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Direct comparison of ozonation and adsorption onto powdered activated carbon for micropollutant removal in advanced wastewater treatment

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ABSTRACT

Organic micropollutants (OMPs) may occur ubiquitously in the aquatic environment. In order to protect the ecosystem and drinking water sources from potentially toxic effects, discharges of an increasing number of OMPs are being regulated. OMP removal from wastewater treatment plant (WWTP) effluents as a point source is a preferred option with removal by adsorption onto powdered activated carbon (PAC) and OMP transformation to presumably harmless compounds by ozonation as the most promising techniques. In this study, effluents of four WWTPs were treated with PAC and ozone in bench-scale experiments to compare the removal efficiencies of seven relevant OMPs. Concentrations of carbamazepine and diclofenac were reduced by more than 90% with 20 mg/L PAC or 5–7 mg/L ozone (0.5 mg O_3 per mg dissolved organic carbon (DOC)). Comparing typical doses for practical applications ozonation proved to be more efficient for abatement of sulfamethoxazole, while removal of benzotriazole and iomeprol was comparatively more efficient with activated carbon. While well known for ozonation, DOC-normalized doses were also applied to PAC and correlated better to relative OMP removal than volume proportional PAC addition. Furthermore, OMP removal efficiencies corresponded well with the reduction of ultraviolet light absorption at 254 nm for both treatment options.

1. Introduction

Numerous organic micropollutants (OMPs) are discharged into the aquatic environment as constituents of treated wastewater (Bueno et al., 2012; Reemtsma et al., 2006). Although the impact of pharmaceutically active OMPs on the environment and humans is not fully elucidated to date, initiatives for advanced wastewater treatment on scientific, technological and political levels are in progress. Two major removal processes are being investigated worldwide in bench, pilot and full scale operation: OMP removal by adsorption onto activated carbon (Hernandez-Leal et al., 2011; Nowotny et al., 2007) and oxidative OMP transformation with ozone (Hollender et al., 2009; Huber et al., 2005; Reungoat et al., 2012; Zimmermann et al., 2011).

Activated carbon has been tested in numerous applications as an advanced wastewater treatment step (Boehler et al.,

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2012; Margot et al., 2013). As the water constituents attach to the surface of the adsorbent, the adsorbed compounds are completely removed from the wastewater. Granular activated carbon (GAC) has been used as a common measure for drinking water purification in the past (Babi et al., 2007; Paune et al., 1998) and has also been studied in WWTPs (Gerrity et al., 2011; Reungoat et al., 2012). Advantages of GAC include its simple application and the possibility for regeneration/reuse of exhausted GAC. However, GAC efficiency might be significantly reduced by the presence of competing organic matter in WWTP effluents. Alternatively, powdered activated carbon (PAC) can be applied in a tertiary treatment step or dosed directly to the biological stage of a WWTP (Boehler et al., 2012; Serrano et al., 2011). Due to its smaller particle size, PAC is typically superior in regard to adsorption kinetics and might be more efficient compared to GAC (Nowotny et al., 2007).

Ozonation is capable of oxidizing micropollutants either by a direct reaction with ozone or indirectly after formation of hydroxyl radicals. As a result, the water constituents are transformed into other compounds and not completely removed from the effluent. The identification of reaction products and pathways is the objective of extensive research (Hübner et al., 2014; Scheurer et al., 2012; Zimmermann et al., 2012). Recent studies assessing the effect of ozonation on wastewater toxicity have been inconclusive (Altmann et al., 2012; Dodd et al., 2010; Schmidt and Brauch, 2008), though biodegradability usually increases after ozonation (Volk et al., 1997; Yavich et al., 2004). In addition to OMP degradation, ozone also provides disinfection capabilities (Xu et al., 2002).

PAC is suitable to adsorb a wide range of micropollutants, but shows a general preference for hydrophobic compounds and has been related to the octanol–water distribution coefficient (K_{ow} or D_{ow}) (Kovalova et al., 2013; Nam et al., 2014). Log D_{OW} values for the micropollutants investigated in this study are listed in Table 1. The efficiency of ozone for OMP removal can be estimated according to respective reaction constants. Published rate constants for the reaction of OMPs with ozone (k_{O3}) and hydroxyl radicals (k_{OH}) are also provided in Table 1. Diclofenac, carbamazepine and sulfamethoxazole with second order rate constants above 10^5 $M^{-1}s^{-1}$ react very quickly with ozone. Removals of these OMPs in WWTP effluents were among the highest in different studies (Hübner et al., 2012; Lee et al., 2012; Schaar et al., 2010). Benzotriazole with a lower reaction rate constant for the reaction with ozone was not completely removed in a full-scale ozonation application (Zimmermann et al., 2011). In comparison, benzotriazole, carbamazepine and diclofenac were almost completely removed in a full-scale PAC application, while sulfamethoxazole was removed to a lesser degree (Boehler et al., 2012). In a pilot-scale investigation comparing ozonation (median dose 0.8 mg O_3/mg DOC) and PAC (12 mg/L) carbamazepine was removed by more than 90% by either treatment, while ozonation performed better for sulfamethoxazole and diclofenac abatement, whereas PAC was more efficient for benzotriazole removal (Margot et al., 2013). Similar results were reported in a comparative evaluation of PAC and ozone for post-treatment of hospital wastewater, with complete removal of carbamazepine, bezafibrate and diclofenac with 23 mg/L PAC or 1.08 mg O_3/mg DOC and better removal of Iomeprol with PAC (Kovalova et al., 2013). However, a direct comparative evaluation of OMP removal from different WWTP effluents by PAC and ozone under standardized conditions has not been reported to our knowledge.

The efficiencies of adsorption and ozonation processes are significantly influenced by effluent dissolved organic matter (DOM) content and composition (Bahr et al., 2007; Worch, 2010). In adsorption processes DOM competes with the target OMPs for adsorption sites or clogs outer pores of the activated carbon and thus restricts access to the inner micropores. DOM is also oxidized by ozone or hydroxyl radicals and thus significantly reduces oxidant exposure. As adjusting ozone doses to DOC concentrations typically lead to similar ozone exposures in different waters, DOC-normalized ozone doses are often utilized in ozone treatment (Buffle et al., 2006; Wert et al., 2009a). Additionally, a strong correlation between abatement of OMPs and corresponding loss of UV light absorption at 254 nm (UVA_{254}) has been reported and suggested as a suitable control parameter for ozonation (Bahr et al., 2007; Wert et al., 2009b). A possible transfer of both concepts to PAC applications has not been reported yet.

The present investigation aimed at directly comparing adsorptive OMP removal with PAC and oxidative OMP transformation with ozone in different municipal WWTP effluents. The primary goals were to (1) assess the efficiencies of PAC and ozone with regard to a range of OMPs under the high background DOC concentrations of Berlin WWTP effluents, (2) seek correlations of OMP removals with UVA_{254} reduction for PAC and (3) investigate the DOC influence on OMP removal and examine a possible normalization of PAC doses similar to ozonation.

Table 1 – Published log D_{OW} values and reaction constants of OMPs with ozone and OH radicals.

Compound	Log D_{OW} pH = 7	k(O_3) [M^{-1} s^{-1}]	k(OH) [10^9 M^{-1} s^{-1}]
Benzotriazole	1.29[a]	36.4 ± 3.8[b]	8.6–10[b]
Iomeprol	−1.45[a]	<0.1[c]	2.5 ± 0.5[c]
Diclofenac	1.37[a]	$1 \cdot 10^6$[d]	7.5 ± 1.5[d]
Carbamazepine	2.77[a]	$3 \cdot 10^5$[d]	8.8 ± 1.2[d]
Bezafibrate	0.97[a]	590 ± 50[d]	7.4 ± 1.2[d]
Primidone	1.12[a]	1.0 ± 0.1[e]	6.7 ± 0.2[e]
Sulfamethoxazole	0.14[a]	$2.5 \cdot 10^6$[d]	5.5 ± 0.7[d]

[a] Kovalova et al. (2013).
[b] Leitner and Roshani (2010).
[c] Jin et al. (2012).
[d] Huber et al. (2003).
[e] Real et al. (2009).

2. Materials and methods

2.1. Experiments

Grab samples of secondary effluents from four different WWTPs were collected and used for bench-scale studies within one day after withdrawal. The WWTPs are all equipped with primary sedimentation, conventional activated sludge treatment with nutrient removal and secondary clarification.