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Application of SAC_{254} measurement for the assessment of micropollutant removal in the adsorptive treatment stage of a municipal wastewater treatment plant

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Abstract

In 2010, the Mannheim wastewater treatment plant was expanded with an adsorptive treatment stage to remove organic micropollutants (OMPs). Differences in the removal efficiencies of the OMPs investigated were determined over four years of operation by applying different powdered activated carbon (PAC) products and a constant volume-proportional dosing of 10 mg PAC/L. Possible influences on the removal efficiency are discussed here on the basis of the data obtained, exemplified for the analgesic diclofenac. The analyses show that the removal efficiency is influenced significantly by the spectral absorption coefficient (SAC) of the biologically treated wastewater at a wavelength of 254 nm (SAC_{254}). Therefore, in order to ensure the constant treatment performance desired, the dosage of PAC should be adjusted to the measured SAC_{254} values. Moreover, as the SAC_{254} reduction correlates with the removal efficiency of OMPs, the additional determination of its reduction allows indirect control of the actual removal performance achieved. The SAC_{254} reduction can also be used for targeted control of the PAC dosage.

Key words: municipal wastewater treatment, optimized dosage, organic micropollutant, powdered activated carbon, spectral absorption coefficient

INTRODUCTION

Municipal wastewater treatment plants (WWTPs) are considered major input paths for organic micropollutants (OMPs) to water bodies, as, in the majority of the cases, they are not designed to remove them (Ternes 2001; Reemtsma *et al.* 2006; Kasprzyk-Hordern *et al.* 2009). Since about 2005, numerous investigations have been carried out, in Germany and Switzerland, to develop suitable process techniques for the targeted removal of OMPs. Based on current knowledge and experience, the application of both adsorptive processes with activated carbon and oxidative processes with ozone are considered the most viable techniques for the effective removal of a large number of OMPs from municipal wastewater (Abegglen & Siegrist 2012; DWA 2015).

The introduction of measures for OMP removal in WWTPs became a legal requirement in Switzerland in 2016 (WPA 2016), whereas in Baden-Württemberg, a federal state in Germany, it was done either voluntarily or under an agreement between the operator and the regulator. Since 2010, eight WWTPs in Baden-Württemberg have been expanded with an advanced treatment stage targeted on

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OMPs. In all cases the method used was treatment with powdered activated carbon (PAC) which had proved to be the most efficient in long-term pilot-scale investigations at Biberach University of Applied Sciences (Metzger 2010). In this method, the PAC is first added to a separate adsorption stage downstream of the biological treatment and subsequently recirculated back into the biological stage for further use in a counter-flow principle. Studies have shown that OMPs are removed to a large extent from the wastewater with as little as 10 mg PAC/L (Rößler & Metzger 2014). Despite using the same PAC product and constant volume-proportional dosage of 10 mg PAC/L, some significant fluctuations occurred in the removal efficiencies of the OMPs investigated at every WWTP studied. It is therefore necessary to learn more about PAC dosage, in order to be able to meet possible future OMP removal requirements. An additional difficulty in operational monitoring of the adsorption stage for the targeted removal of OMPs is that these substances cannot readily be analyzed *in situ* directly in the facility's own laboratory. Thus, real time control of the OMP removal performance can only be achieved by measurement of a surrogate parameter. A comparatively simple, robust and inexpensive measurement is needed, if it is to be practical in use in both small and large WWTPs. Altmann *et al.* (2014) and Zietzschmann *et al.* (2014) have obtained good correlation, in laboratory experiments, between OMP removal performance and reduction of the spectral absorption coefficient (SAC) at 254 nm wavelength (SAC_{254}). As far as is known, there are no reports to date of experience applying this surrogate parameter on an industrial scale.

The objective of this study, based on long-term operating data, is to indicate possible influences on the OMP removal performance in an adsorption stage, and, based on these findings, to derive a possible strategy for the monitoring and control of PAC dosage.

METHODS

Implementation of the adsorption stage with PAC at the Mannheim WWTP

The first full-scale implementation of an adsorption stage for OMPs occurred in summer 2010 at the Mannheim WWTP (capacity 725,000 PE), Baden-Württemberg. In order to obtain initial operating experience with the new technology, it was first implemented for a partial stream with a maximum flow of 300 L/s (Alt & Mauritz 2010). It was operated like that until the beginning of 2015. Subsequently the adsorption stage was extended so that a flow of 1,500 L/s, representing approximately 90% of the annual average wastewater flow, could be treated with PAC from summer 2016 (Kapp 2012).

The process principle and integration of the adsorption stage in the treatment train are shown in Figure 1. Fresh PAC is first added to the biologically treated wastewater in the contact reactor. The activated carbon is precipitated in the subsequent settling tank using polymers and flocculant, and then fed back, as 'return carbon', into the contact reactor to improve utilization. While the designed minimum wastewater retention time in the contact reactor is approximately 40 minutes, the PAC remains for about seven days on average in the adsorption stage due to continuous circulation, before final discharge to the biological stage. There it is mixed with the activated sludge and is finally removed from the system with the excess sludge. Since the PAC cannot be separated completely by sedimentation (Metzger *et al.* 2011; Platz *et al.* 2012), a flocculant filter is installed downstream as a final process step to ensure that the WWTP effluent is almost free of suspended solids.

Until the end of October 2012 the adsorption stage feed was quantity-based for the maximum flow of 300 L/s. During this time the average inflow was 160 L/s on days with dry weather conditions, while the retention time in the contact reactor was 75 minutes. From November 2012 until the beginning of 2015 a constant flow rate of 200 L/s was treated adsorptively. The retention time in this case

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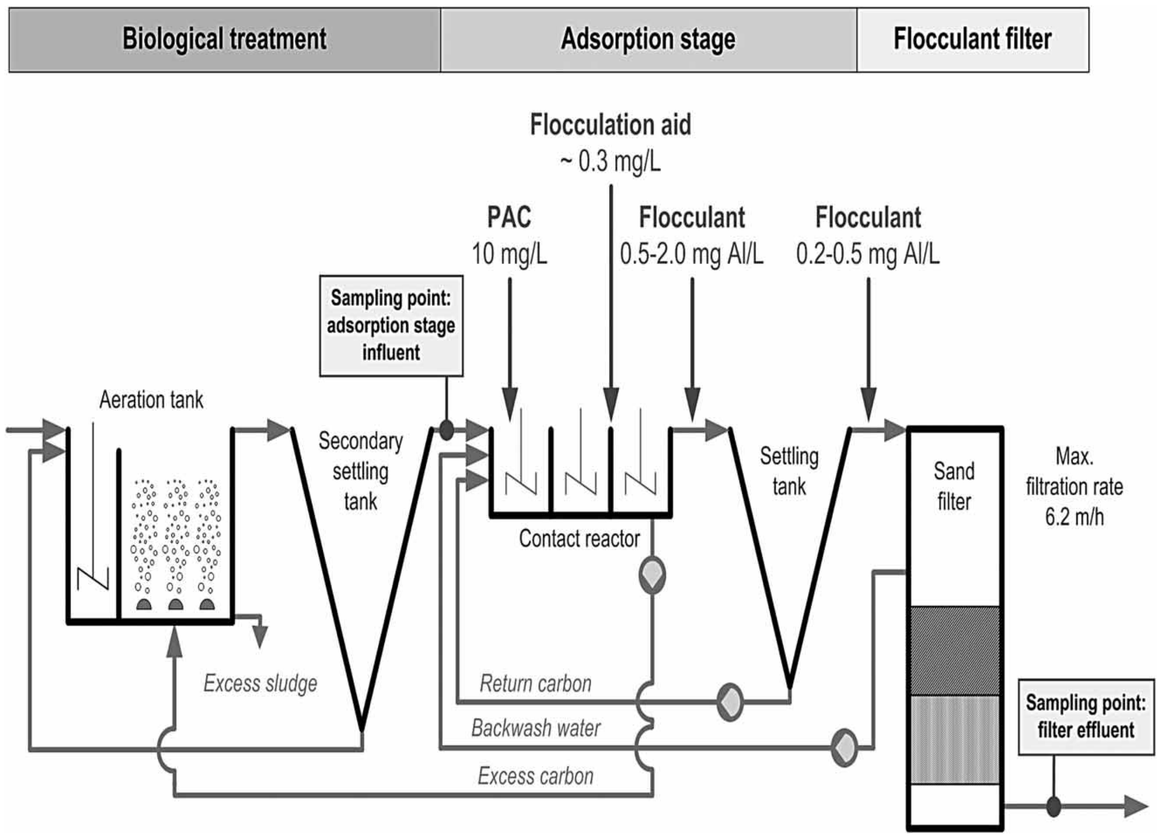

Figure 1 | Process diagram of the OMP adsorption stage at the Mannheim WWTP.

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was 60 minutes. However, the different retention times have no effect on OMP removal efficiency according to the results of own investigations (Metzger 2010).

Operation of the adsorption stage was under the scientific supervision of the Biberach University of Applied Sciences from 2010 to 2012, during which time detailed research was performed to investigate OMP removal by PAC (Metzger *et al.* 2012). In addition, the reduction in the estrogen effect of the wastewater was verified using active fish monitoring with male rainbow trout (Rößler & Kapp 2012). Afterwards the operation was continued without scientific supervision. Later, in 2014, further extensive measurements were done within a new investigation campaign by KomS.

Chemical dosing

Four different PAC products were tested during the approximately four-year period of operation. They were – 'Norit SAE Super' from Cabot, 'AquaSorb 5000P' from Jacobi, 'Carbopal AP' from Donau Carbon and 'PAK C 880 SR' from CarboTech.

The suitability of 'Norit SAE Super' for OMP removal had already been verified in several studies (Metzger 2010; Boehler *et al.* 2012; Kovalova *et al.* 2013; Margot *et al.* 2013). The other three PACs have been shown in investigations carried out by KomS as well as in other published studies removal performances comparable to 'Norit SAE Super' (Zietzschmann *et al.* 2014). In this paper the products are mentioned anonymously (PACs A-D). The treatment efficiencies presented were achieved with a dosage of 10 mg PAC/L in all cases.

Throughout the operating period, polyaluminium chloride was used as a flocculating agent both in the adsorption stage and upstream of the flocculant filter. In the period 2011/12, total flocculant dosing varied between 1.9 and 2.3 mg Al/L, while in 2014 dosing was at 1.2 mg Al/L. Both anionic and cationic polymers were used as flocculation aids.

Evaluation of the treatment performance

Treatment efficiency was evaluated by collecting 24-hour composite samples, taken in a flow-proportional manner from the adsorption stage influent and the flocculant filter effluent. The performance of the adsorption stage was not considered on its own due to the necessity for a downstream filter unit. The improvement in wastewater quality was rather evaluated through the selection of the two sampling points, indicating the overall performance of the 'adsorptive system' (=adsorption stage + filter). Before analysis, all samples were filtered using membranes (cellulose nitrate, pore size 0.45 μm, Sartorius, Germany).

The SAC_{254} was measured using a UV-VIS spectral photometer DR 5000 (Hach-Lange, Germany) and determination normally took place on working days.

In order to evaluate OMP removal performance in the adsorptive stage, it is sufficient to analyze only a few individual substances (Jekel & Dott 2013). The choice, however, should take into account substances that are permanently present in the secondary settling stage effluent and can also be removed to varying degrees by adsorption. For this purpose, the concentrations of the pharmaceuticals metoprolol, carbamazepine and diclofenac, the industrial chemical benzotriazole and the radio opaque substance iopamidol in the wastewater samples were determined at regular intervals. Metoprolol and carbamazepine are both very easily, benzotriazole is readily and iopamidol moderately adsorbed on PAC (Metzger *et al.* 2012). Samples for the determination of OMPs were taken only under dry weather conditions.

The analyses were performed with HPLC-MS by the DVGW (German Technical and Scientific Association for Gas and Water) Technology Centre for Water in Karlsruhe. The limit of determination was 50 ng/L in all cases.

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RESULTS AND DISCUSSION

Operating results

The percentage removal of diclofenac in the system 'adsorption stage + filter' over four years is shown in Figure 2. The removal rates for other OMPs are shown in the Supplementary Information in Figures S1 and S2. It appears that diclofenac is removed steadily to a high degree with a dosage of 10 mg PAC/L. Despite the constant volume-proportional dosing of PAC, removal efficiency varied between about 70 and 90%. Considering the removal rates in Figure 2 with regard to the different PAC products, it appears that PACs A and B achieved higher percentage removals than PACs C and D. However, it cannot be determined from Figure 2 whether the lower removal rates are due to poorer quality of either the PAC product or the particular load delivered, as commonly supposed.

Figure 3 illustrates the percentage of SAC_{254} reduction arising from the applied adsorptive technology over several years of operation. The SAC_{254} reduction arises primarily from adsorption of

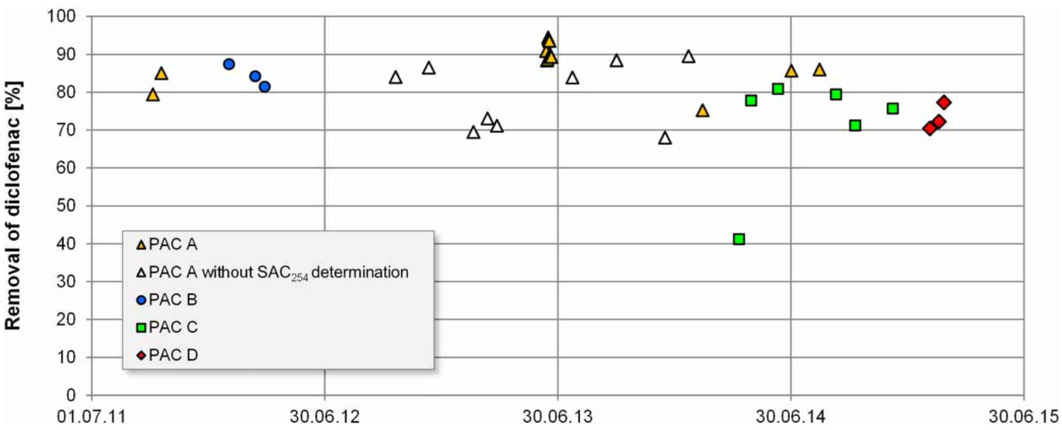

Figure 2 | Removal of diclofenac with a dosage of 10 mg PAC/L.

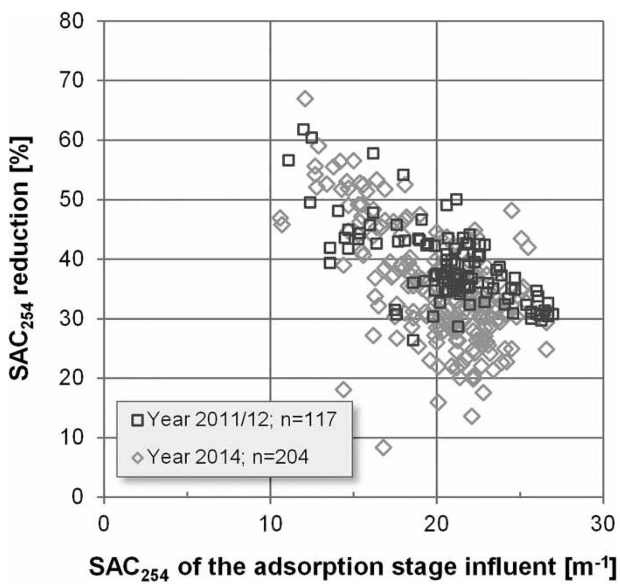

Figure 3 | SAC_{254} reduction versus the SAC_{254} of the adsorption stage influent at a dosage of 10 mg PAC/L.

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dissolved residual organic matter on the PAC. Part of the reduction is also due to an effect of the flocculant (Altmann *et al.* 2015). Beyond this, it is possible that biological processes in the activated carbon sludge of the adsorption stage and the filter bed can cause a reduction in SAC_{254} as well. No clear statement can be made, however, on the precise factors leading to SAC_{254} reduction.

Although the SAC_{254} reductions corresponding to influent wastewaters with the same SAC_{254} value fluctuate in a broad range, there is a general trend that with increasing SAC_{254} influent value, the percentage SAC_{254} reduction decreases when applying 10 mg PAC/L. Thus, if an SAC_{254} value of 15 m^{-1} is measured after biological treatment, then, on average, a reduction of 50% is observed, whereas at an SAC_{254} input value of 25 m^{-1}, a reduction of only about 30% is detected.

Effects on OMP removal

Often, the influence of the quality of the PAC applied, as well as the inflow concentrations of the substances analyzed and the dissolved residual organic matter, on the OMP removal efficiency is questioned. Figure 4 shows the diclofenac removal percentage with respect to these two factors.

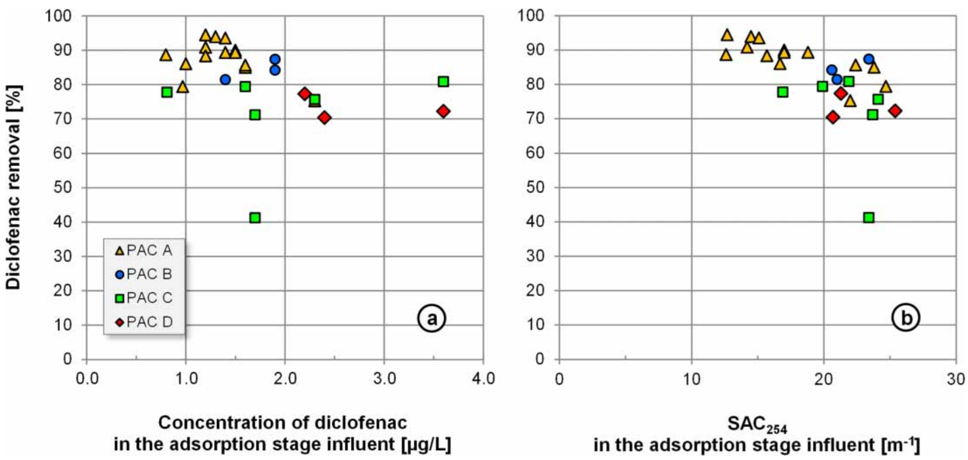

Figure 4 | Diclofenac removal at a dosage of 10 mg PAC/L varying with the concentration of diclofenac in the adsorption stage influent (a) and with the SAC_{254} of the adsorption stage influent (b).

Figure 4(a) indicates that higher input concentrations of diclofenac tend to result in lower percentage removal, regardless of the type of PAC used. With an input concentration of about 1.5 µg/L, the removal rate is between 80 and 90%, but it is 10 percentage points less with an adsorption stage influent concentration of 3.5 µg/L. However, if the results in Figure 4(a) are considered in terms of the different PAC products, it appears that PAC C has a slightly poorer removal performance than PACs A and B, as implied in Figure 2.

If, however, the influence of the dissolved residual organic matter on diclofenac removal, expressed by the SAC_{254}, is also taken into account (Figure 4(b)), no differences can be identified between the removal performances of the four PACs. The lower diclofenac removal rates, between 70 and 80% with PAC C, are thought to arise from the fact that, on the corresponding days, a comparatively high SAC_{254} of more than 20 m^{-1} was measured in the adsorption stage influent.

Accordingly, the percentage removal of diclofenac appears to be influenced significantly by the SAC_{254} of the biologically treated wastewater, and rather less by the input concentration of diclofenac or the supposedly different removal performances of the four PAC products or delivered loads. It is concluded that, to achieve a specific treatment target, PAC dosage must be adjusted to the SAC_{254} of the adsorption stage influent.

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Control and regulation of the PAC dosage

To remove diclofenac continuously in the adsorption stage by, say, 80%, at Mannheim WWTP, an SAC_{254} specific dosage of 0.5 mg PAC/(L·m^{-1}) related to the adsorption stage influent would be necessary (Figure 5(a)). These control specifications for PAC dosage, however, assume that the PAC applied would achieve removal performances comparable with those of PAC products A to D.

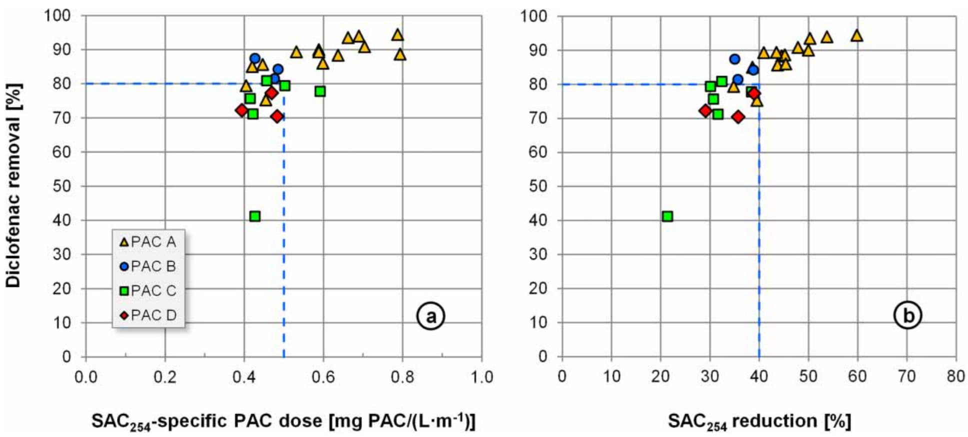

Figure 5 | Control and regulation parameters for a demand-based PAC dosage using the diclofenac removal example.

An additional measurement of the SAC_{254} in the effluent of the filter would also enable determination of the SAC_{254} reduction and thus, as Figure 5(b) shows, the indirect control of the scope of diclofenac removal. The SAC_{254} reduction can also be drawn on for the deliberate regulation of PAC dosage. Thus, for Mannheim WWTP, an SAC_{254} reduction of 40% is required to achieve a diclofenac removal of 80% in the adsorption stage, independent of the SAC_{254} in the adsorption stage influent. For other OMPs, corresponding correlations between percentage removal and the SAC_{254}-specific PAC dosage, respectively the SAC_{254} reduction, are presented in the Supplementary Information in Figures S3 and S4.

CONCLUSIONS

In this study, based on long-term operating data from a WWTP, it is shown that steady removal of OMPs can be achieved by using 10 mg PAC/L in an adsorption stage. Despite the constant volume-proportional PAC input, differences were observed in OMP removal efficiency for the substances investigated. These are conditioned significantly by the SAC_{254} of the biologically treated wastewater, e.g., for the analgesic diclofenac. In order to comply with possible future requirements regarding the removal efficiencies for individual substances, it will thus not be sufficient to dose the PAC proportionally to the wastewater flow. It would be better to use an SAC_{254}-specific PAC dosage rate, to achieve the constant level of treatment desired. The actual removal performance achieved can be controlled indirectly by the additional determination of the SAC_{254} reduction, which would enable a regulated PAC dosage, corresponding to the particular demand.

The analyses shown in this study are based on SAC_{254} values of membrane-filtered, 24-hour composite samples. If future regulations require that the PAC dosage has to be defined in relation to continuous determination of the SAC_{254} reduction, further research will be needed to investigate the suitability of SAC sensors for the application. In particular, it will be necessary to examine how well the influence of particles can be compensated for and whether any additional sample preparation is required in order to determine the SAC_{254} sufficiently accurately. If the findings of this study are to

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be generalized, it will be important to clarify whether the characteristic values determined for the Mannheim WWTP can be transferred to others using the same adsorptive process technology.

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SUPPLEMENTARY INFORMATION

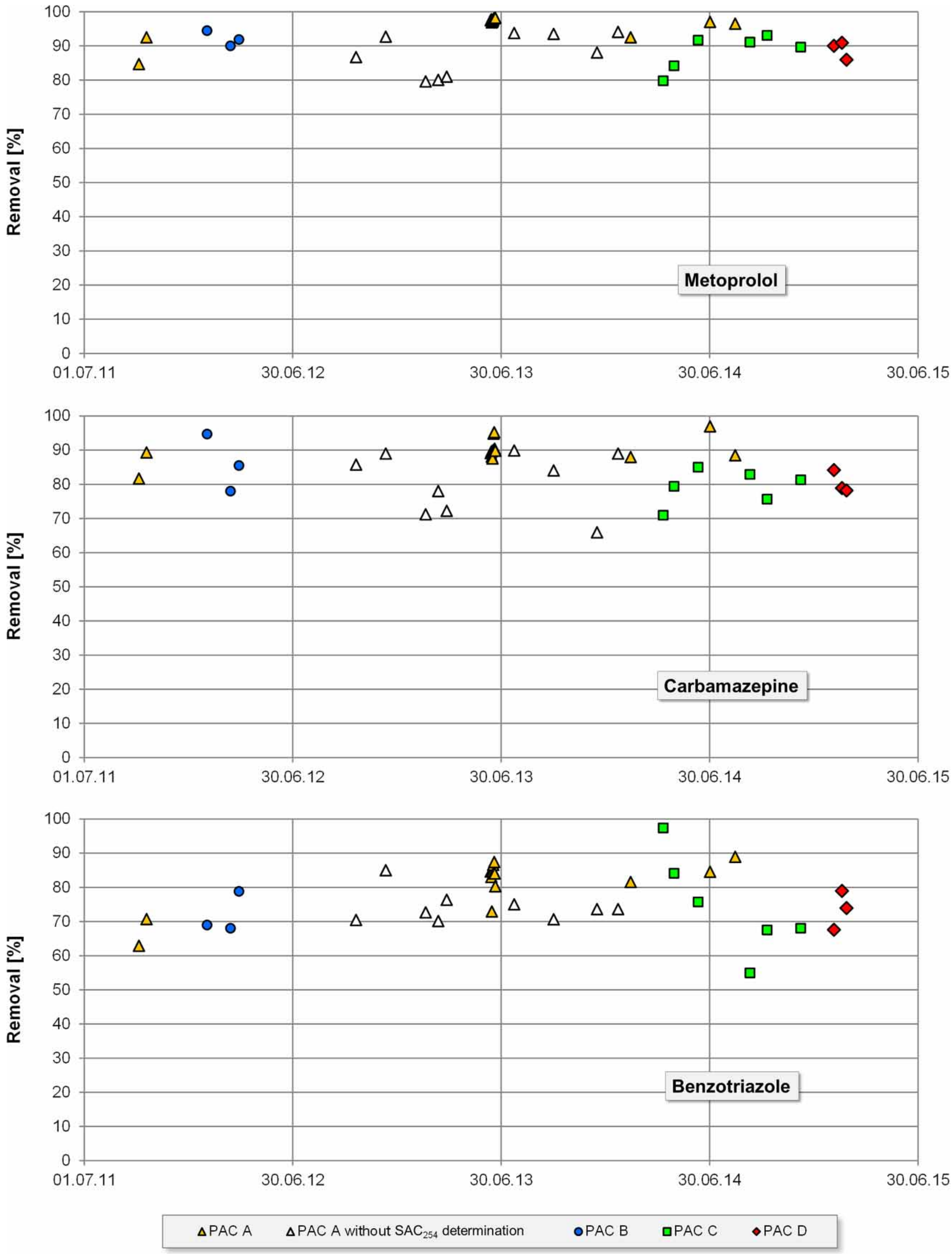

Figure S1 | Removal of metoprolol, carbamazepine and benzotriazole with a dosage of 10 mg PAC/L.

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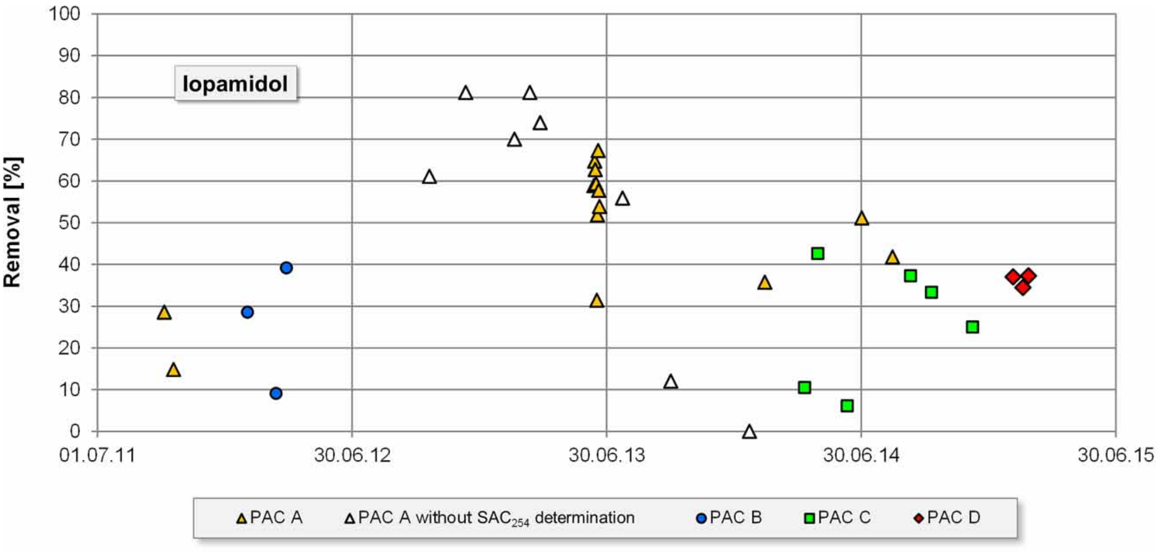

Figure S2 | Removal of iopamidol with a dosage of 10 mg PAC/L.

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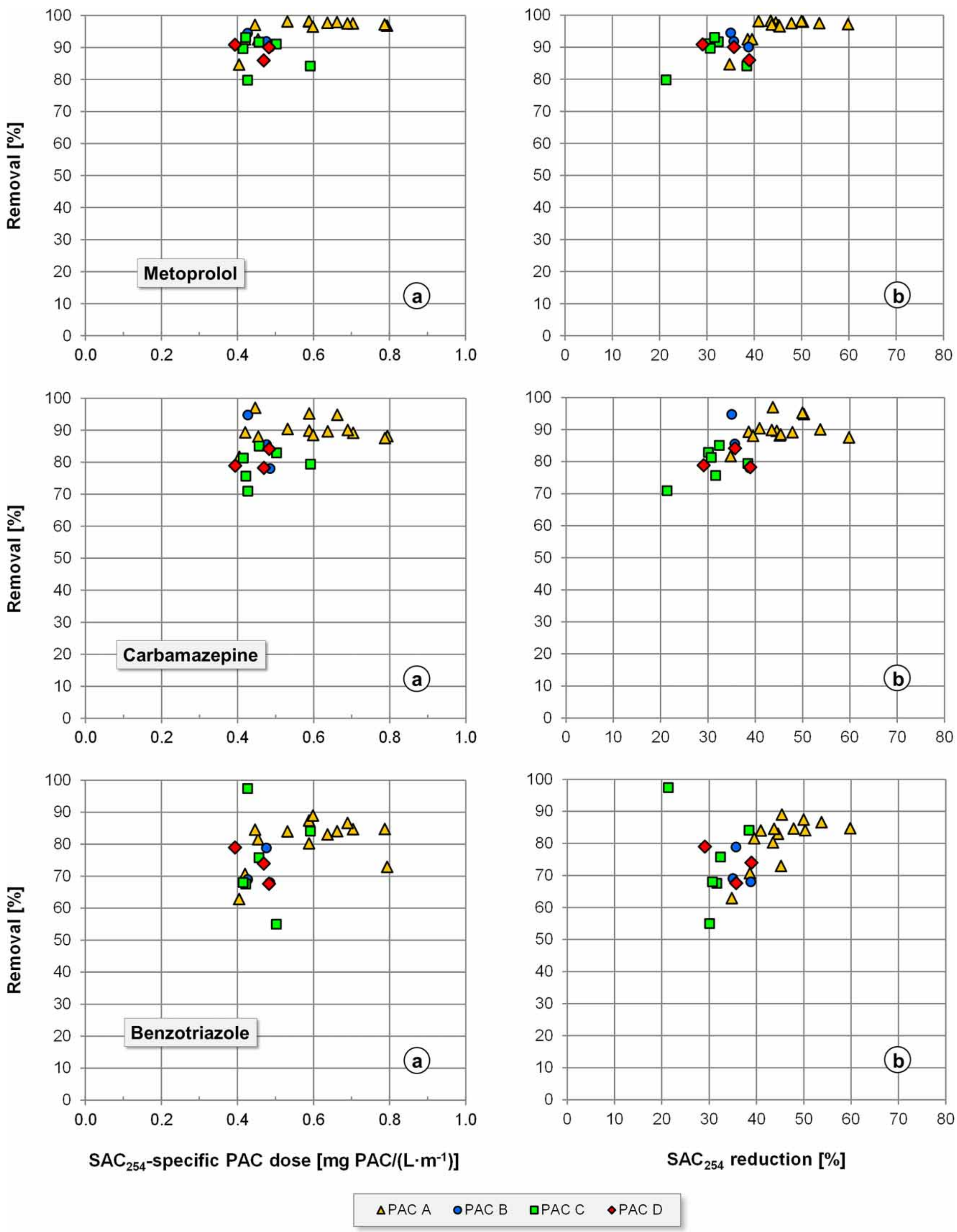

Figure S3 | Removal of metoprolol, carbamazepine and benzotriazole dependent on the SAC_{254}-specific PAC dosage (a) and on the SAC_{254} reduction (b).

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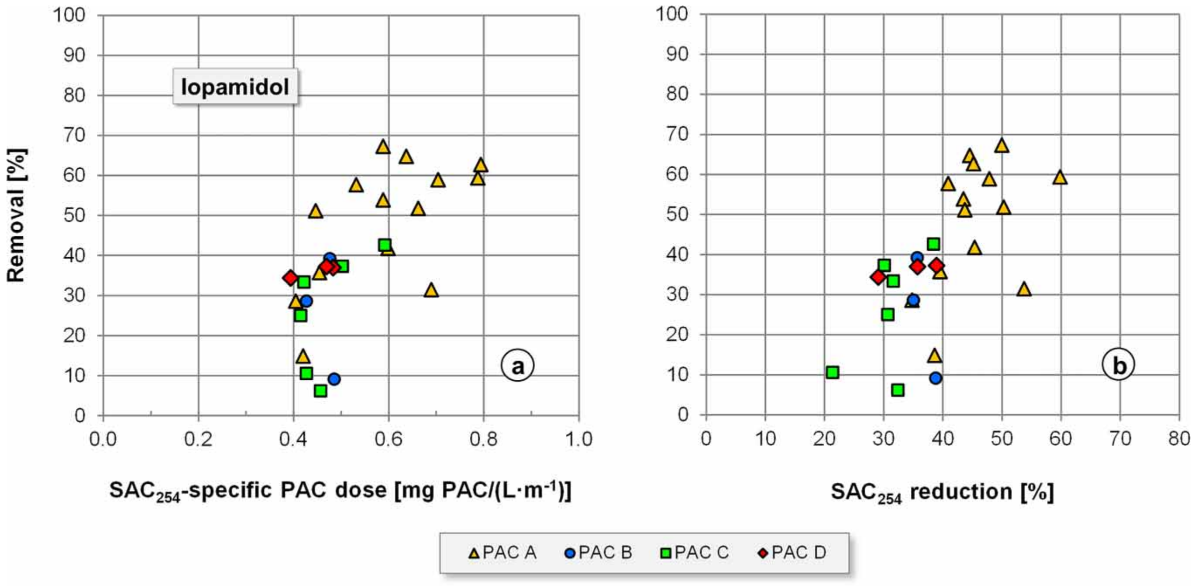

Figure S4 | Removal of iopamidol dependent on the SAC_{254}-specific PAC dosage (a) and on the SAC_{254} reduction (b).