EfOM size on competition in activated carbon adsorption of organic micro-pollutants from treated wastewater

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ABSTRACT

The competitive impacts of different fractions of wastewater treatment plant effluent organic matter (EfOM) on organic micro-pollutant (OMP) adsorption were investigated. The fractionation was accomplished using separation by nanofiltration (NF). The waters resulting from NF were additionally treated to obtain the same dissolved organic carbon (DOC) concentrations as the initial water. Using size exclusion chromatography (LC-OCD) it could be shown that the NF treatment resulted in an EfOM separation by size. Adsorption tests showed different competitive effects of the EfOM fractions with the OMP. While large EfOM compounds that were retained in NF demonstrated a reduced competition as compared to the raw water, the NF-permeating EfOM compounds showed an increased competition with the majority of the measured OMP. The effects of small size EfOM are particularly negative for OMP which are weak/moderate adsorbates. Adsorption analysis was carried out for the differently fractionized waters. The small sized EfOM contain better adsorbable compounds than the raw water while the large EfOM are less adsorbable. This explains the observed differences in the EfOM competitiveness. The equivalent background compound (EBC) model was applied to model competitive adsorption between OMP and EfOM and showed that the negative impacts of EfOM on OMP adsorption increase with decreasing size of the EfOM fractions. The results suggest that direct competition for adsorption sites on the internal surface of the activated carbon is more substantial than indirect competition due to pore access restriction by blockage. Another explication for reduced competition by large EfOM compounds could be the inability to enter and block the pores due to size exclusion.

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1. Introduction

Organic micro pollutants (OMP) such as pharmaceuticals are increasingly found in all kinds of water sources such as wastewater, surface water, groundwater, and drinking water (Putschew et al., 2000; Reemtsma et al., 2006). OMP concentrations are rising in many cases because the consumption of drugs and other OMP is increasing and demographic aging will probably lead to an intensification of these trends (Dieter et al., 2010). The occurrence of OMP in our water sources is problematic because to this date, it is not fully understood which potentially harmful effects can be caused by OMP. Most OMP have very small concentrations and adverse impacts are not easily detectable (Dieter and Mückter, 2007). Furthermore, the combinatory/cumulative and chronic effects of exposition to OMP are not satisfactorily investigated (Bergmann et al., 2008). Due to the increasing concentrations of OMP in our water sources, the installation of additional water treatment steps in drinking water/wastewater treatment plants will be necessary in the forthcoming years (Jekel et al., 2013; Snyder et al., 2003). Activated carbon is a promising treatment technology in this respect and has been applied successfully in drinking water and reservoir water treatment (Worch, 2012). It is now also being tested with wastewater treatment plant (WWTP) effluent aiming at decreasing the pollution of receiving water bodies (Altmann et al., 2014; Boehler et al., 2012). In order to minimize activated carbon consumption and to attain high efficiencies, the activated carbon capacity should mainly be used for the target compounds, i.e. the OMP that are to be removed. This goal is not always achievable because several effects can impede OMP adsorption.

The affinity of OMP or adsorbing soluble organics (adsorbates) towards activated carbon depends on a variety of factors, e.g. properties of the applied activated carbon, such as internal surface area and chemistry (Newcombe et al., 2002a; Quinlivan et al., 2005). Stronger impacts on the activated carbon affinity of an adsorbate are due to the structural and chemical properties of the respective adsorbate itself, such as the hydrophilicity/solubility and the molecular size (Knappe et al., 2003). In activated carbon adsorption from natural waters the most crucial factor impacting OMP adsorption is the competition caused by other soluble organic substances of the respective natural organic matter (NOM). (In WWTP effluents, the NOM is usually denominated effluent organic matter – EfOM). The general two interference mechanisms are direct competition for adsorption sites on the activated carbon surface and indirect competition due to pore blockage which can impede OMP transport within the activated carbon pore structure. Distinction between the two mechanisms is not easy but direct competition for adsorption sites at the activated carbon internal surface is considered to be more fundamental in WWTP effluent treatment (de Ridder et al., 2011). Differences between OMP and EfOM regarding concentration as well as the affinity towards activated carbon can have substantial impacts on adsorption (Matsui et al., 2003). If the concentration of the bulk EfOM compounds present in WWTP effluents is considered, it is obvious that OMP adsorption can be impeded substantially (Newcombe et al., 2002b). In the case of Berlin, Germany, which is in the focus of this study, the WWTP effluent DOC concentration is normally between 10 and 15 mg/L (~20–30 mg/L EfOM) which is about 10^3–10^5 times the concentration of most of the OMP considered. However, it has been noted that only a fraction of the EfOM present in natural waters is effectively competing in adsorption with OMP (Graham et al., 2000; Knappe et al., 1998). This is accounted for the different accessibilities of the pore structure areas within the activated carbon which cannot always be entered equally easily by all present EfOM molecules (Hepplewhite et al., 2004; Newcombe et al., 2002a).

Because of the potentially high amount of EfOM competing with OMP in activated carbon adsorption, it was the objective of the current study to better understand which compounds of the WWTP effluent EfOM are the major competitors in OMP adsorption. If the entire EfOM of a WWTP effluent sample are evaluated in their competitiveness against OMP adsorption, the attribution to EfOM classes or fractions is not possible because of the vast variety of EfOM (measured via the bulk parameter DOC). Chromatographic techniques like liquid size exclusion chromatography with online carbon detection (LC-OCD) allow for some fragmentation but the chromatographic peaks overlap. Furthermore, EfOM adsorption onto activated carbon is nonspecific and this impedes concise statements as to the adsorbability of different EfOM fractions when all these fractions are present at the same time. Therefore, and since most OMP of interest have molecular masses between 100 and 1000 g/mol, the EfOM of a Berlin WWTP effluent sample was fractionized using nanofiltration which has a molecular weight cutoff in this range. This approach allowed for the separate investigation of the adsorption competition caused by differently sized WWTP effluent EfOM fractions.

2. Materials and methods

2.1. Study approach & pre-treatments

Prior to all other pre-treatments, particles/microorganisms and macromolecules were removed with ultrafiltration (UF) from the initial WWTP effluent sample to obtain higher microbial/chemical stability (for a comparison of the OMP adsorption in WWTP effluent and ultra-filtered WWTP effluent, see Supplemental Information). The resulting "raw water" was modified, using nanofiltration (NF), reverse

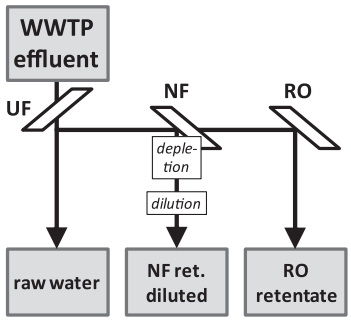

Fig. 1 – Water treatment scheme prior to adsorption testing (UF – ultrafiltration, NF – Nanofiltration, RO – reverse osmosis, ret. – retentate).