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The benefits of powdered activated carbon recirculation for micropollutant removal in advanced wastewater treatment

F. Meinel [a, *], F. Zietzschmann [a], A.S. Ruhl [a], A. Sperlich [b], M. Jekel [a]

[a] Technische Universität Berlin, Chair of Water Quality Control, KF4, Str. des 17. Juni 135, D-10623 Berlin, Germany
[b] Berliner Wasserbetriebe, Research & Development, Neue Jüdenstr. 1, 10179 Berlin, Germany

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ABSTRACT

PAC adsorption is a widespread option for the removal of organic micropollutants (OMP) from secondary effluent. For an optimal exploitation of the adsorption capacity, PAC recirculation is nowadays a common practice, although the mechanistic interrelations of the complex recirculation process are not fully resolved. In this work, extensive multi-stage batch adsorption testing with repeated PAC and coagulant dosage was performed to evaluate the continuous-flow recirculation system. Partly loaded PAC showed a distinct amount of remaining capacity, as OMP and DOC removals considerably increased with each additional adsorption stage. At a low PAC dose of 10 mg PAC L^{-1}, removals of benzotriazole and carbamazepine were shown to rise from <40% in the first stage up to >80% in the 11th stage at 30 min adsorption time per stage. At a high PAC dose of 30 mg PAC L^{-1}, OMP and DOC removals were significantly higher and reached 98% (for benzotriazole and carbamazepine) after 11 stages. Coagulant dosage showed no influence on OMP removal, whereas a major part of DOC removal can be attributed to coagulation. Multi-stage adsorption is particularly beneficial for small PAC doses and significant PAC savings are feasible. A new model approach for predicting multi-stage OMP adsorption on the basis of a single-stage adsorption experiment was developed. It proved to predict OMP removals and PAC loadings accurately and thus contributes towards understanding the PAC recirculation process.

1. Introduction

Adsorption of organic micropollutants (OMP) onto powdered activated carbon (PAC) is a promising option to reduce OMP emissions from wastewater treatment plants (WWTP) into the aquatic environment and drinking water sources (Eggen et al., 2014; Jekel et al., 2013). In advanced wastewater treatment, PAC is typically dosed continuously into the WWTP effluent and separated after a certain contact time by sedimentation or filtration (Boehler et al., 2012; Margot et al., 2013; Meinel et al., 2015).

Typical residence times of the PAC in the range of minutes to a few hours until separation are not sufficient to fully exploit the adsorption capacity of the PAC. High solid phase OMP concentrations on the PAC and thus high efficiencies are desired for economic and environmental reasons. Different process options are known to extend the residence time of the PAC in order to achieve higher loadings: Besides immobilization of the PAC in filters, recirculation of partly loaded PAC is a widespread technique. Coagulation as common phosphorus elimination process may take place simultaneously to adsorption. Several industrial-scale plants involving PAC recirculation for advanced wastewater treatment have been successfully put into operation within the last years in Switzerland and Southern Germany.

Additionally to an enhanced PAC residence time, the recirculation process, as schematically shown in Fig. 1, involves a countercurrent principle recycling partly loaded PAC from the first adsorption stage and mixing it with more concentrated influent water. Higher PAC loadings and higher removals of dyes and OMP, respectively, have been reported (Metzger, 2010; Nicolet and Rott, 1999; Nicolet-Mißlbeck, 2000); however, the mechanistic interrelations of this complex system are still not fully resolved.

In addition to the procedural complexity, competitive adsorption between dissolved organic matter and the target OMP as well as possible impacts of coagulation complicate understanding and evaluation of the recirculation process: Besides the target OMP, dissolved organic matter (usually expressed via dissolved organic carbon, DOC), also adsorbs onto the PAC and thus competes for

* Corresponding author.
E-mail address: felix.meinel@tu-berlin.de (F. Meinel).

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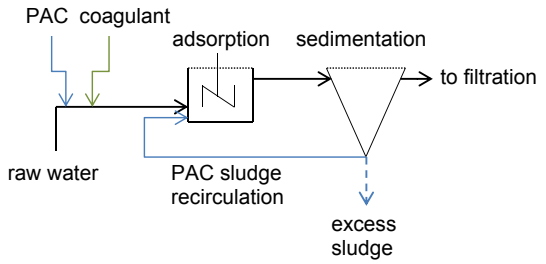

Fig. 1. Schematic of a continuous-flow recirculation process.

adsorption sites (Kovalova et al., 2013; Najm et al., 1990; Zietzschmann et al., 2014). In treated wastewater, DOC typically occurs in concentrations of several mg L^{-1} which is 3–5 magnitudes higher than concentrations of individual OMP.

Furthermore, OMP may be eliminated during coagulation besides the desired adsorptive removal (Nam et al., 2014). Different OMP, including carbamazepine, diclofenac and sulfamethoxazole, are reported to be removed to a low extent (≤15%), but other factors besides coagulation such as sorption onto particles and photodegradation may play an important role (Vieno et al., 2007; Stackelberg et al., 2007). Generally, elimination through coagulation is regarded ineffective (Huerta-Fontela et al., 2010; Luo et al., 2014).

For a detailed understanding of the recirculation process and possible removal predictions, an adsorption model representing the multi-stage loading of PAC under realistic conditions would be desirable. In a previous work, it could be shown that multiple-stage loading of PAC without fresh PAC addition can increase the OMP removal efficiency under competition conditions and irrespective of the OMP's adsorption properties (Zietzschmann et al., 2015). Furthermore, it was shown that in a single-stage process, coagulation exerts no influence on OMP adsorption (Altmann et al., 2015). The next step towards understanding OMP removal in a continuous-flow recirculation system is the inclusion of fresh PAC dosing into multi-stage batch experiments reusing PAC. In the present investigation, extensive experiments with treated wastewater and 14 subsequent stages reproducing PAC recirculation were conducted with the objective to help understand how PAC loadings and OMP removals behave in PAC recirculation systems. A new model approach was developed to consider the combination of fresh PAC with loaded PAC from previous stages in order to predict PAC loadings and OMP removals under realistic conditions.

2. Materials and methods

2.1. Materials

All experiments were conducted with grab samples taken from the influent of Phosphorous Elimination Plant (PEP) Tegel after mechanical treatments by a coarse screen (30 mm) and a coarse sieve (6 mm). PEP Tegel influent consists of WWTP effluent diluted approx. 1:2 with surface water (Schimmelpfennig et al., 2012) and has a mean DOC concentration of 11 mg L^{-1} (2014). OMP concentrations as measured during bench scale tests (cf. 2.3) are presented in Table 1.

Table 1
Concentrations of selected OMP in PEP Tegel influent.

OMP	Concentration [μg L^{-1}]
benzotriazole	4.49
carbamazepine	0.89
sulfamethoxazole	0.18
4-formylaminoantipyrine	1.56

Stock solutions and suspensions were prepared in ultrapure water (ELGA Berkefeld LabWater, Germany). PAC was AquaSorb 5000 P (PAC-S, Jacobi, Germany). A coagulant solution of 19.4 g Fe^{3+} L^{-1} was prepared by diluting a commercial $Fe_2(SO_4)_3$ solution with deionized water.

2.2. Isotherm experiments

PAC was dried overnight at 105 °C and cooled in a desiccator. A 10 g L^{-1} PAC suspension was prepared with ultrapure water. A 0.5 g L^{-1} PAC suspension was prepared by diluting 1 mL of the 10 g L^{-1} suspension with ultrapure water. PAC suspension was dosed into 9 identical batches of 100 mL PEP Tegel influent with target concentrations of 0.5, 1, 2.5, 5, 10, 20, 30, 50 and 100 mg PAC L^{-1}, while an additional batch was used as a reference. Initial OMP concentrations were 2.18 μg L^{-1} (benzotriazole), 0.52 μg L^{-1} (carbamazepine) and 0.85 μg L^{-1} (4-formylaminoantipyrine), sulfamethoxazole was not detectable (≤0.01 μg L^{-1}). The batches were agitated on a horizontal shaker for 20 h, as prior tests with the same water had shown that the adsorption equilibrium is reached after 20 h. Samples were then taken and immediately filtered for OMP analyses.

2.3. Bench scale tests for multi-stage loading of PAC

To simulate the continuous recirculation of PAC, multi-stage experiments were carried out implementing dosing of fresh PAC in addition to reused PAC from prior stages (as a modification of a previously developed method, Zietzschmann et al., 2015). For this purpose, PAC doses of 10 and 30 mg PAC L^{-1}, respectively, were added to 150 mL PEP Tegel influent water in centrifuge tubes. Additionally, 10 mg Fe^{3+} L^{-1} were dosed as coagulant to obtain similar P removal conditions and total suspended solids (TSS) composition as in a technical-scale PAC recirculation process. In another approach, no coagulant was dosed at a PAC dose of 30 mg PAC L^{-1} to examine the influence of coagulation and iron sludge accumulation on adsorption. A blank test was prepared without PAC or coagulant dosage. After 30 min of shaking on a horizontal shaker at 200 rpm, flocs consisting of ferric hydroxides, PAC and influent solids were separated in a centrifuge (Hettich Rotanta, Germany) at 3000 rpm during 10 min 140 mL of the supernatant clear water was removed cautiously with a bulb pipette without disturbing the sediment and was used for analyses. In the second stage, 140 mL new raw water, PAC and coagulant (where applicable) were added to the sediment from the previous stage and shaken, representing the second contact of the activated carbon with new influent water after sludge recirculation. On the whole, 11 stages with new water, carbon and coagulant were performed accumulating the sludge inside the tubes. Three more stages with new water but without PAC or coagulant addition were performed to investigate the adsorption onto preloaded PAC excluding the adsorption onto fresh PAC. The blank test was shaken and centrifuged like the other approaches and analyzed after the last stage to determine OMP removal by biodegradation, sorption onto solids and abiotic transformations.

Removals of OMP and DOC were calculated as $1-(c/c_0)$ with c_0 being the influent concentration and c being the concentration at the end of the respective experimental stage. Solid phase concentrations (loadings) of all stages were calculated on the basis of mass balances. The results of the 1st stage of this experiment were used as single-stage modeling input (cf. 2.5).