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Adsorption/precipitation prototype agent for simultaneous removal of phosphorus and organic micropollutants from wastewater

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ABSTRACT

In this study, the effectiveness of a novel adsorbent/precipitant containing powdered activated carbon (PAC) and poly aluminum chloride (PACl) was evaluated for the simultaneous removal of organic micropollutants (OMP) and phosphorus. Results showed better performance with the prototype suspension at similar PAC/DOC doses, possibly due to changes in surface chemistry caused by PAC's suspension in the acid precipitant. Further lab tests with wastewater treatment plant (WWTP) effluent samples confirmed the prototype's effectiveness for different matrices. They highlighted the need for optimizing PAC content based on the total phosphorus and DOC content of the wastewater to use both PAC and PACl most efficiently. Full-scale testing at a specific PAC/DOC ratio of 2 over one month demonstrated the prototype's suitability for simultaneous phosphorus and OMP removal under real WWTP conditions. OMP removal increased by $>$ 90 % for carbamazepine, $>$ 50 % for diclofenac and metoprolol, and 30 % for benzotriazole; overall, $>$ 80 % elimination was achieved for all investigated proxy substances. The full-scale experience confirmed that the prototype is easier to store and to apply. It can be immediately used in existing P-dosing systems without additional investment costs, making it advantageous over other OMP removal technologies.

1. Introduction

Organic micropollutants (OMP)- including pharmaceuticals, personal care products, and industrial chemicals - are abundant in water bodies and potentially affect the environment and human health [6,25,40]. WWTP effluents represent a critical point source, and advanced treatment is necessary to prevent further pollution and sustain downstream water quality [24,43]. Many technologies, e.g., oxidative processes, adsorption, membrane filtration, or combined systems, have been studied and developed recently [46]. However, due to the enhanced costs and demands on the operating personnel, their practical implementation is particularly challenging for small WWTPs that require advanced treatment for several reasons (e.g., low dilution rate in the receiving water; direct reuse, discharge to a sensitive region).

This work evaluates a novel chemical prototype agent combining adsorption and precipitation properties, thus, being able to simultaneously tackle OMP and P removal. A major advantage is the suspended, liquid form of the agent, which enables dosage via pumps and storage systems already existing for P removal. This allows immediate advanced wastewater treatment with low investment costs and fewer safety concerns usually associated with PAC storage (e.g., dust explosion risks) [12].

PAC is conventionally dosed into the biological stage or a subsequent tank. The first option involves less process complexity and favors integration into the sludge flocs, biomass growth, and biological activity but requires a higher PAC/DOC dose due to competition with dissolved organic matter [11,23,26,47,50]. The binding of OMP to activated carbon (AC) mainly relies on van der Waals forces, π-π, and electrostatic interactions and is affected by temperature, concentration, adsorbent, and adsorbate properties. Small molecular size, positive charge, hydrophobicity, and aromatic groups, appear to enhance the adsorption of OMP to AC [36,37,57].

Iron and aluminum salts only marginally affect the OMP removal but are used to precipitate dissolved phosphorus fractions [4,35]. They compensate the negative charges of flocs/ suspended PAC and promote the formation of larger particle agglomerates. They are commonly used for chemical P removal but also serve as coagulants during the separation of PAC in downstream filters [30], and interactions with OMP and

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PAC were investigated in this context. Two studies reported reduced adsorption of micropollutants and trace benzenes on the AC when a coagulant was added and interpreted this observation by competition effects or pore blockage on the AC [10,42]. However, other authors did not observe an apparent effect of prior, simultaneous, or subsequent addition of a coagulation agent on the adsorption capacity of the AC [4, 38].

Based on these contradictory results, we first investigated the impact of the precipitant (PACl) on the adsorption of OMP in comparative lab tests performed at three specific PAC/DOC ratios. Samples were analyzed for OMP proxy substances and in vitro bioassays by CALUX® for two modes of action (estrogenicity and toxic PAH xenobiotics metabolism). Secondly, lab tests with effluent samples of three WWTPs with different matrix characteristics aimed to determine the required PAC content in the product formulation for a broad range of WWTP effluent characteristics and assess the applicability. Finally, the prototype agent was applied at a WWTP (6000 p.e. design capacity) for one month to demonstrate OMP and phosphorus removal at full-scale. The objectives of the study were:

i) to assess the effect of the coagulant on the adsorption capacity of the PAC
ii) to define the required PAC content in the product formulation for simultaneous removal of micropollutants and phosphorus
iii) to demonstrate OMP/ P removal by the novel adsorption/ precipitation prototype under real conditions

2. Materials & methods

2.1. Description of the adsorbents

The tested DonauPAC-AQUACLEAR® prototype suspension (Donau Chemie AG, Austria) contained 16.5w % PAC (Carbopal AP®), poly aluminum chloride coagulant, and additional inorganic formulation compounds. The latter's role lies in compensating the PAC charges in the acidic milieu, thus supporting the suspension of the PAC within the coagulant. The reagents within the prototype agent are chemically stable. During long-term storage (>2 years), a slight separation due to sedimentation occurs, which is physically limited and can be remedied by stirring. For the common usage period on a WWTP (<2 years), however, sedimentation does not play a decisive role. The formulation used in the experiments was optimized to the effluent concentration range of P and DOC (5 mg L^{-1}), which are typical for small to medium-sized WWTPs. The total solids content of the prototype sample was 36.9 %, with a pH below 1. The active agent concentration for P removal was 1.9 mol kg^{-1}, which refers to a specific amount of 0.012 L per g of P.

For comparative laboratory tests, we used PAC Carbopal AP® (Donau Carbon, Germany); the same charge used to manufacture the prototype agent.

The point of zero charges (PZC) of the PAC was determined according to the procedure described by Rivera-Utrilla et al. [45]. First, a 0.01 molar sodium chloride solution was prepared and aerated with nitrogen to stabilize the pH. Then, the initial pH (6.4) was adjusted by adding either sodium hydroxide (0.1 molar) or hydrochloric acid (0.1 molar) to obtain an initial pH range between 3 and 9. Next, 150 mg of PAC was added. After 3 h, pH values were measured again and plotted against the initial ones. Accordingly, the PAC's PZC is 8.67.

2.2. Concept of lab experiments

Four effluent samples from three WWTPs differing in size and effluent characteristics were investigated. All WWTPs are operated according to the best available technologies, i.e., conventional, low-loaded activated sludge treatment with carbon, nitrogen (nitrification and denitrification) removal and chemical phosphorus precipitation. Characteristics are described in Table S1 – Supplementary Information (SI).

Table 1 gives an overview of the lab tests. Tests A1 and A2 compared the adsorption of OMP by the adsorption/precipitation prototype and PAC only at three similar PAC/ DOC ratios in physical triplicates. OMP were analyzed in the initial and final samples. For the in vitro bioassays, the triplicates were merged into one composite sample. Tests A3, B, and C assessed the general applicability of the prototype for implementation at WWTPs with differing DOC effluent characteristics.

Lab experiments were conducted with effluent samples, which originated from a WWTP applying chemical P removal (0.15–0.5 mg L^{-1} total P) and aimed to evaluate the OMP removal. The combined effect of the prototype suspension was evaluated in the full-scale application, in which the tested agent replaced the routinely applied P- precipitant. The effluent samples showed a total suspended solid content below 1 mg L^{-1} and were used without prior filtration. Each Erlenmeyer glass flask contained a fixed sample volume (between 200 mL and 400 mL) and a known amount of adsorbent (PAC or adsorption/precipitation prototype) related to three targeted doses (1, 1.5, and 2 g PAC g^{-1} DOC) tested in physical triplicates. Blank tests (effluent without adsorbent) were included in duplicates to assess a potential bias caused by the adsorption onto the glass walls or by photocatalytic effects. Mixing was realized by horizontal shaking with CERTOMAT® U (B. Braun, Germany) at 120 rpm and room temperature (approximately 23 °C). After 24 h of contact time, the suspended PAC was removed by VWR (USA) 1 μm glass fiber filters, and the filtrate obtained was analyzed for OMP.

2.3. Full-scale application at WWTP A

The suspension dose was selected according to two criteria: i) to fulfill P-emission limits and maintain the operated β-value of 0.8 (β-value: parameter for assessment of coagulation effectiveness as molar ratio between precipitant and P to be precipitated), and ii) to provide sufficient PAC to realize a DOC/PAC ratio 2. The amount needed was calculated based on the mean P-concentration of the influent (three years of operational protocols) and the mean DOC measured during the reference period.

The prototype suspension was dosed at a constant rate of 90 L d^{-1} and 126 kg d^{-1}, respectively, by a peristaltic pump (DULCO flex - Prominent, Germany) into the inflow of the biological stage for four weeks, replacing iron(III) chloride usually used at that WWTP as a coagulant. The total test period covered eight weeks (56 days), including two weeks of reference period before dosing started and two more weeks of washout phase after prototype addition was stopped and switched back to iron(III) chloride. Beginning with the second week, the dosing scheme was changed from continuous to intermittent at 15-minute intervals to increase flow velocity in the pipes and avoid clogging, as observed in the first week. The total adsorption/precipitation product amount used during the entire period was 2 700 L (3 500 kg).

Sample collection of flow-proportional daily composite effluent samples covered the total experimental period. The samples were stored

Table 1
The lab tests assessed the coagulant's effect on the PAC adsorption capacity (A1 and A2) and the applicability for the treatment of different WWTP effluents (A3, B, and C).

Tests	Adsorbent	WWTP	DOC (mg L^{-1})	PAC/ DOC ratios	OMP analysis	In vitro bioassays
A1	Carbopal AP®	A	4.5	1/1.5/ 2	x	x
A2	DonauPAC-AQUACLEAR®	A	4.5	1/1.5/ 2	x	x
A3	DonauPAC-AQUACLEAR®	A	5.9	1/1.5/ 2	x	
B	DonauPAC-AQUACLEAR®	B	5.6	1/1.5/ 2	x	
C	DonauPAC-AQUACLEAR®	C	15.4	1/1.5/ 2	x	

at 4 °C and analyzed within seven days. The spectral absorption coefficient at 254 nm wavelength (SAC_{254}), a standard surrogate parameter for OMP removal, was assessed in all daily effluent samples. Furthermore, DOC was measured in 12 daily effluent samples. Based on the SAC_{254} measurement and the recorded wastewater loads, 21 daily influent and corresponding effluent samples out of the 56 samples were selected and analyzed for OMP. In order to compensate for fluctuations in daily composite samples, all collected influent and effluent samples were merged into eight flow-proportional weekly composite samples and analyzed for the following parameters: OMP, SAC_{254}, DOC, orthophosphate, and total suspended solids (TSS) contents.

2.4. Selected OMP proxy parameters

Adsorption of OMP onto AC is influenced by the adsorbent physicochemical properties as given in Table 2 for ten different OMP. The selected OMP, which were analyzed in both the lab and full-scale experiments, are considered as suitable proxy parameters for evaluating advanced wastewater treatment. The parameter log D_{OW} is used for the differentiation between hydrophilicity and hydrophobicity [37,49,61]. Furthermore, the compounds' charge affects electrostatic interactions with the AC surface, which may be positively ($pH < PZC$) or negatively charged ($pH > PZC$) [36].

2.5. Chemical analysis

Organic micropollutants were extracted by online SPE with Phenomenex Strata X extraction cartridges (20 × 2.0 mm, 25 µm) and measured by LC-MS using Phenomenex Luna C-18 (150 × .0 mm; 5 µm) and Phenomenex C18-Security guard cartridges (40 ×3.0 mm) analytical columns with a linear gradient using two eluents: 0.1 % acetic acid and acetonitrile with 0.1 % acetic acid). A linear trap ion trap mass spectrometer QTRAP 6500 (Applied Biosystems, USA) was used for detection. Ion spray voltage was − 4500 V, and the temperature was 400 °C. The sample injection volume was 10 mL.

OMP concentration was determined by external calibration using different concentrations of multicomponent standards. All chemicals were purchased from Sigma-Aldrich. Details regarding the elution program for online SPE and HPLC and other parameters, like ionization mode used, mass-to-charge ratios, and LOQs can be found in SI.

Dissolved organic carbon was analyzed according to EN 1484 with the TOC-L analyzer by Shimadzu (Japan). The SAC_{254} was measured with a UV/VIS spectrometer Lambda 35 (Perkin Elmer, USA). Orthophosphate (PO_4-P/ISO 6878) and TSS content were determined in the weekly composite effluent samples, which were additionally subjected to greyscale tracking tests described by Metzger et al. [39]. Conventional wastewater parameters, like temperature, pH, electrical conductivity, biological and chemical oxygen demand (BOD/DIN 38 4099 and COD/ISO 6060–1989), ammonia (NH_4-N/ISO 7150–1,), nitrate (NO_3-N/DIN 38405 D9–2), nitrite (NO_2-N/ ISO 26777), total nitrogen, and total phosphorus (TP/ISO 6878:2004), as well as the dry matter content of the activated sludge, were abstracted from the operational protocol of WWTP A.

2.6. In vitro bioassays

Composite samples based on the triplicates and the blanks from experiments A1 and A2 were concentrated by solid-phase extraction (SPE) with Oasis HLB cartridges (500 mg, 6cc, Waters 186000115; Waters Corporation, Taunton, MA, USA) according to an adapted protocol of BioDetection Systems (Amsterdam, The Netherlands), as described by Phan et al. (2021). One procedure blank sample (deionized water) was included for quality control. All extracts were analyzed by BioDetection Systems (Amsterdam, the Netherlands) with two CALUX® reporter gene assays comprising estrogenicity (ERα) and toxic PAH xenobiotics metabolism (PAH). *In vitro* bioassays account for mixture effects, which are translated into bioanalytical equivalent concentrations (BEQ) of reference chemicals. The BEQ for the ERα bioassay was expressed as 17-β-estradiol equivalent (EEQ), and BEQ for the PAH bioassay was benzo[*a*]pyren equivalents (B[*a*]P-EQ). BEQ values were compared to specific effect-based trigger values (EBT) currently discussed, defining acceptable levels for different modes of action. According to literature, for a given mode of action different EBT values are provided, depending on the applied bioassay and the defined target. For ERα, the range lies between 0.1 ng L^{-1} and 0.5 ng L^{-1} EEQ, while the relatively wide range of EBT values for PAH CALUX® encompasses values between 6.2 ng L^{-1} and 150 ng L^{-1} B[*a*]P-EQ [7,20,54]. To guarantee comparability to former studies, we applied EBT values provided by the joint NORMAN and Water Europe Position Paper "New and emerging challenges and opportunities in wastewater reuse" [41], which were 0.1 ng L^{-1} EEQ and 6.2 ng L^{-1} B[*a*]P-EQ.

2.7. Data evaluation and calculations

The initial ($C_{i,0}$) and final (C_i) micropollutant concentrations as well as BEQ biotest results were used to calculate removal according to Eq. (1). The initial concentration was taken as the mean value of two control samples without adsorbents added. The SAC_{254} reduction was calculated using mean SAC_{254} values instead of concentrations.

$$removal \quad (\%) = \frac{C_{i,0} - C_i}{C_{i,0}} \tag{1}$$

3. Results & discussion

3.1. Lab-scale tests

3.1.1. Effect of the coagulant on OMP adsorption

Comparative tests with standard PAC (test A1) and the prototype

Table 2
Analyzed OMP in the samples from the lab experiments and the full-scale application test.

Substance	Abbreviation	CAS	Compound class	LOQ (ng L^{-1})	log D_{OW} ($pH = 7$–7.5)	charge at $pH = 7$	Adsorptive removal
acesulfame K	ACS	55589-62-3	sweetener	0.2	-2.23^{a}	neutral	medium**
benzotriazole*	BTA	95-14-7	complexing agent	1.6	1.29^{c}	neutral	high**
bezafibrate	BZF	41859-67–0	lipid-lowering agent	1.0	0.97^{b}	negative	high**
carbamazepine*	CBZ	298-46-4	antiepileptic	0.2	2.77^{a}	neutral	high**
diclofenac*	DCF	15307-79-6	analgesic	0.4	0.82^{a}	negative	high**
diuron	DCMU	330–54–1	herbicide	62.8	2.53^{b}	neutral	n.a.
ibuprofen	IBP	31121-93-4	analgesic	6.7	1.48^{d}	negative	medium**
metoprolol*	MTP	37350-58-6	beta blocker	6.0	-0.81^{b}	positive	high**
sulfamethoxazole	SMX	723-46-6	antibiotic	0.6	-0.40^{a}	negative	medium
trimethoprim	TMP	738-70-5	antibiotic	1.7	1.12^{a}	neutral	n.a.

*Included in the proxy substance list suggested for revising the UWWTD [21]
**According to Jekel et al. [28]
[a] [61]; [b] [27]; [c] [29]; [d] [17].

(test A2) were performed at specific PAC/DOC ratios of 1, 1.5, and 2 for each adsorbent, which resulted in PAC doses between 4.5 and 9 mg L^{-1}. Fig. 1 shows the removal of metoprolol, benzotriazole, carbamazepine, and diclofenac. Removal data for the other detected OMP, sulfamethoxazole, bezafibrate, and ibuprofen is shown in Table S4 and Figure S1 in SI. The initial pH of the wastewater sample was 7.86. After 24 h of contact time, pH values were 7.77–8.10 in samples treated by the prototype and 7.74–8.03 in samples treated by PAC. All values were below the PZC of the PAC, which was 8.67.

Individual OMP adsorption by the prototype agent follows the pattern from standard PAC experiments conducted under similar conditions [3,4,9]. Although the pH of the WWTP effluent sample was lower than the PZC of the applied AC, negatively charged adsorbed organic matter may switch the surface charge, thus leading to the binding of positive compounds, e.g. metoprolol, by electrostatic interactions [36,58]. According to literature, the adsorption of neutral and negatively charged substances is largely influenced by the hydrophobicity and molecular structure [9,37]. High removal of benzotriazole, carbamazepine, and trimethoprim (with log D_{OW} values > 1) is thus likely attributed to hydrophobic interactions [37,61]. Removal rates of negatively charged compounds were generally lower, probably due to increased repulsion by the PAC surface [36]. Diclofenac removal amounted to 28 ± 3 % and 37 ± 16 % by PAC and the adsorption/precipitation prototype, respectively. The reduction for bezafibrate and ibuprofen was inconclusive; given the high standard deviations for a PAC/DOC ratio of 2, a dose-dependent differential effect is insignificant for these compounds. Removal of sulfamethoxazole was below 10 % in samples treated with PAC and the prototype suspension. This substance is generally known for its low/moderate adsorbability. Nevertheless, the rates were slightly higher for the prototype suspension. Acesulfame K and diuron concentrations lay below the LOQ in the initial effluent samples, and subsequent removal could not be calculated.

Almost all OMP, independent of molecular size, charge, or octanol-water distribution coefficient, showed a higher removal by the prototype suspension than by standard PAC treatment. This is likely due to the acidic character of the coagulant/ precipitant, which leads to an increased chemical activation of the AC surface, thus enabling additional electrostatic interactions between the AC and the OMP. Former studies showed that an acidic and oxidizing pre-treatment of the AC causes alterations in the surface chemistry. This results in the formation of surface oxygen acidic groups, thereby increasing the adsorbent's net negative surface charge [8,48]. The coagulant removes mostly higher molecular weight organic matter, which is of minor importance to OMP competitive adsorption and thus should not influence the adsorption capacity, as shown in former studies [4,15,38].

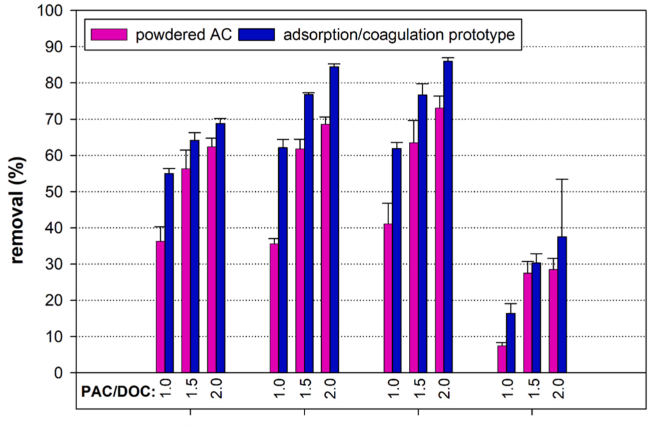

Fig. 1. Comparison of metoprolol (MTP), benzotriazole (BTA), carbamazepine (CBZ), and diclofenac (DCF) removal by PAC (Carbopal AP®) and the adsorption/precipitation prototype (DonauPAC-AQUACLEAR®) at PAC/DOC ratios of 1, 1.5, and 2 from WWTP effluent sample A1.

3.1.2. *Toxicity reduction*

The analysis of the extraction quality control sample (deionized water) resulted in concentrations below the LOQ (0.018 ng L^{-1}) for EEQ and 41 ng L^{-1} for B[*a*]P-EQ, the latter being considerably higher than the EBT value of 6.2 ng L^{-1} for this parameter. Increased blank results (background level) for the PAH CALUX® bioassay were formerly reported in other studies and seemed to be influenced by the solvents' impurities, impacting the analysis [13]. The BEQ concentrations in the untreated effluent samples (based on the experiments' control samples) were 1.90 ng L^{-1} EEQ and 120 ng L^{-1} B[*a*]P-EQ for ERα and PAH, respectively. EEQ lies above the range given in a former study on nine different Austrian WWTPs (0.32–1.30 ng L^{-1} EEQ). The effluent PAH concentration is in line with the range reported in the literature (0.38–210 ng L^{-1} for B[*a*]P-EQ) [13]. The BEQ values after treatment with standard PAC and the prototype product are given in Fig. 2.

Consistent with the OMP results, EEQ reduction increased with the dose applied and was higher for samples treated with the adsorption/ precipitation prototype than those treated with standard PAC. The EEQ removal increased from 79 % to 95 % and from 42 to 77 % with the prototype and PAC doses, respectively. Standard PAC removals agree well with values reported in the literature, approximately 75 % for specific PAC/DOC ratios ranging from 0.8 to 4 [56]. Treatment with the prototype exceeded this value. The B[*a*]P-EQ results are of lower significance due to the high BEQ in the blank sample, which was in the same range as the samples treated by the adsorbents. The toxicity reductions were 68–71 % and 23–63 % by the prototype product and PAC, respectively, showing an apparent differential effect at the lowest PAC/DOC ratio.

Comparing the BEQs with EBT values, as described by Alygizakis et al. [5], shows that acceptable toxicity levels (a factor between BEQ/EBT of below 1) of the treated effluent and not considering any dilution by the receiving waterbody was only achieved for EEQ at the highest dose of the adsorption/precipitation agent tested. After treatment with PAC alone, both ERα and PAH-like toxicity were still above EBT, which indicates that resampling and further actions would be needed to identify specific substances that trigger the test's cell response. For PAH-CALUX®, the obtained BEQ/EBT factors were between 5 and 14, meaning further source identification and monitoring are appropriate [5]. Notably, for PAH-CALUX®, a broader range of EBT values is available in the literature. Been et al. suggest a higher EBT value of 24.4 ng L^{-1} B[*a*]P for drinking water, which would accordingly lead to significantly lower factors. The significant deviation of EBTs reported is based on varying methods for EBT derivation, depending whether the ecosystem's protection or human health is targeted [7].

3.1.3. *Applicability of the adsorption/precipitation prototype for different WWTPs*

Lab tests A3, B, and C, aimed to optimize the prototype's PAC content for efficient and economic OMP elimination at various WWTPs. Fig. 3 shows the triplicate removal rates of four OMP, detected in all investigated effluent samples at three PAC/DOC ratios. The applied amount of the prototype product was between 37 -77 mg L^{-1}, 30–76 mg L^{-1} and 64–122 mg L^{-1} for A, B, and C, respectively. Results for additional OMP are given in SI (Table S5-S7). The initial pH values of effluents A, B, and C were 7.55, 7.66, and 8.55, respectively, and increased in all samples by a maximum of 0.2.

The location-dependent characteristic wastewater matrix has a substantial effect on the removal of OMP by PAC, whereby specifically the low molecular organic acids are considered competitors for adsorption sites [59,60]. Thus, similar product doses result in varying removal rates, as is also visible in our data.

Metoprolol concentration was reduced by more than 80 % in samples A and B at a PAC/DOC ratio of approximately 2. The required dose for C was even lower at about 1.5. Compared to A, where about 2.5 PAC/DOC

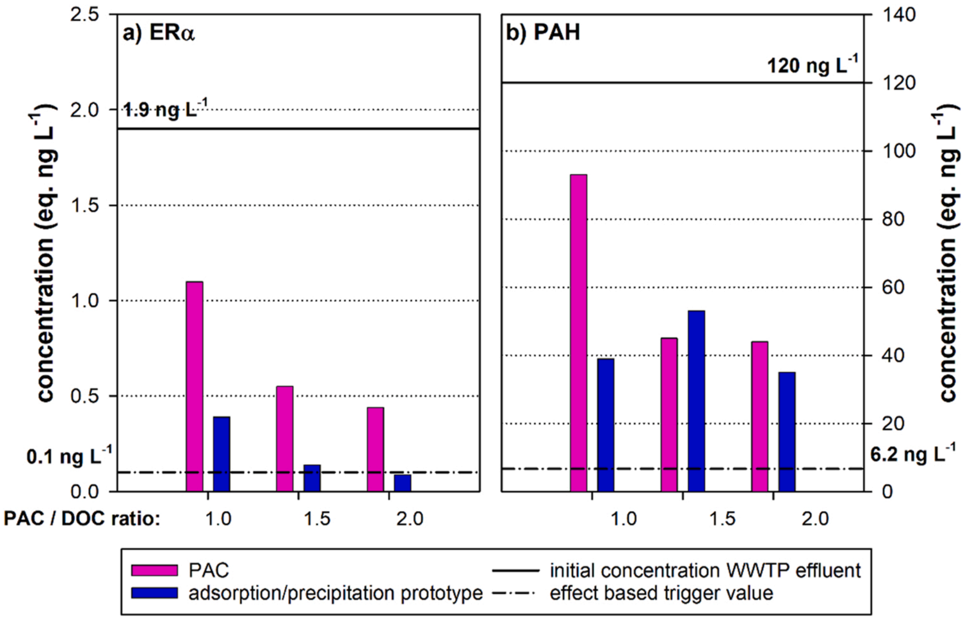

Fig. 2. : Comparison of ERα and PAH-CALUX® removal by PAC and the adsorption/precipitation prototype at specific doses of 1, 1.5, and 2 g PAC/ g DOC from WWTP effluent sample A1.

would be needed to achieve 80 % removal, the removal of benzotriazole and carbamazepine was higher in samples B and C with a required PAC/DOC ratio of 1.5. Diclofenac adsorption was found to have the slightest variation, and the required dose for all three effluents was linearly extrapolated to 3 g PAC g^{-1} DOC. Other OMP, known to be biodegradable during conventional treatment, were not detected in all of the initial samples. Bezafibrate was detected in WWTP B and C, not in WWTP A. Its removal in tests with effluent B increased from 13 % to 86 % with rising PAC/DOC ratios applied. Treatment of effluent C with the prototype resulted in a lower dose-dependent increase and ranged between 40 % and 50 % removal. The moderately adsorbable proxy substances (sulfamethoxazole, acesulfame K, and ibuprofen) were only detected at low concentrations. Concentrations of the finally treated samples were below the LOQ, and subsequently removal calculation was impossible. Treatment by the adsorption/precipitation prototype resulted in a maximal sulfamethoxazole removal of 18 % in sample B. No removal for A and C was observed. Ibuprofen concentrations lay below the LOQ in all samples. Acesulfame K could only be detected in sample A at a concentration of 19.0 ± 1.0 ng L^{-1} and removal decreased from 90-100 % at the lowest dose to 58–68 % at the highest one. Acesulfame K is known for its poor adsorptive removal properties, and fluctuating removal rates may result from analytical bias. In addition, this substance is susceptible to photocatalytic and biodegradation, which is considered by examining final control values. The PAC may however impose a shielding effect at higher doses, thus making such degradation pathways less likely. Nevertheless, this substance could only be detected in this wastewater (sample A). Therefore, it was not possible to verify this controversial behavior. Both compounds, ibuprofen and acesulfame K, are biodegradable, and conventional treatment has already achieved efficient elimination.

Commonly, an OMP proxy-substance of 80 % for the sum of all substances is targeted and calculated between the influent and effluent of the WWTP. This value originates from legal regulations, which are in force in Switzerland and Germany and have been adapted within the draft for revising the European Urban wastewater treatment directive [21]. Thus, OMP reduction during conventional treatment must be considered when determining the required PAC/DOC dose. In particular, carbamazepine (no biological removal) and diclofenac (20–50 % biological removal [11,55]) are critical due to their persistence against biodegradation and low sorption affinity to activated sludge [16].

Applying the prototype agent in combination with biological treatment at a PAC/DOC ratio of 2.5–3, 80 % removal for almost all compounds analyzed can be achieved. Only sulfamethoxazole, with biological removal rates between 30 % and 50 % [11], would probably result in less than 80 % removal even at a high PAC/DOC ratio of 3. The required dose is consistent with literature studies recommending a PAC/DOC ratio between 2 and 3 when PAC is dosed into the biological stage [44,50]. For the full-scale tests at WWTP A, we selected a PAC/DOC ratio of 2 to observe a noticeable effect without completely removing all compounds (below LOQ) to gain insight into adsorption dynamics.

3.2. *Optimum product formula*

The required P removal for WWTPs discharging into eutrophication-sensitive areas, according to legal guidelines is currently 80 % [1]. As described above, for OMP removal, 80 % removal requirement may be expected.

To achieve the required removal of both parameters, the required dosage for the simultaneous addition to the biologically activated sludge process depends on the influent's phosphorus content and effluent's DOC; therefore, it is essential to consider both parameters during the product formulation and dosage. While typical total phosphorus concentrations in the influents of the different investigated WWTPs, obtained from operation protocols of the WWTPs under investigation, ranged between 4.7 and 5.7 mg L^{-1}, the mean DOC of the samples varied between 4.5 and 15.4 mg L^{-1}. Since DOC limits the adsorption capacity for OMP it is important to consider the fixed PAC mass fraction of the product. The impact of the ratio between these two relevant parameters (total phosphorus to be removed and DOC) on the prototype PAC content was assessed in Figure S3 and Figure S4. The required mass fraction derived for PAC in the adsorption/precipitation product under matrix conditions typical for small to medium-sized WWTPs in Austria, as represented by WWTP A and B (5 mg L^{-1} DOC and 4 mg L^{-1} P, which must be chemically removed), is 12 %. The elevated DOC at WWTP C (15.4 mg L^{-1} DOC/ 4.3 mg L^{-1} P, which has to be chemically removed) requires a higher PAC content with a minimum of 29 %. Since the product is commercialized for the use in different wastewaters, the PAC fractional dose should be optimized to the specific matrix applied. However, dosing pump specifications certainly can limit the possible

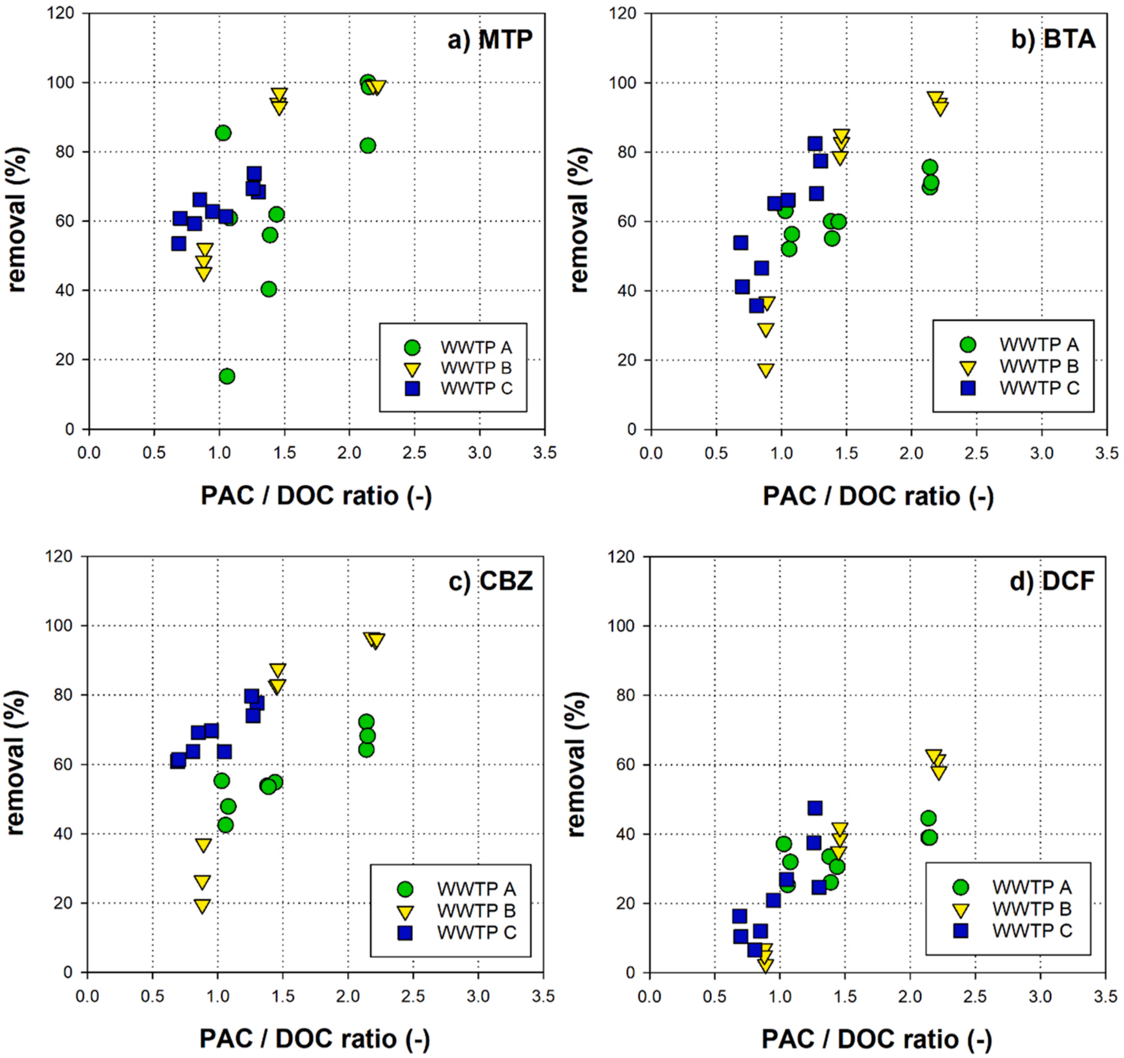

Fig. 3. Removal of a) metoprolol (MTP), b) benzotriazole (BTA), c) carbamazepine (CBZ), and d) diclofenac (DCF) from three different WWTP effluent samples vs. the applied PAC/DOC ratio.

mass fraction due to total solids content. Further on, excessive coagulant dosing is neither an economically meaningful nor resource-efficient option, which may lead to undesired effects such as charge reversal thus affecting flocs/PAC coagulation and sedimentation [33].

To summarize, wastewater characteristics, particularly the ratio between to be removed phosphorus and DOC, are core criteria for the product formulation. Those site-specific effluent matrix characteristics should be considered when determining the required PAC mass fraction, which typically lies between 12 % and 20 % (5 g L^{-1} P in the influent and a DOC between 5 and 10 mg L^{-1}).

3.3. *Full-Scale test*

3.3.1. *General performance and conventional parameter abatement*

The advanced wastewater treatment by the prototype under investigation was implemented on-site at the WWTP within a few hours since dosing equipment was already on-site for a P-precipitation, demonstrating the approach's easy implementation. After initial operational difficulties arising from the dosage pump (clogging due to low flow velocity in the existing distribution pipes) were solved within a week by shifting from continuous pumping to intermittent dosing at 15-minute intervals, a stable operation was achieved for the rest of the test period. Dosing was set at a fixed flowrate (90 L per day), therefore the system did not require additional equipment such as sensors or analyzers, and maintenance for the treatment plant operators was limited to a check of functionality.

Figure S5 shows the wastewater inflow at WWTP A during the whole experimental period. The grey area indicates the period when the adsorption/precipitation prototype was applied. The mean inflow during dry weather conditions in the previous years (2019–2021; 1 547 m^3 d^{-1}) was used to calculate the amount of product dosage. However, the mean flow during the reference period (mean load of 939 ± 64 m^3 d^{-1}) was significantly lower than the long-term dry weather flow but increased to more than 2 000 m^3 d^{-1} during the test period. The peaks in wastewater flow result from the takeover of retained stormwater after weekends. SAC_{254} measurements of daily-composite samples were the primary tool to follow and assess the purification performance and functionality of the test approach (see Figure S6). It is evident that both parameters, SAC_{254} and DOC, decreased continuously during the dosing period and increased again during the washout period after the dosing was stopped.

Mean COD removal during the reference period (95 ± 2 %) and test period (92 ± 2 %) were in a similar order of magnitude. Mean total nitrogen removal increased slightly from 87 ± 5 % to 94 ± 2 %. Phosphorus removal, dependent on the amount of coagulant applied, was 92 ± 3 % during the reference time and slightly lower (86 ± 6 %) during the test period, nonetheless above the targeted value of 80 %. The average effluent total P- concentration during the reference and test period were 0.48 ± 0.04 mg L^{-1} and 0.47 ± 0.05 mg L^{-1}, respectively. The allowed emission standard of 1 mg L^{-1} total phosphorus and 0.5 mg L^{-1} ortho-phosphate were thus met at all times. Conventional parameters are displayed in Figure S7. Suspended solids were assessed in the weekly composite samples to assess PAC loss. Concentrations were between 0.9 mg L^{-1} to 1.2 mg L^{-1} and, therefore, in the range reported for effluents after filtration to remove residual PAC [31]. Accompanying greyscale tracking measurements showed no PAC in the composite effluent samples (see Figure S8). However, it should be noted that this method is affected by the background matrix and shows little accuracy at a concentration range below 1 mg L^{-1} of total suspended solids. The totals suspended solid content of the sludge was approximately 3 % higher than usual, which is caused by the additional solids (PAC and inorganic stabilizators) introduced by the prototype agent. The sludge volume index as an indicator for sedimentation in the secondary clarifier decreased from approximately 120 mL g^{-1} to 60 mL g^{-1}, and as a consequence, visibility depth in the secondary clarifiers increased too. Microscopic images of activated sludge samples collected during the last two weeks of the test period showed PAC particles incorporated into the sludge flocs.

Benefits of PAC dosing into the biological stage, such as improved nitrification and sludge settling properties, are well documented in the literature [14,47] and are visible during the application of the adsorption/precipitation prototype in our study. Based on these observations, we conclude that the applied PAC has been successfully integrated into the sludge flocs and that separation in the secondary clarifier was sufficient to prevent PAC loss, even in the case of higher inflow conditions.

3.3.2. Removal of OMP

Fig. 4a shows the removal of metoprolol, benzotriazole, carbamazepine, and diclofenac, during the reference and test time. In addition, acesulfame K, bezafibrate, and ibuprofen were analyzed. Since their removal exceeded 90 % in the biological step during the reference period, these parameters were not evaluated in detail. During the reference period, the removal of metoprolol, benzotriazole, and diclofenac was 31 ± 7 %, 39 ± 4 %, and 23 ± 2 %, respectively. Carbamazepine, however, was not at all removed. The highest abatement during the test period with prototype dosage was observed for metoprolol and carbamazepine, reaching and maintaining removal efficiencies above 80 % after test week 2 until reference week 3 (one week after PAC dosing was stopped). For benzotriazole, removal fluctuated around 80 % in test weeks 2, 3, and 4. Also diclofenac abatement was close to 80 % in test weeks 2 and 3 but slightly lower (69 %) in week 4.

Besides the weekly composite samples, 21 daily influent and effluent samples were analyzed to assess OMP removal in detail (see Fig. 4b). As mentioned, continuous dosing encountered operational difficulties in test week 1, resulting in a lower applied dose than intended, which explains the comparably low removal of OMP on the 12th and 19th of July. On August 1st, a reduced removal was noted for diclofenac and benzotriazole, most probably due to a stormwater event of 2 302 m^3, leading to a significantly reduced hydraulic retention time (approximately 17 instead of 36 h) and contact time between the wastewater and the PAC-enriched sludge.

After stable removal was obtained following week 1, OMP removal rates as predicted by physical-chemical properties, were met. Replacing the P-precipitant with the prototype agent improved the abatement by more than 80 % for carbamazepine, 60–80 % for metoprolol, and 40–60 % for benzotriazole and diclofenac. Benzotriazole and diclofenac removals were slightly lower than the targeted 80 %. Sorption behaviour generally reflected the results of the lab experiments, which agree with removal values obtained for PAC application at other WWTPs [22,34].

3.4. Comparison with other technologies

The results obtained in lab and full-scale tests proved the suitability of the prototype agent for simultaneous phosphorus and OMP abatement. Nevertheless, the competitiveness of the technology against other approaches depends on economic, environmental, and operational aspects.

Compared to the standard PAC treatment, where coagulant and PAC are added separately, the prototype solution can be applied using the existing infrastructure, which represents a clear advantage. Nevertheless, dosing the prototype suspension within the biological stage is also linked to disadvantages, e.g., the higher amount of DOC resulting in a higher competition of OMPs with the background matrix [50]. A possibility to overcome this issue is to apply the prototype after the biological stage in a subsequent contact reactor. In this case, a separation stage (deep bed filtration, clog filtration, ultrafiltration) is necessary to avoid a PAC loss via the effluent [31]. Although investment is needed in this configuration, PAC's improved surface chemistry and adsorption capacity still represents an asset when it is compared to the standard PAC application. In both cases, dosing into the biological stage and a subsequent reactor, it has to be considered that the PAC is mixed with the excess sludge and cannot be reused, which is a drawback in terms of

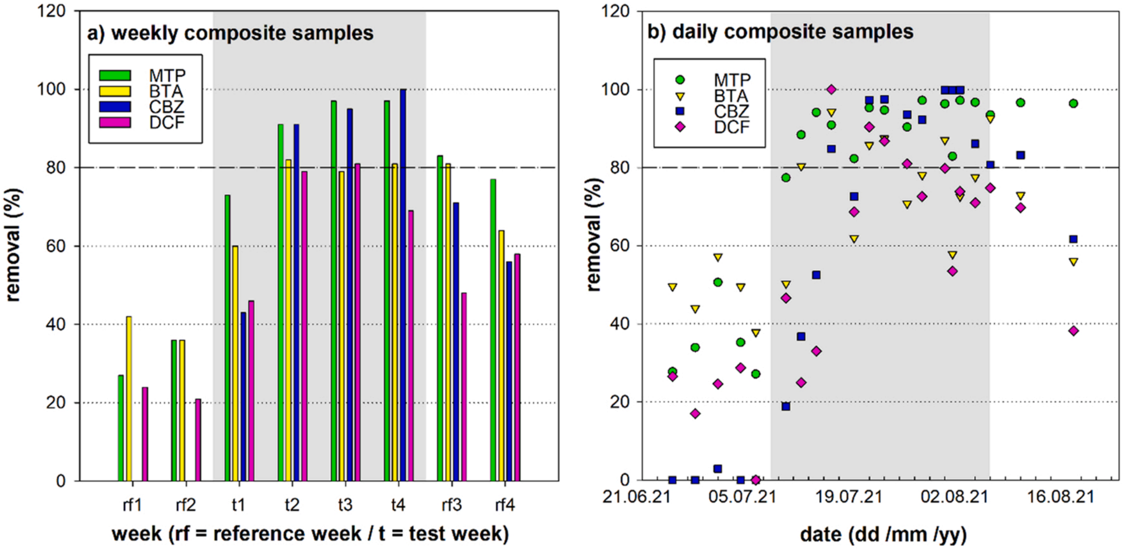

Fig. 4. Removal of metoprolol (MTP), benzotriazole (BTA), carbamazepine (CBZ), and diclofenac (DCF) during the full-scale tests in a) weekly composite samples and b) daily composite samples.

sustainability.

Another option to achieve simultaneous phosphorus and OMP removal is to combine coagulation with GAC filtration. In this case, the coagulant is added before GAC filtration to precipitate additional phosphorus from the WWTP effluent. Furthermore, the GAC filter removes suspended solids and adsorbs OMP [2,52]. To implement this option, dosing pumps and filters are required, and the filter's adsorption capacity must be monitored during operation to avoid a breakthrough, which enhances operational efforts. A benefit of this approach is that the GAC can be regenerated and reused. Besides adsorptive treatment, phosphorus and OMP can be removed simultaneously within MBBR (moving bed bioreactors) systems by controlling redox conditions and feeding regime. However, the reported removal rates for OMP are below 80 % [19,51,53]. Otherwise, algae treatment is another eco-friendly treatment technology described in the literature, but implementation is linked to high land use, enough solar irritation, and average moderate temperatures throughout the year, which restricts it's application in countries like Austria [32].

4. Conclusions & outlook

The novel adsorption/precipitation prototype agent was investigated via lab and full-scale tests and proved to be effective in removing OMP and phosphorus simultaneously. The main findings of this study are:

- The prototype suspension achieved a higher OMP removal and toxicity reduction than standard PAC at similar specific PAC doses. Most probably, this can be attributed to the prototypes' acidic character that causes AC surface chemistry alterations.
- Phosphorus and DOC in the wastewater matrix are core criteria for determining the required mass fraction of PAC. The PAC mass fraction should be optimized for the site-specific effluent matrix characteristics; it typically ranges between 12 % and 20 % (5 g L^{-1} P to be precipitated and 5–10 mg L^{-1} DOC).
- Requirements for P removal were met during the full-scale application, and a targeted PAC/DOC ratio of 2, enhanced OMP removal by $>$ 90 % for carbamazepine, $>$ 50 % for diclofenac and metoprolol and 30 % for benzotriazole. The total removal during stable prototype dosing was: 95.0 $\pm$ 3.5 % for metoprolol, 80.7 $\pm$ 1.5 % for benzotriazole, 95.3 $\pm$ 4.5 % for carbamazepine and 76.3 $\pm$ 6.4 % for diclofenac.
- Applying the adsorption/precipitation prototype is possible with the existing infrastructure and equipment for P-precipitation, no additional investment is needed.

The prototype suspension is especially an interesting option for small- to medium-sized WWTP with a comparably lower level of technical standards, in which investment costs per treated m^3 of wastewater generally are proportionally higher or limitations in space impede the implementation of more elaborate technologies. The adsorption/precipitation agent can also help treat peak loads or industrial effluents containing OMP, which are only produced for a defined period or applied during maintenance work at existing advanced systems. Furthermore, the pre-suspension of PAC in the coagulant enables a combination of different properties. These should be optimized site-specifically to achieve increased adsorbent-adsorbate interactions, which is still considered one of the critical challenges in adsorption technologies [18]. Such possible optimizations can be achieved for a specific or broad range of substances, enhancing process efficiency and decreasing resource demand. The adsorption/precipitation prototype represents an innovative promising product in the portfolio of established treatment technologies, and further development is recommended.

CRediT authorship contribution statement

D. Reif: Conceptualization, Methodology, Investigations, Formal analysis, Writing – original draft. **L. Weisz:** Investigations, Formal analysis, Writing – review & editing. **K. Kobsik:** Investigations, Formal analysis. **H. Schaar:** Methodology, Writing – review & editing. **E. Saracevic:** Investigations, Validation. **J. Krampe:** Supervision. **N. Kreuzinger:** Project administration, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2023.110117.

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