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Where to dose powdered activated carbon in a wastewater treatment plant for organic micro-pollutant removal

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HIGHLIGHTS

- Competition of pollutants with background organic matter along wastewater treatment.
- Slightly more competition during denitrification and nitrification than in effluent.
- Good correlations with DOC normalized dosages and partly with UVA_{254} reductions.
- Differences in removals partly compensated by longer contact times.
- Comparable results with five different commercial powdered activated carbons.

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ABSTRACT

Emissions of many organic micro-pollutants (OMP) into the aquatic environment can be efficiently reduced with advanced treatment at wastewater treatment plants (WWTP). Post-treatment with activated carbon is currently considered as one of the most promising options, but powdered activated carbon (PAC) could also be dosed into the existing biological treatment process instead. Due to much greater concentrations of suspended and dissolved constituents the adsorptive OMP removal was expected to be severely hindered. Systematic comparative adsorption tests with samples from different process steps of a large conventional WWTP were conducted to investigate differences in adsorption competition and removal efficiencies. The results show that much greater competition occurs in the WWTP influent and in the anaerobic tank but removal efficiencies in the anoxic and aerobic tank and in the WWTP effluent were more similar than expected. Suspended solids thus seem not to severely affect OMP adsorption. Similar results were obtained in a comparison of different commercial PAC in all for the respective matrices. OMP removals showed a relation with the PAC dosage normalized to the concentration of dissolved organic carbon. In the anoxic and aerobic tank and in the WWTP effluent, a uniform correlation of OMP removals and reductions of UV light absorption was observed.

1. Introduction

Wastewater treatment plants (WWTP) are considered as the main point source of organic micro-pollutant (OMP) emissions into the aquatic environment as numerous OMP such as pharmaceuticals or industrial chemicals are not or only partly removed in WWTP (Jekel et al., 2015; Michael et al., 2013; Oulton et al., 2010; Reemtsma et al., 2006; Verlicchi et al., 2012a). Currently intensive research is in progress to optimize OMP removals in WWTP in order to protect the aquatic environment and drinking water sources (Eggen et al., 2014; Joss et al., 2008).

Advanced wastewater treatment with powdered activated carbon (PAC) is a promising option to reduce OMP emissions (Altmann et al., 2014; Boehler et al., 2012; Meinel et al., 2015). Adsorption of OMP onto PAC requires sufficient mixing and contact time, typically provided in additional reactors for post-treatment after the secondary sedimentation (Boehler et al., 2012; Mailler et al., 2015; Margot et al., 2013). Existing reports indicate that an additional filter is needed for the reliable removal of suspended PAC and recent studies indicated that the PAC deposition in a pumice fixed bed filter contributes to the OMP removal (Altmann et al., 2015; Ruhl et al., 2014a).

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Simultaneous adsorption of OMP onto PAC during the activated sludge process is a promising alternative that has been proposed for the removal of phenols almost 40 years ago (Grieves et al., 1977). The combination of microbial processes and adsorption onto PAC was assumed to provide different advantages such as the elimination of substances that are toxic to bacteria, additional surfaces for bacteria attachment and their protection against shear force (Olmstead and Weber, 1991). However, competition by elevated concentrations of organic constituents and coating of the PAC by biofilms have been reported to decrease the efficiency of dichlorophenol adsorption in the activated sludge process (Widjaja et al., 2004). The addition of PAC into the biological treatment of municipal wastewater not only removed adsorbable organic halogens (AOX) but also improved the sedimentation of activated sludge (Bornhardt et al., 1997). Furthermore, the discontinuous addition of 0.1 and 0.5 g/L (Nguyen et al., 2013) or 1 g/L (Serrano et al., 2011) into a membrane bioreactor achieved great removals of e.g. diclofenac. The addition of PAC into the activated sludge in a conventional WWTP has been reported to require greater PAC dosages compared to a post-treatment for the removal of OMP (Boehler et al., 2012).

The present study aimed at elucidating specific differences of OMP adsorption onto PAC at different points along the process steps of an exemplary WWTP. Different batch experiments focused on required dosages and differences in adsorption competition by dissolved organic carbon (DOC) and potential negative impacts of sludge (suspended solids). However, the complex recirculations for biological phosphorous removal and denitrification and sludge retention times of several days could not be addressed in the present study. Five PAC products were compared to quantify potential differences between different commercial products for the use in simultaneous adsorption. The adsorption kinetics were additionally studied to determine the impact of contact times for the different stages and to differentiate concomitant biological degradation and adsorption onto sludge.

2. Experimental

2.1. WWTP

The experiments were conducted in the WWTP Ruhleben, one of the major WWTP of Germany's largest city Berlin. The WWTP has a capacity of 240,000 m^3 per day. The treatment consists of screening, primary sedimentation, biological phosphorous removal (anaerobic tank), denitrification (anoxic tank), nitrification (aerobic tank) and secondary clarification. The sludge recirculation from the secondary clarifier to the anaerobic tank for biological phosphorous removal was approximately 100% of the influent with a sludge retention time of approximately 15 days. The recirculation from the end of the aerobic tank to the influent of the anoxic tank for denitrification was approximately 500% of the influent (exemplary volume flows are shown in Fig. S1 in the supplementary material).

Grab samples were manually taken from 1) the influent of the primary clarifier, 2) the beginning of the anaerobic tank, 3) after ca. 20% of the anoxic tank volume, 4) after ca. 30% of the aerobic tank and 5) from the effluent of the secondary clarifier. The samples were taken at different days in April or May between 10 and 12 o'clock a.m. and batch experiments were conducted onsite in the WWTP directly after sample withdrawal to minimize sample alteration.

2.2. Test methods

PAC dosages of 20, 50 and 100 mg/L PAC were added to freshly withdrawn samples filled into glass flasks on a magnetic stirrer. The high dosage of 100 mg/L was tested as severe competition was expected for the samples withdrawn from the bioreactors. Comparably short contact times of 60 min were chosen for most of the experiments to avoid changes of the matrix. Different PAC products from different suppliers for advanced wastewater treatment were compared in another campaign with dosages of 50 mg/L PAC. An additional campaign with contact times up to 24 h was performed in the laboratory to investigate near-equilibrium conditions (Nowotny et al., 2007) and possible biological degradation in a reference batch. However, real conditions of a WWTP with recirculation and changing redox-conditions could not be simulated in the laboratory. Biological sample alterations were determined in parallel control batches without PAC addition. After the respective contact times, the PAC and the suspended solids were removed by membrane filtration (0.45 μm pores size) and samples were analyzed within 24 h.

2.3. Adsorbents

All experiments were conducted with the PAC ColorSorp 5000P PAC-S provided by Jacobi (PAC A in Table 1). Other PAC products from different suppliers, of different origins and with different properties were tested for comparison. These PAC are recommended for advanced wastewater treatment by their respective providers.

2.4. Analyses

Suspended solids were quantified by measuring the weight increase of a membrane filter (0.45 μm pore size, cellulose nitrate, dried at 105 °C) before and after filtration.

The UV light absorption at 254 nm wavelength (UVA_{254}) was analyzed with a dual beam spectrometer (Lambda 12, Perkin Elmer). Dissolved organic carbon (DOC) was quantified with a VarioTOC cube (Elementar Analysensysteme). DOC was further characterized by size-exclusions chromatography (SEC or LC-OCD (Huber et al., 2011)) with continuous organic carbon detection (SEC-OCD) and UVA_{254} measurement (SEC-UVD) as described elsewhere in more detail (Haberkamp et al., 2007; Ruhl and Jekel, 2012).

OMP were analyzed by liquid chromatography coupled with tandem mass spectrometry as described elsewhere in detail (Zietzschmann et al., 2014a). Benzotriazole and carbamazepine were quantified as process indicator substances (Jekel et al., 2015). Diclofenac and metoprolol are discussed for the long-term batch-test since they revealed significant removals without PAC. The limit of quantification was 100 ng/L. Possible matrix effects by high concentrations of organics in the WWTP influent were controlled by two different techniques: 1) Samples from the primary clarifier were diluted up to a ratio of 1:1000 to reduce potential matrix effects and 2) standard addition was done to investigate the analytical recovery. Both techniques revealed that matrix effects in the analyzed samples were negligible.

3. Results and discussion

3.1. Differences in the matrix

Great differences of suspended solids and DOC were observed between samples from the WWTP influent, the biological tanks and the WWTP effluent as shown in Fig. 1. While the biological tanks contained up to 3 g/L suspended solids due to the return of activated sludge and the recycle for denitrification, almost no residual sludge was found in the WWTP effluent after the sedimentation.

As expected, significantly higher DOC concentrations were