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Impacts of coagulation on the adsorption of organic micropollutants onto powdered activated carbon in treated domestic wastewater

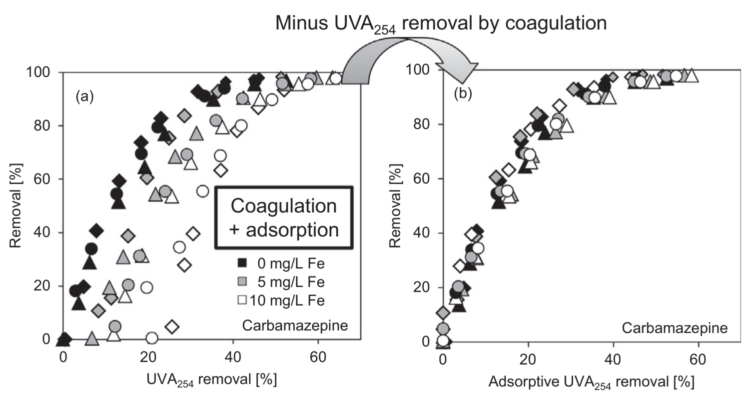
Johannes Altmann [a,*], Frederik Zietzschmann [a], Eva-Linde Geiling [a], Aki Sebastian Ruhl [a], Alexander Sperlich [b], Martin Jekel [a]

[a] Technische Universität Berlin, Chair of Water Quality Control, Str. des 17. Juni 135, 10623 Berlin, Germany
[b] Berliner Wasserbetriebe, Cicerostr. 24, 10709 Berlin, Germany

HIGHLIGHTS

- Coagulation and adsorption remove different organic matter fractions from wastewater.
- Dosing sequence of coagulant and PAC not relevant for micropollutant removal.
- Correlations between UVA_{254} and OMP removal affected by coagulation.
- Adsorptive UVA_{254} predicts OMP removal independent of coagulation.

GRAPHICAL ABSTRACT



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ABSTRACT

The application of powdered activated carbon (PAC) as an advanced wastewater treatment step for the removal of organic micropollutants (OMP) necessitates complete separation of the PAC particles, e.g. by coagulation. In this study, potential positive or negative indirect or direct effects of coagulation on the adsorption of OMPs onto PAC in treated wastewater were investigated. Although the concentration of dissolved organic matter (DOM) was significantly reduced by coagulation, the selective removal of mainly larger DOM components such as biopolymers and humic substances did not improve subsequent OMP adsorption onto PAC, demonstrating that coagulation has minor effects on DOM constituents that are relevant for direct competition or pore blocking. The combination of coagulation and adsorption yielded the sum of the individual removals, as adsorption predominantly affected smaller compounds. While the formation of flocs led to visible incorporation of PAC particles, no significant mass transfer limitations impeded the OMP adsorption. As a result, the dosing sequence of coagulant and PAC is not critical for efficient adsorption of OMPs onto PAC. The relationships between adsorptive OMP removal and corresponding reduction of UV absorption at 254 nm (UVA_{254}) as a promising surrogate correlation for the real-time monitoring and PAC adjustment were affected by coagulation, leading to individual correlations depending on the water composition. Correcting for UVA_{254} reduction by coagulation produces adsorptive UVA_{254} removal, which correlates highly with OMP removal for different WWTP effluents and varying coagulant doses and can be applied in combined adsorption/coagulation processes to predict OMP removal and control PAC dosing.

* Corresponding author.
E-mail address: johannes.altmann@tu-berlin.de (J. Altmann).

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1. Introduction

The occurrence of pharmaceuticals, personal-care products and industrial chemicals in the aquatic environment has become a cause for concern over the last decade (Reemtsma et al., 2006; Ternes, 2007), leading to ongoing discussions and intensified research regarding possible health effects (Grummt et al., 2013). While the impacts of anthropogenic organic micropollutants (OMP) on the environment and humans are not fully elucidated to date, negative effects have been reported for laboratory bioassay tests and real-life test organisms (Leusch et al., 2014; Liang et al., 2014). As municipal wastewater treatment plants (WWTPs) are major sources of OMPs found in the aquatic environment (Loos et al., 2013; Michael et al., 2013), additional wastewater treatment steps are currently being investigated to reduce discharges into receiving waters. Advanced treatment stages can include oxidation with ozone or adsorption onto activated carbon (Margot et al., 2013; Altmann et al., 2014). Ozonation typically leads to transformation products, many of which are still unknown (Wert et al., 2007). Activated carbon can be applied in granular (GAC) or powdered form (PAC). The abatement of UV absorption at 254 nm wavelength (UVA_{254}) correlates specifically with the removals of various OMPs in both ozonation (Bahr et al., 2007b; Wert et al., 2009) and adsorption onto activated carbon (Altmann et al., 2014; Zietzschmann et al., 2014a) and thus represents a valuable surrogate parameter.

The practical application of PAC typically consists of dosing into an adsorption stage followed by sedimentation/filtration or direct addition to a filtration unit (Margot et al., 2013). In both processes, coagulant is typically applied to improve separation of the fine PAC fraction (Böhler et al., 2012). The addition of coagulant can lead to two major effects: (1) As a direct negative effect, the incorporation of PAC particles into flocs can obstruct the mass transfer to the PAC surface and thus decrease the adsorption efficiency and (2) as an indirect positive effect, competition between OMPs and dissolved organic matter (DOM) for adsorption sites on the PAC surface and pore blocking by larger DOM molecules can be reduced. Coagulation is generally assumed to yield ineffective OMP removals from wastewater with both alum and ferric coagulant (Luo et al., 2014), while some studies report relevant eliminations of selected OMPs from surface waters by alum coagulation (Diemert and Andrews, 2013) and with polyaluminum chloride addition in a coagulation/flocculation stage of a water treatment plant (Nam et al., 2014).

Cook et al. (2001) observed adverse direct effects of coagulation with alum on the adsorption of taste and odor compounds in a high turbidity source water and concluded that tight binding of the PAC in dense flocs led to a decreased removal efficiency. Similarly, Ho and Newcombe (2005) reported an increasing negative influence of alum coagulation on the odor removal with increasing alum doses due to the growing size of the flocs around PAC particles and reduced mixing efficiencies and diffusion kinetics of the target compound.

The presence of DOM (quantified as dissolved organic carbon (DOC)) decreases the adsorption capacity toward target compounds compared to pure water (Newcombe et al., 2002; Zoschke et al., 2011). Coagulation prior to adsorption might reduce adsorption competition. Hepplewhite et al. (2004) and Zietzschmann et al. (2014b) reported that small molecules exhibited the greatest competition for adsorption sites. In a study conducted with synthetic wastewater and comparably high PAC and coagulant doses ($1\ g\ L^{-1}$ PAC, $58\ mg\ L^{-1}$ $FeCl_3$) coagulation removed the majority of large molecular-weight organics while adsorption was only efficient in removing small molecular-weight DOM (Guo et al., 2005). Haberkamp et al. (2007) reported that adsorption and coagulation complement each other with regard to DOC removal and that the dosing sequence had no influence on DOC removal under the conditions studied ($50–1000\ mg\ L^{-1}$ PAC and $2.5–50\ mg\ L^{-1}$ Fe). Zoschke et al. (2011) found that coagulation/flocculation of surface water with low DOM concentration (DOC = $2.7\ mg\ L^{-1}$) had nearly no influence on low molecular-weight fractions but only removed DOM without competitive effect on removal of taste and odor compounds.

As shown by the literature, different studies reported either adverse effects of coagulation on PAC adsorption (due to PAC incorporation into flocs), or no impact on adsorptive DOM and micropollutant removal depending on the experimental conditions and the water matrix studied, e.g. surface water, wastewater. The direct or indirect impacts of coagulation on the adsorptive removal of anthropogenic OMPs by PAC in WWTP effluents have not yet been studied sufficiently.

The present study aimed at elucidating the impact of coagulation on simultaneous adsorption of OMPs and competing DOM from WWTP effluent with high DOM contents. Bench-scale experiments were conducted to investigate the removal of competing DOM by coagulation, the subsequent OMP removal and the effect of PAC incorporation into flocs. The relevance of the dosing sequence for optimum OMP removal in combined treatments was examined under practical aspects. Because coagulation also reduces UVA_{254}, it was further investigated how the correlations between OMP removals and corresponding UVA_{254} reduction are affected by coagulation and whether UVA_{254} measurements are still suitable as surrogate parameter for OMP removal by PAC in practical applications.

2. Materials and methods

2.1. Experiments

2.1.1. Secondary effluent

Unfiltered grab samples of secondary effluents were taken from three different WWTPs and stored for maximum one night at <8 °C before use. Each effluent was sampled three times for replicate experiments. The WWTPs are equipped with primary sedimentation, conventional activated sludge treatment with nutrient removal (including biological P-elimination and denitrification) and secondary clarification. Each experiment was conducted with at least two different water sources and additionally replicated on different dates. The ranges of DOC, UVA_{254} and concentrations of carbamazepine, diclofenac and sulfamethoxazole of each effluent are shown in Table 1. A detailed listing of the individual samples used for each experiment with concentrations of further OMPs is given in Table S1. All samples were taken during dry-weather conditions. While not determined for the specific water samples, pH values of 7.2–7.6 and a conductivity of 1000–1300 μS/cm have been reported for the effluent of WWTP C (Bahr et al., 2007a). Furthermore, the tested effluents generally exhibit a turbidity <10 NTU. All experiments were conducted at room temperature.

Table 1
Ranges of DOC, UVA_{254} and OMP concentrations of the effluent samples taken from WWTPs A-C ($n = 3$).

Secondary effluent	WWTP A	WWTP B	WWTP C
DOC ($mg\ L^{-1}$)	13.0–15.8	13.0–15.4	11.9–12.3
UVA_{254} ($1\ m^{-1}$)	33.0–42.8	27.0–42.8	30.4–31.4
Carbamazepine ($\mu g\ L^{-1}$)	1.3–1.9	2.1–2.3	1.2–5.9
Diclofenac ($\mu g\ L^{-1}$)	3.1–6.5	5.4–8.1	2.9–5.5
Sulfamethoxazole ($\mu g\ L^{-1}$)	0.27–0.33	0.25–0.38	0.28–0.35