The role of coagulation on the fate of PFAS, brominated flame retardants and other trace contaminants in tertiary wastewater treatment for phosphorus control

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HIGHLIGHTS

- Dissolved organic matter type affected the fate of trace organics in coagulation.
- Humic acid led to highest removals due to complexation and co-removal.
- Seven short-chain PFAS underwent <30 % removal under all tested conditions.
- Three BDEs and three long-chain PFAS were removed by at least 50 % depending on DOM.

GRAPHICAL ABSTRACT
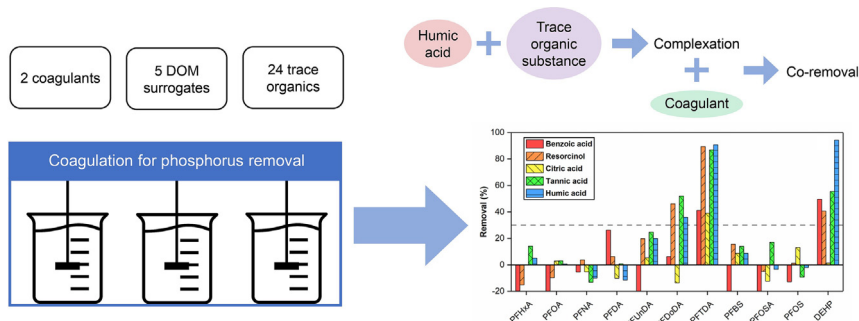
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ABSTRACT

Coagulant dosing to achieve low phosphorus concentrations in wastewater effluents may favour the removal of trace organics such as pharmaceuticals, plasticisers and flame retardants. Nevertheless, the behaviour of trace organics in coagulation processes is currently poorly understood because of the complex interactions between these compounds, the coagulants and dissolved organic matter (DOM). This study assessed the coagulation removal from synthetic secondary effluent of twenty-four compounds including ten PFAS and four brominated flame retardants. Testing involved two coagulants (alum, ferric chloride) and five DOM surrogates (resorcinol, benzoic acid, citric acid, tannic acid, humic acid); DOM surrogates had assorted molecular weights, structures, charges, and hydrophobicity. With coagulant doses of 14 mg Fe/L and 4 mg Al/L, ten trace organics were removed by >30 % in the presence of at least one DOM surrogate. Humic acid effected the highest removals owing to complexation of trace organics and subsequent co-removal by adsorption or sweep floc. For instance, removal extents for three brominated diphenyl ethers were 60 to 75 % with Al and 50 to 88 % with Fe (initial concentration 0.4 to 0.8 ng/L); PFTDA, a long-chain PFAS, was removed by 87 and 91 % with Fe in the presence of tannic or humic acid, respectively (initial concentration 0.03 μg/L). The varying coagulation performance of different treatment works in terms of trace substance removal can be explained because of the site-specific DOM characteristics. Addition of humic acids as complexing agents has the potential to improve the removal of hydrophobic trace substances, including some long-chain PFAS and brominated flame retardants.

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1. Introduction

The discharge of phosphorus-containing effluent from wastewater treatment plants into the environment is a major cause of eutrophication in surface waters (Preisner et al., 2020). Hence, the introduction of tightened regulations on wastewater phosphorus release has translated into enhanced chemical dosing for phosphorus removal, either during secondary treatment or in dedicated tertiary treatment processes (Alibardi et al., 2021). To illustrate, typical molar ratios of 4–5:1 (coagulant:phosphorus) are required to achieve levels below 0.5 mg P/L with alum, while extremely high doses are required to achieve sub 0.1 mg P/L concentrations (Bratby, 2016). Increasing the dose of standard coagulants (e.g. ferric chloride, alum) has two general impacts: (1) the dissociation of the coagulant consumes alkalinity (1 mg/L alum consumes 0.51 mg/L of $CaCO_3$, 0.93 mg/L for ferric) which can cause the pH of the water to become increasingly acidic, and (2) precipitate is formed (1 mg/L alum forms 0.35 mg/L solids; 0.66 mg/L for ferric) providing additional area for adsorption. The added coagulant interacts with the available phosphorus as well as other components within the water.

Such behaviour raises questions on whether dosing for very low phosphorous discharges might impact on other quality determinants. Importantly, these include trace concentrations of diverse organic contaminants (e.g., pharmaceutically active compounds, biocides, plasticisers and flame retardants) present in tertiary wastewater (Comber et al., 2018; Proctor et al., 2021). Deploying additional treatment steps is often necessary to reduce the hazards posed by these substances, which include mixture toxicity and endocrine-disrupting action, to aquatic ecosystems and human health (Bhandari et al., 2015; Eggen et al., 2014). This is especially important for *per*- and poly-fluoroalkyl substances (PFAS) and brominated flame retardants such as brominated diphenyl ethers (BDEs) that have a high bioaccumulation and biomagnification potential (Choo et al., 2019; Cousins et al., 2020). Nevertheless, advanced treatment specifically designed for the elimination of trace contaminants is usually costly and energy intensive (Rahman et al., 2018).

Previous work has indicated the possibility of coagulant dosing providing a co-benefit in this regard. For instance, a recent study of wastewater treatment plants in the United Kingdom showed that the concentrations of certain trace chemicals were lower in the effluent of plants dosing iron for phosphorus removal when compared to effluents of plants without phosphorus control (Comber et al., 2021). The position remains equivocal as numerous studies reported low or no removal of trace organics in coagulation applied for primary wastewater treatment (Kooijman et al., 2020), tertiary wastewater treatment (Müller et al., 2019; Sheng et al., 2016) or drinking water treatment (Stackelberg et al., 2007; Wray and Andrews, 2014). Moreover, high removals have been observed under certain conditions, e.g., in the presence of natural organic matter such as humic acids (Ballard and MacKay, 2005; Vieno et al., 2006).

In coagulation, depending on the organic matter characteristics and the background water chemistry, colloidal and dissolved organic matter (DOM) incorporates into particulate aggregates by interacting with the metal and the metal hydrolysis species through adsorption, complexation, entrapment, and charge neutralisation, (Jarvis et al., 2004). In this process, pH is particularly important since it controls the dissociation of both coagulants and organics. Acidic conditions where the charge load delivered by the coagulant is maximised (pH 4.5 for ferric and 5.5 for alum) favour charge-based interactions. At near neutral conditions solubility is minimised and hence precipitation is maximised (pH 8.0 for ferric and 6.2 for alum), which leads to adsorption-based mechanisms (Crittenden et al., 2012). The situation is further complicated owing to the presence of organics, both bulk and trace, that can undergo a series of complexation reactions.

For trace organic contaminants, interactions with bulk organic matter as well as with the coagulant are relevant for removal. Sorption of hydrophobic substances on particles or colloids (including precipitated coagulant) has been suggested as the main mechanism of removal of trace organics in coagulation and has been linked to the impact of hydrophobic interactions (Ballard and MacKay, 2005; Kooijman et al., 2020). However, some bulk organics may stabilise trace organic contaminants within the water body and/or inhibit aggregation preventing removal. Accordingly, it is posited that the diverse physicochemical properties of both bulk organic matter and trace organic contaminants generate the equivocal nature of the current evidence base from full scale trials and warrant a more systematic investigation to elucidate the true potential of trace contaminant management through enhanced coagulant dosing. This approach can be achieved with the use of appropriate probe compounds or surrogates of DOM that represent a range of molecular weights and structures that are encountered in environmental samples (Bond et al., 2010; Finkbeiner et al., 2019). When selecting trace organic contaminants, the focus should be on priority substances such as PFAS and brominated flame retardants that are subject to current and future regulations including the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2020).

The aim of this study was to establish an evidence-based framework to understand the relative mechanistic roles of the coagulant and the background organic matter in providing a pathway for trace organic removal during enhanced coagulant doses for phosphorus removal. For this purpose, a series of coagulation experiments was conducted with five model compounds as DOM surrogates showing a range of molecular weight, structure, charge, and hydrophobicity combined with trace organics and a consistent background water chemistry. The target trace substances were selected based on previous results of a UK-wide programme involving extensive sampling of wastewater treatment works, the National Chemical Investigations Programme (CIP), and include ten PFAS, four brominated flame retardants, and ten other organic compounds. Ferric chloride and aluminium sulphate (alum) were used as the most applied coagulants.

2. Materials and methods

2.1. Chemicals and wastewater effluent

Chemicals and analytical consumables were purchased from Merck or Fisher Scientific. Ultrapure water used for stock solutions (resistivity 18.2 MΩ.cm), and deionized (DI) water used for the experiments were produced with an ELGA water purification system. For coagulation experiments, the DI water was balanced to produce a consistent background water quality as a synthetic wastewater effluent based on previous studies (Carra et al., 2016). Only one of five DOM surrogates (resorcinol, benzoic acid, citric acid, tannic acid, humic acid) was added at a time. The humic acid used was of technical grade from Sigma Aldrich. Two different water matrices were used: a) initial experiments were performed with DI water containing $CaSO_4$, $MgSO_4$, KCl, $(NH_4)_2SO_4$, $NaHCO_3$, plus one DOM surrogate (DOC of 2 mg C/L), while b) experiments on trace contaminant removal were performed with the full synthetic effluent recipe (SI, Table S1) including one DOM surrogate (total DOC of 10 mg C/L).

The five DOM surrogates were chosen based on their different physicochemical properties (Table 1). Resorcinol is a relatively small (0.11 kDa) aromatic compound with two hydroxyl groups protonated at neutral pH (charge density of 0.08 meq/mg_{DOC}) and expressing low hydrophobicity ($logK_{ow}$ 0.8). Benzoic acid is a benzene-base single carboxylic acid deprotonated at pH above 4.5 (charge density of 11.9 meq/mg_{DOC}) with a relatively small size (0.12 kDa) and moderate hydrophobicity ($logK_{ow}$ 1.9). Citric acid is a small (0.19 kDa) and hydrophilic ($logK_{ow}$ − 1.6) tricarboxylic acid fully deprotonated at pH above 4.5 with a high charge density of 41.2 meq/mg_{DOC}. Tannic acid is an aromatic compound with high molecular weight (1.7 kDa) including multiple hydroxyl groups and classifying as hydrophobic ($logK_{ow}$ 6.2) with a low charge density of 0.56 meq/mg_{DOC}. Humic acids are naturally occurring macromolecules (1–50 kDa) composed of substituted aromatic and aliphatic groups negatively charged at pH above 4 with a low charge density within the range of 0.005–0.010 meq/mg_{DOC}.

The target trace organic contaminants also have diverse characteristics, with a focus on perfluorinated and polybrominated compounds (Table 1). The synthetic effluent was dosed with small volumes of a stock solution

Table 1
Main properties of model compounds used as DOM surrogates and of target trace organic contaminants.

Compound			MW (Da)	pK$_a$	logK_{ow}	Charge density (meq/mg$_{DOC}$)
DOM model compounds		Citric acid (CA)	192.1	2.8	−1.6	41.23[e]
		Resorcinol (RES)	110.1	9.3, 11.1	0.8	0.08[e]
		Benzoic acid (BA)	122.1	4.2	1.9	11.88[e]
		Tannic acid (TA)	1701.2	4.9, 7.4[b]	6.2	0.56[e]
		Humic acid (HA)	1000–50,000[a]	4.0, 9.0[c]	n/a	0.005–0.010[f]
Trace organic contaminants	Perfluorinated	PFHxA (6 carbons)	314.1	−0.2	3.5	
		PFOA (8 carbons)	414.1	1.3	4.8	
		PFNA (9 carbons)	464.1	−0.2	5.5	
		PFDA (10 carbons)	514.1	0.5[d]	6.3	
		PFUnDA (11 carbons)	564.1	0.5[d]	6.9	
		PFDoDA (12 carbons)	614.1	0.5[d]	7.6	
		PFTDA (14 carbons)	714.1	0.5[d]	9	
		PFBS (4 carbons)	300.1	−3.3	1.8	
		PFOSA (8 carbons)	499.2	7.0[d]	5.8	
		PFOS (8 carbons)	500.1	−3.3[d]	4.5	
	Brominated	BDE-28	406.9	n/a	5.5	
		BDE-47	485.8	n/a	6.2	
		BDE-99	564.7	n/a	6.8	
		HBCD	641.7	n/a	7.1	
	Other	benzotriazole	119.1	8.4	1.4	
		tolyltriazole	133.2	8.7[d]	1.4	
		DEHP	390.6	n/a	7.6	
		diclofenac	296.1	4.2	4.5	
		ciprofloxacin	331.3	6.1, 8	0.3	
		triclosan	289.5	7.9	4.8	
		EE2	296.4	10.2[d]	3.7	
		TBT	290.1	n/a	n/a	
		cypermethrin	416.3	n/a	6.6	
		nonylphenol	220.4	10.2[d]	5.8	

References: PubChem (literature or calculated values), except for [a](Beckett et al., 1987; Kawahigashi et al., 2005), [b](Lin et al., 2009), [c](Choppin and Kullberg, 1978), [d]predicted values obtained from SciFinder, [e](Finkbeiner et al., 2019), [f](Edzwald, 1993), n/a: Not available.

of trace organics, to achieve concentrations reported in literature (results from Phases 1 and 2 of the UK National Chemical Investigations Programme unless those were not available, see Table S2 for details). The trace organics stock solution was prepared in methanol. Methanol constituted 0.001 % *v*/v of the synthetic effluent solutions.

Coagulation experiments were also performed with the final effluent of an activated sludge pilot plant (ASP effluent) that was fed with synthetic wastewater dosed with the same trace organics. The pilot plant ran continuously over one year under different operating conditions (Campo et al., 2023). It was known from previous analysis that most of the trace substances were present in the ASP effluent because they were incompletely removed by the activated sludge treatment. The characteristics of the two types of effluent are shown in Table 2.

2.2. Coagulation jar tests

The coagulants used were anhydrous ferric chloride and aluminium sulphate octadecahydrate (97 % purity). Coagulant stock solutions were prepared by dissolving 40 g/L ferric chloride or 45 g/L aluminium sulphate in ultrapure water. The pH of the synthetic effluent was adjusted to 7 by addition of a small amount of hydrochloric acid solution before coagulant addition. Coagulant was dosed into pH 7 without pH control to represent the common approach to coagulant dosing for phosphorus removal. After

Table 2
Main characteristics of synthetic wastewater effluent and activated sludge final effluent used in coagulation experiments.

Parameter	Synthetic effluent	ASP effluent
Total Chemical Oxygen Demand (COD, mg/L)	n/a	128
Soluble COD (mg/L)	n/a	44
Total Suspended Solids (TSS, mg/L)	n/a	100
Alkalinity (mg CaCO$_3$/L)	57	550
pH	7.8	7.8
Dissolved Organic Carbon (DOC, mg C/L)	9.7	11.2
Soluble Reactive Phosphorus (SRP, mg P/L)	1.1	1.4

coagulant addition, rapid mixing was immediately established at 225 rpm for 2 min, followed by slow mixing at 40 rpm for 15 min. The jars were then left without agitation for at least 30 min before sampling.

Dose-response curves testing different coagulant concentrations were conducted in 1-L glass beakers. A series of six 1-L jars included one control without coagulant addition plus five coagulant doses. The supernatant was sampled from approximately 25 mm below the surface with a syringe, filtered through 0.45 μm and analysed for dissolved organic carbon (DOC), soluble reactive phosphorus (SRP), the DOM surrogates and selected trace organics.

Experiments evaluating the removal of all trace substances at a set coagulant dose (selected based on dose-response results) were conducted in 2-L glass beakers. A series of six 2-L jars included three triplicate control jars plus three triplicate jars with the same coagulant dose. To achieve the high sample volumes required for analysis of all compounds, the supernatant from three triplicate jars was combined by decanting it into a glass vessel, taking care not to transfer the settled flocs (when present). This was analysed for all trace organics. Removal percentages were calculated by comparing the concentration of coagulated samples with the concentration of the control. When concentrations were below the reporting limit (RL) after coagulation, the removal was calculated assuming a concentration equal to RL/2. RLs are shown in Table S2. The analytical and experimental error for the removal of trace organics was assumed to be equal to 30 %.

2.3. Analysis

Four DOM surrogates (citric acid, benzoic acid, resorcinol, tannic acid) were analysed by high pressure liquid chromatography (HPLC) with UV detection with an Agilent 1260 Infinity II system equipped with a Phenomenex Gemini C6-Phenyl column. Further details are provided in the SI, Text S1. Two trace organics (diclofenac, ciprofloxacin) were analysed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) in a Sciex Exion LC equipped with an Acquity UPLC BEH C18 column and coupled to a QTRAP 6500 + MS/MS. Further details are provided in the SI, Text S2.

DOC was measured as non-purgeable organic carbon (NPOC) with a Shimadzu TOC-L analyser. SRP was measured after filtration through 0.45 μm following the phosphomolybdate method (Spectroquant Phosphate Cell Test, Merck). Total suspended solids (TSS) and alkalinity were measured according to standard methods.

Total concentrations of twenty-four trace organics were measured by an ISO17025 accredited external laboratory (RPS, Bedford, UK). The methods used were liquid chromatography-tandem mass spectrometry (LC-MS/MS), gas chromatography–mass spectrometry (GC–MS) and gas chromatography-inductively coupled plasma mass spectrometry (GC-ICPMS).

3. Results and discussion

3.1. Coagulation of DOM surrogates

The probe compounds followed the anticipated response congruent with their physico-chemical properties when coagulated individually and in the absence of phosphate, bulk organics, and trace organics (Fig. 1). The different probe compounds delivered the desired range of impacts. Tannic acid was the DOM surrogate that underwent the highest removal reaching a residual of 0.4 mg/L after a dose of 2 mg Fe/L, while humic acid followed a similar pattern (data not shown). The high removal of these compounds by coagulation is consistent with their high molecular weight and charge (Bond et al., 2010). Citric acid was partly removed, with visible flocs only present at the highest iron dose of 18 mg Fe/L. Citric acid inhibits floc formation by forming multidentate ligand-metal complexes, a process that competes with the hydrolysis of the metal salt (Boyd et al., 2012; Zhang et al., 2021). The small, neutral molecule of resorcinol was not removed by coagulation, in agreement with previous work (Bond et al., 2010). Benzoic acid has a weak negative charge but showed the same behaviour as resorcinol. Previous studies have reported that benzoic acid can adsorb on metal hydroxides to a much smaller extent than other carboxylic acids that have a higher negative charge density, such as phthalic acid (Guan et al., 2006; Zhang et al., 2021).

3.2. Coagulation of synthetic effluent and ASP effluent

The coagulation of the five variations of synthetic wastewater containing all trace organics was studied with different doses of the two coagulants (Fig. 2). The addition of the highest coagulant dose to the pH-
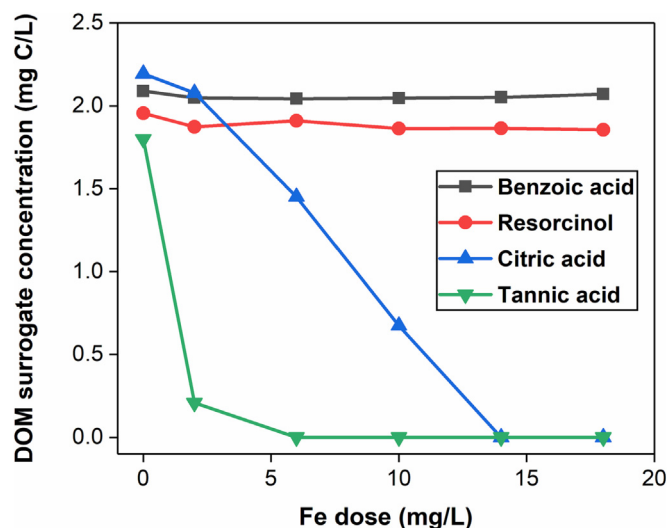

Fig. 1. Dose response curves of the individual DOM surrogates as the sole source of DOC (water matrix: DI water containing $CaSO_4$, $MgSO_4$, KCl, $(NH_4)_2SO_4$, $NaHCO_3$) at initial pH 7 with ferric chloride. The concentrations are shown as DOC concentrations.

adjusted synthetic wastewater (started at pH 7) reduced the pH to 5.3 for ferric chloride and 5.6 for alum (see SI, Fig. S1). These changes in pH shift the pervading mechanism of action from one of precipitation towards charge interaction. In the case of alum, the low doses represent optimum pH for precipitation and the higher doses optimum pH for charge interactions. In contrast, for ferric chloride the pH ranges missed the optimum levels for either pathway (4.5 for charge interactions, 8.0 for precipitation). This manifested in the respective doses required to meet a similar level of removal. To illustrate, in the case of tannic acid, a DOC residual of 5 mg/L was measured at a dose of 10 mg Fe/L and 4 mg Al/L. Overall, at the maximum coagulant dose, there was a residual DOC of 5 to 6 mg C/L when tannic, humic or citric acid were present. This represents the non-sorbable fraction of the synthetic wastewater DOC (Kastl et al., 2004). For benzoic acid and resorcinol, the residual DOC concentration was higher as it also included the remaining DOM surrogate. At coagulant doses up to 14 mg Fe/L and 4 mg Al/L, citric acid inhibited the DOC removal compared to the other four DOM surrogates by preventing floc formation.

The impact of the different probe compounds on SRP removal was more diverse when using ferric chloride compared to alum (Fig. 2). Effective removal of SRP was observed in the presence of resorcinol for both coagulants leading to concentrations near or below the detection limit of 0.05 mg P/L with a coagulant dose of 6 mg Fe/L and 4 mg Al/L. This reflects the lack of interaction between resorcinol and either the SRP or the coagulant, hence having no inhibitory impact. In the case of alum, slight retardation in removal was observed when the water contained benzoic, tannic, or humic acids all of which had a similar impact. In contrast, the different probe compounds resulted in distinct response curves when using ferric chloride, indicating that ferric exhibited a greater sensitivity to competing reactions impacting the SRP removal pathway as well as competition for adsorption sites (Chen et al., 2018). The greatest impact was observed with respect to citric acid which either added a lag to the dose required (alum) or partially inhibited the pathway for all but very high doses (ferric chloride), consistent with the high charge density of the compound exerting demand on the coagulant.

In addition, two trace organics (diclofenac and ciprofloxacin) were analysed for the ferric chloride experiments to explore the impact on the probe compounds. Due to very low concentrations near the limit of detection, the results can be viewed qualitatively (Fig. S2). Despite some scattering of the data, it appears that diclofenac was not removed with any coagulant dose/DOM surrogate combination. There is mixed information in the literature regarding the fate of diclofenac in coagulation (Alexander et al., 2012). High removal has been reported for ferric sulphate at pH 4.5 (Vieno et al., 2006), which is near diclofenac's pK_a of 4.2 and the optimum pH for maximising charge reactions with ferric (Sharp et al., 2006). Ciprofloxacin was removed with Fe doses ≥ 6 mg/L in the presence of resorcinol and benzoic acid, with Fe doses ≥ 10 mg/L for humic acid and tannic acid, and with Fe doses ≥ 18 mg/L for citric acid. Ciprofloxacin has a low K_{ow} so is not expected to be removed by physical adsorption. Instead, its observed removal is caused by the formation of a bidentate complex with an iron atom (Gu and Karthikeyan, 2005). This was inhibited in the presence of citric acid, which was present at a much higher concentration than ciprofloxacin.

To consolidate the trends observed with synthetic effluent through comparison with a more complex matrix, ferric chloride coagulation was also performed with the effluent of an activated sludge pilot plant (ASP effluent). At the time of the experiment, the ASP effluent contained high residual TSS, COD and alkalinity (Table 2). The synthetic wastewater did not contain any particulate organic matter, therefore higher iron concentrations were used for dose-response experiments with ASP effluent (Fig. S3). The pH underwent a small decrease with increasing Fe doses due to the high alkalinity. The residual DOC at Fe dose ≥ 30 mg/L was 6 mg C/L, with SRP < 0.05 mg P/L. In agreement with synthetic effluent data, there was no removal of diclofenac, but partial removal of ciprofloxacin, increasing with the coagulant dose.
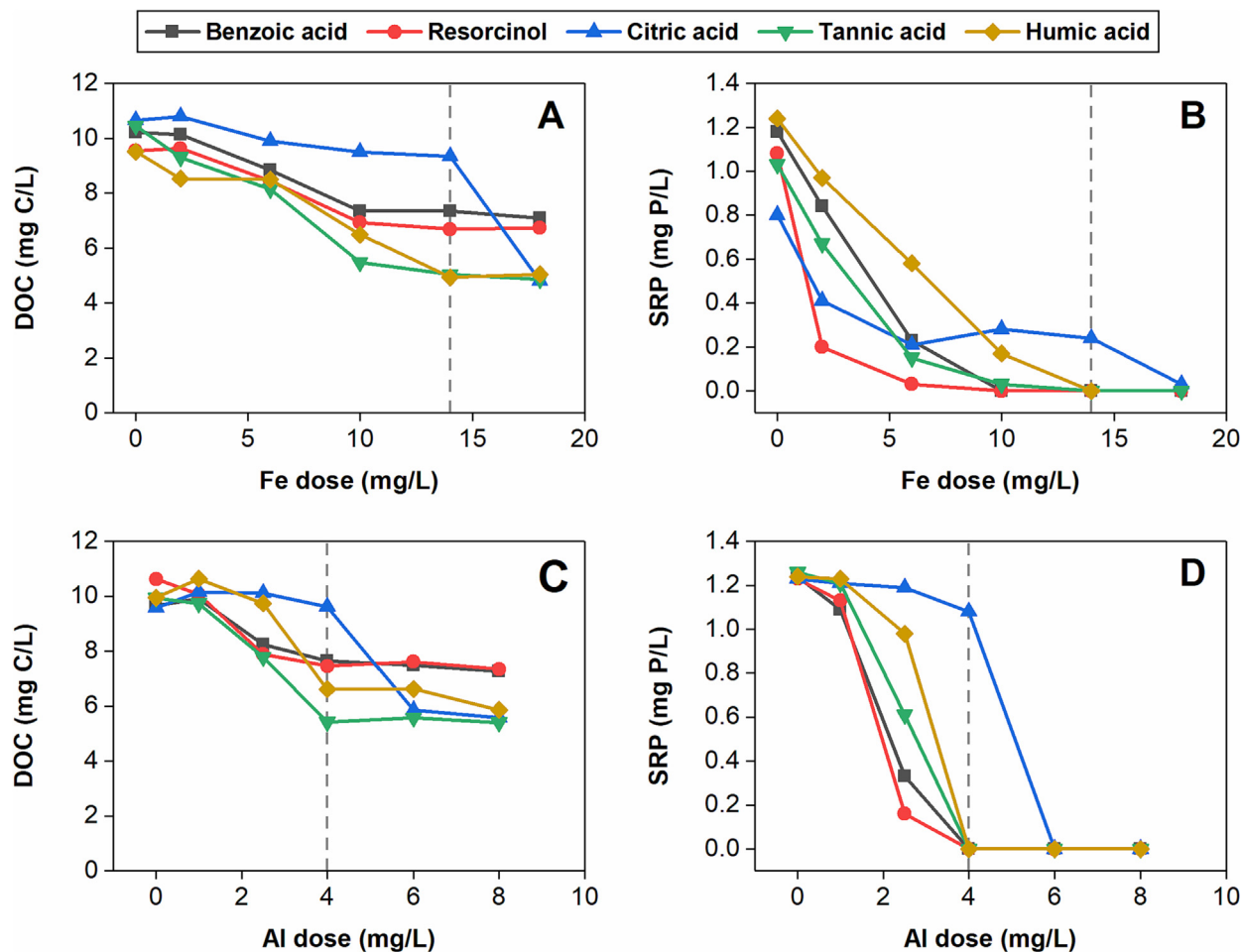
Fig. 2. Dissolved organic carbon and soluble reactive phosphorus in dose response experiments with five variations of synthetic effluent (initial pH 7) using ferric chloride (A and B) and aluminium sulphate (C and D). The dashed lines indicate 14 mg Fe/L and 4 mg Al/L.

3.3. Fate of trace organics in coagulation with different DOM types

The removal of all trace substances was measured at doses of 14 mg Fe/L and 4 mg Al/L for the synthetic effluent and 25 mg Fe/L for the ASP effluent based on minimisation of the SRP to sub 0.1 mg/L concentrations (see vertical dashed lines in Fig. 3; bulk parameters shown in Table S3). The trace organics were analysed in the supernatant of the jars, which was decanted and not filtered before analysis, so that settled flocs were excluded

from the samples while avoiding losses due to filtration (Figs. 3,4 and SI Table S4). Fourteen compounds, including two triazoles and seven short-chain PFAS, underwent <30 % removal with all DOM surrogates (Table S4). These removals are within the analytical and experimental error associated with trace concentrations, so these compounds can be considered not to be influenced by coagulation pathways. Note that negative removals were also observed although mostly within the 30 % threshold. Ten compounds had at least one removal percentage above 30 %. For three of them (DEHP,
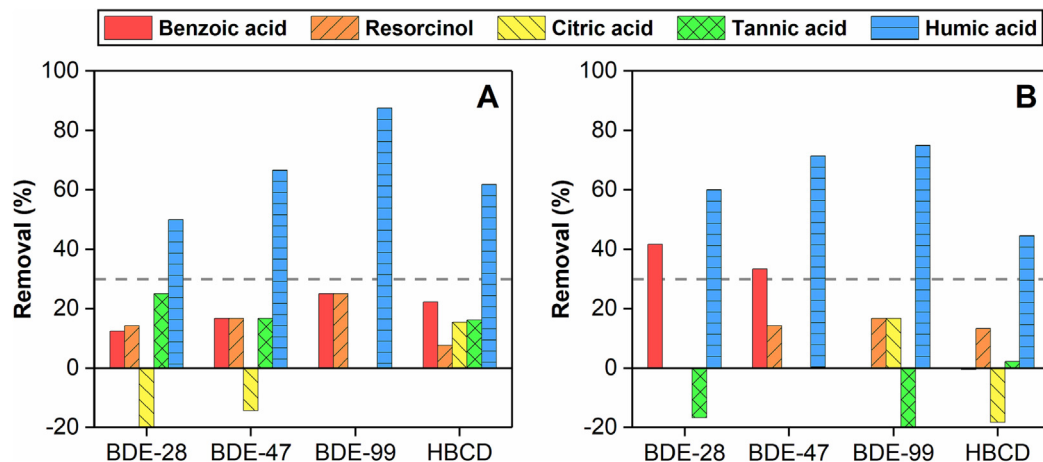

Fig. 3. Removal of brominated flame retardants in coagulation of five variations of synthetic effluent using A. ferric chloride (14 mg Fe/L) and B. aluminium sulphate (4 mg Al/L). The dashed line indicates 30 % removal.
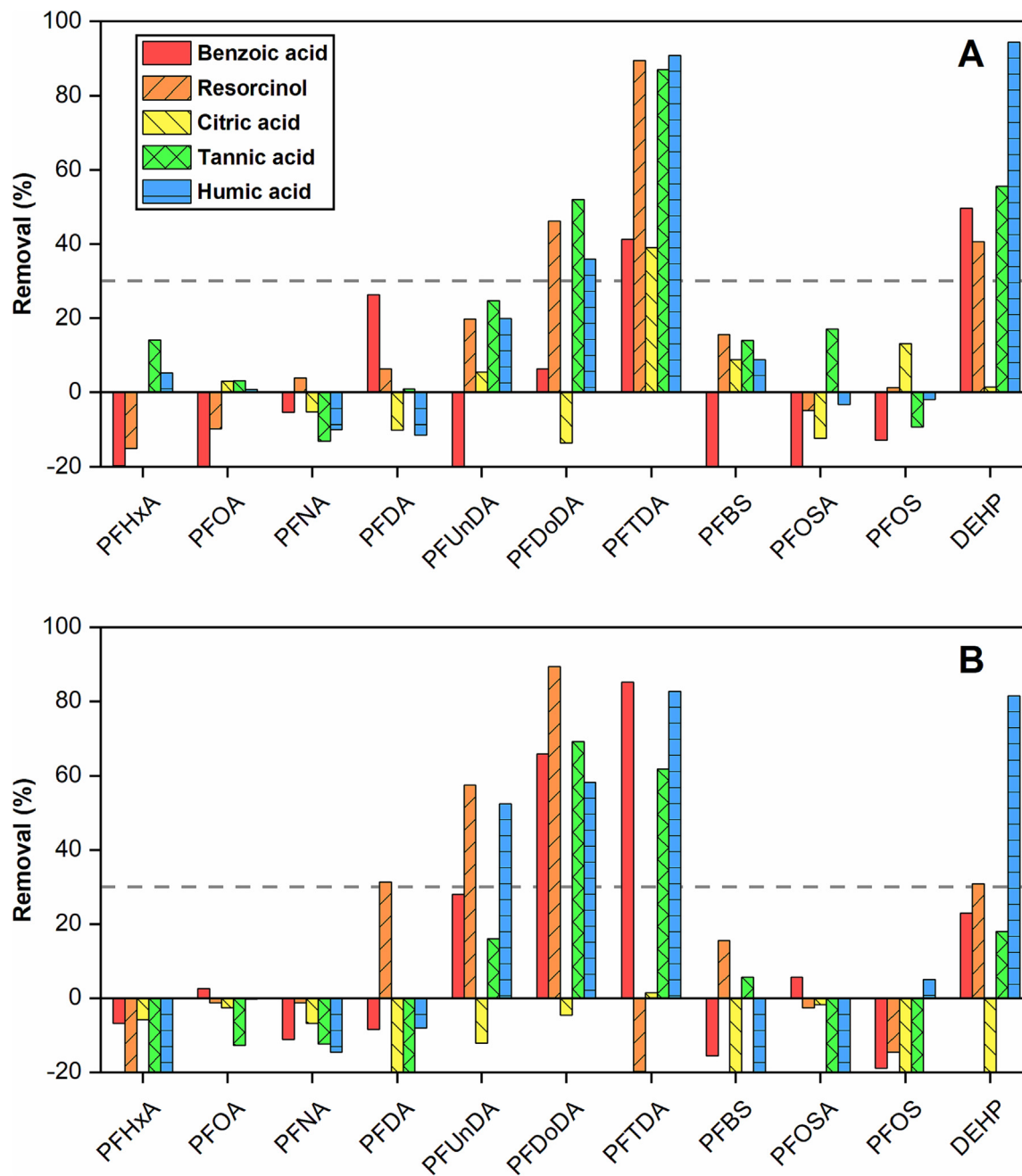
Fig. 4. Removal of PFAS and DEHP in coagulation of five variations of synthetic effluent using A. ferric chloride (14 mg Fe/L) and B. aluminium sulphate (4 mg Al/L). The dashed line indicates 30 % removal.

HBCD and cypermethrin) decreased effluent concentrations in UK wastewater treatment plants employing iron dosing have been previously reported (Comber et al., 2021).

The coagulation removal of trace organics depended strongly on DOM nature. Presence of humic acid led to the highest removals and of citric acid to the lowest removals. The positive impact of humic acid is due to complexation of trace organics and co-removal as humic acid adsorbs onto precipitates or is enmeshed in sweep floc (Rebhun et al., 1998; Zheng et al., 2009). This mechanism was particularly relevant for the four brominated flame retardants which are neutral, moderately hydrophobic molecules. BDEs were only removed in the presence of humic acid owing to its inherent hydrophobicity and size (Fig. 3). This supports the previous observation that the removal pathway of BDEs in primary wastewater sedimentation with alum addition was due to complexation with colloidal organic matter (Song et al., 2006).

DEHP and three long-chain PFAS (PFUnDA, PFDoDA, PFTDA) were partly removed in experiments with alum; DEHP, PFDoDA and PFTDA were also partly removed in experiments with ferric chloride, depending on the presence of different DOM probe compounds (Fig. 4). Alum removals with humic acid were 53, 58 and 83 % for PFUnDA, PFDoDA, and PFTDA, respectively. Ferric removals with humic acid were 36 and 91 % for PFDoDA and PFTDA, while similar removals were observed in the presence of tannic acid and resorcinol. In comparison, there was less consistency in the case of alum, with benzoic acid and tannic acid assisting removal for PFDoDA and PFTDA, and resorcinol assisting removal for PFUnDA and PFDoDA.

DEHP is neutral while PFAS compounds are negatively charged; both are hydrophobic with the hydrophobicity of PFAS compounds increasing with the length of the carbon chain (Ahrens et al., 2010). Since the shorter PFAS compounds were not removed (Fig. 4), it is posited that

hydrophobicity and molecular size of both the trace compounds and the background organics are the defining characteristics for the efficacy of removal through a coagulation pathway. The result is three possible pathways: a) direct electrostatic binding between the negatively charged PFAS species and the positively charged metal hydrolysis species (Bao et al., 2014), b) adsorption on the precipitated metal coagulant through a hydrophobic interaction with the higher efficacy associated with aluminium coagulants ascribed to the more hydrophobic nature of the resultant precipitates compared to ferric (Lin et al., 2015), c) binding of PFAS compounds to the background organics which can then react with the coagulant through a combination of charge, complexation-based precipitation and adsorption mechanisms to enable removal. Both pathway (a) and (b) require the background organics to not outcompete or inhibit the interaction but were not observed for any of the short-chain PFAS as evidenced by their lack of removal. Pathway (c) was illustrated for long-chain PFAS by tannic and humic acid and offers the future potential to condition wastewater to aid removal of such compounds by adding an appropriate agent such as humic acid.

The removal of trace organics in ASP effluent is shown in Fig. S4. Despite differences in the characteristics of the aqueous matrix and the applied coagulant dose, the results confirm the conclusions drawn from synthetic effluent data. PFTDA, the three BDEs, DEHP, ciprofloxacin and cypermethrin were partly removed. Two additional compounds (triclosan and TBT) showed moderate removals, but their concentrations were very close to the RL even before coagulation. Low BDEs removals (26 to 37 %) suggest that the ASP effluent contained little DOM of humic-like nature. The removal of the other substances was due to hydrophobic interactions with both suspended solids and DOM.

4. Conclusions

The ability to remove recalcitrant trace organics as a co-benefit associated with coagulant dosing for low phosphorus discharges was investigated. Positive evidence of a removal pathway was demonstrated for four brominated flame retardants (BDE-28, BDE-47, BDE-99, HBCD), DEHP and three long chain PFAS compounds (PFUnDA, PFDoDA, PFTDA). The posited mechanism is associated with the background organics present within the water matrix that combine with the trace organics through a hydrophobic interaction pathway. The combined species are then able to interact with the added coagulant through a combination of adsorption and/or a precipitation mechanism to be removed. This provides an explanation to the equivocal data currently reported on removal; treatment sites deficit in background organics such as humic acids will have poorer removal than those with sufficient humic-like organics. Further, this offers a potential enhancement route for coagulation processes through dosing of such compounds to ensure that the pathway exists.

CRediT authorship contribution statement

Garyfalia A. Zoumpouli: Investigation, methodology, validation, formal analysis, visualization, writing - Original Draft.
Dean Herron Writing: Project administration, writing - Review & Editing.
Arthur Thornton: Conceptualization, funding acquisition.
Bruce Jefferson: Conceptualization, methodology, validation, writing - Review & Editing, funding acquisition.
Pablo Campo: Conceptualization, methodology, validation, writing - Review & Editing, project administration, funding acquisition.

Data availability

No data was used for the research described in the article.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Pablo

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.163982.

References

Ahrens, L., Taniyasu, S., Yeung, L.W.Y., Yamashita, N., Lam, P.K.S., Ebinghaus, R., 2010. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. Chemosphere 79, 266–272. https://doi.org/10.1016/j.chemosphere.2010.01.045.

Alexander, J.T., Hai, F.I., Al-aboud, T.M., 2012. Chemical coagulation-based processes for trace organic contaminant removal: current state and future potential. J. Environ. Manag. https://doi.org/10.1016/j.jenvman.2012.07.023.

Alibardi, L., Vale, P., Bajón Fernández, Y., 2021. Full-scale trials to achieve low total phosphorus in effluents from sewage treatment works. J. Water Process Eng. 40. https://doi.org/10.1016/j.jwpe.2021.101981.

Ballard, B.D., MacKay, A.A., 2005. Estimating the removal of anthropogenic organic chemicals from raw drinking water by coagulation flocculation. J. Environ. Eng. 131, 108–118. https://doi.org/10.1061/(asce)0733-9372(2005)131:1(108).

Bao, Y., Niu, J., Xu, Z., Gao, D., Shi, J., Sun, X., Huang, Q., 2014. Removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from water by coagulation: mechanisms and influencing factors. J. Colloid Interface Sci. 434, 59–64. https://doi.org/10.1016/j.jcis.2014.07.041.

Beckett, R., Jue, Z., Giddings, J.C., 1987. Determination of molecular weight distributions of fulvic and humic acids using flow field-flow fractionation. Environ. Sci. Technol. 21, 289–295. https://doi.org/10.1021/es00157a010.

Bhandari, R.K., Deem, S.L., Holliday, D.K., Jandegian, C.M., Kassotis, C.D., Nagel, S.C., Tillitt, D.E., vom Saal, F.S., Rosenfeld, C.S., 2015. Effects of the environmental estrogenic contaminants bisphenol a and 17α-ethinyl estradiol on sexual development and adult behaviors in aquatic wildlife species. Gen. Comp. Endocrinol. 214, 195–219. https://doi.org/10.1016/j.ygcen.2014.09.014.

Bond, T., Goslan, E.H., Parsons, S.A., Jefferson, B., 2010. Disinfection by-product formation of natural organic matter surrogates and treatment by coagulation, MIEX® and nanofiltration. Water Res. 44, 1645–1653. https://doi.org/10.1016/j.watres.2009.11.018.

Boyd, C.C., Duranceau, S.J., Tharamapalan, J., 2012. Impact of carboxylic acid ultrafiltration recycle streams on coagulation. J. Water Supply: Res. Technol. - AQUA 61, 306–318. https://doi.org/10.2166/aqua.2012.005.

Bratby, J., 2016. Coagulation and Flocculation in Water and Wastewater Treatment. third ed. IWA Publishing, London https://doi.org/10.2166/9781780407500.

Campo, P., Dai, Z., Herron, D., Jefferson, B., Thornton, A., Zoumpouli, G., 2023. The National Chemical Investigations Programme 2020–2022 Volume 8 Mechanisms of Chemical Removal (22/EQ/01/29).

Carra, I., Sánchez Pérez, J.A., Malato, S., Autin, O., Jefferson, B., Jarvis, P., 2016. Performance of different advanced oxidation processes for tertiary wastewater treatment to remove the pesticide acetamiprid. J. Chem. Technol. Biotechnol. 91, 72–81. https://doi.org/10.1002/jctb.4577.

Chen, K.Y., Hsu, L.C., Chan, Y.T., Cho, Y.L., Tsao, F.Y., Tzou, Y.M., Hsieh, Y.C., Liu, Y.T., 2018. Phosphate removal in relation to structural development of humic acid-iron coprecipitates. Sci. Rep. 8. https://doi.org/10.1038/s41598-018-28568-7.

Choo, G., Lee, I.-S., Oh, J.-E., 2019. Species and habitat-dependent accumulation and biomagnification of brominated flame retardants and PBDE metabolites. J. Hazard. Mater. 371, 175–182. https://doi.org/10.1016/j.jhazmat.2019.02.106.

Choppin, G.R., Kullberg, L., 1978. Protonation thermodynamics of humic acid. J. Inorg. Nucl. Chem. 40, 651–654. https://doi.org/10.1016/0022-1902(78)80381-9.

Comber, S., Gardner, M., Sörme, P., Leverett, D., Ellor, B., 2018. Active pharmaceutical ingredients entering the aquatic environment from wastewater treatment works: a cause for concern? Sci. Total Environ. 613–614, 538–547. https://doi.org/10.1016/j.scitotenv.2017.09.101.

Comber, S.D.W., Gardner, M.J., Ellor, B., 2021. Effects of iron dosing used for phosphorus removal at wastewater treatment works; impacts on forms of phosphorus discharged and secondary effects on concentrations and fate of other contaminants. Sci. Total Environ. 767, 145434. https://doi.org/10.1016/j.scitotenv.2021.145434.

Cousins, I.T., DeWitt, J.C., Glüge, J., Goldenman, G., Herzke, D., Lohmann, R., Miller, M., Ng, C.A., Scheringer, M., Vierke, L., Wang, Z., 2020. Strategies for grouping per- and polyfluoroalkyl substances (PFAS) to protect human and environmental health. Environ Sci Process Impacts 22, 1444–1460. https://doi.org/10.1039/D0EM00147C.

Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J., Tchobanoglous, G., 2012. Coagulation and flocculation. In: Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J., Tchobanoglous, G. (Eds.), MWH's Water Treatment: Principles and Design, Third edition https://doi.org/10.1002/9781118131473.ch9.

Edzwald, J.K., 1993. Coagulation in drinking water treatment: particles, organics and coagulants. Water Sci. Technol. 27, 21–35. https://doi.org/10.2166/wst.1993.0261.

Eggen, R.I.L., Hollender, J., Joss, A., Schärer, M., Stamm, C., 2014. Reducing the discharge of micropollutants in the aquatic environment: the benefits of upgrading wastewater treatment plants. Environ. Sci. Technol. 48, 7683–7689. https://doi.org/10.1021/es500907n.

Finkbeiner, P., Moore, G., Tseka, T., Nkambule, T.T.I., Kock, L. de, Jefferson, B., Jarvis, P., 2019. Interactions between organic model compounds and ion exchange resins. Environ. Sci. Technol. 53, 9734–9743. https://doi.org/10.1021/acs.est.9b02139.

Gu, C., Karthikeyan, K.G., 2005. Sorption of the antimicrobial ciprofloxacin to aluminum and iron hydrous oxides. Environ. Sci. Technol. 39, 9166–9173. https://doi.org/10.1021/es051109f.

Guan, X.H., Chen, G.H., Shang, C., 2006. Combining kinetic investigation with surface spectroscopic examination to study the role of aromatic carboxyl groups in NOM adsorption by aluminum hydroxide. J. Colloid Interface Sci. 301, 419–427. https://doi.org/10.1016/j.jcis.2006.05.031.

Jarvis, P., Jefferson, B., Parsons, S.A., 2004. Characterising natural organic matter flocs. Water Supply 4, 79–87. https://doi.org/10.2166/ws.2004.0064.

Kastl, G., Sathasivan, A., Fisher, I., van Leeuwen, J., 2004. Modeling DOC removal by enhanced coagulation. J. Am. Water Works Assoc. https://doi.org/10.1002/j.1551-8833.2004.tb10557.x.

Kawahigashi, M., Sumida, H., Yamamoto, K., 2005. Size and shape of soil humic acids estimated by viscosity and molecular weight. J. Colloid Interface Sci. 284, 463–469. https://doi.org/10.1016/j.jcis.2004.10.023.

Kooijman, G., de Kreuk, M.K., Houtman, C., van Lier, J.B., 2020. Perspectives of coagulation/flocculation for the removal of pharmaceuticals from domestic wastewater: a critical view at experimental procedures. J. Water Process Eng. 34. https://doi.org/10.1016/j.jwpe.2020.101161.

Lin, D., Liu, N., Yang, K., Zhu, L., Xu, Y., Xing, B., 2009. The effect of ionic strength and pH on the stability of tannic acid-facilitated carbon nanotube suspensions. Carbon N Y 47, 2875–2882. https://doi.org/10.1016/j.carbon.2009.06.036.

Lin, H., Wang, Y., Niu, J., Yue, Z., Huang, Q., 2015. Efficient sorption and removal of perfluoroalkyl acids (PFAAs) from aqueous solution by metal hydroxides generated in situ by electrocoagulation. Environ. Sci. Technol. 49, 10562–10569. https://doi.org/10.1021/acs.est.5b02092.

Müller, J., Levai, S., Titzschkau, L., Popović, N., Carevic, D., Drewes, J.E., Hübner, U., 2019. Role of reduced empty bed contact times and pre-treatment by coagulation with Fe(III) salts on the removal of trace organic compounds during sequential biofiltration. Sci. Total Environ. 685, 220–228. https://doi.org/10.1016/j.scitotenv.2019.05.361.

Preisner, M., Neverova-Dziopak, E., Kowalewski, Z., 2020. Analysis of eutrophication potential of municipal wastewater. Water Sci. Technol. 81, 1994–2003. https://doi.org/10.2166/wst.2020.254.

Proctor, K., Petrie, B., Lopardo, L., Muñoz, D.C., Rice, J., Barden, R., Arnot, T., Kasprzyk-Hordern, B., 2021. Micropollutant fluxes in urban environment – a catchment perspective. J. Hazard. Mater. 401, 123745. https://doi.org/10.1016/j.jhazmat.2020.123745.

Rahman, S.M., Eckelman, M.J., Onnis-Hayden, A., Gu, A.Z., 2018. Comparative life cycle assessment of advanced wastewater treatment processes for removal of chemicals of emerging concern. Environ. Sci. Technol. 52, 11346–11358. https://doi.org/10.1021/acs.est.8b00036.

Rebhun, M., Meir, S., Laor, Y., 1998. Using dissolved humic acid to remove hydrophobic contaminants from water by complexation−flocculation process. Environ. Sci. Technol. 32, 981–986. https://doi.org/10.1021/es9707163.

Sharp, E.L., Parsons, S.A., Jefferson, B., 2006. Seasonal variations in natural organic matter and its impact on coagulation in water treatment. Sci. Total Environ. 363, 183–194. https://doi.org/10.1016/j.scitotenv.2005.05.032.

Sheng, C., Nnanna, A.G.A., Liu, Y., Vargo, J.D., 2016. Removal of trace pharmaceuticals from water using coagulation and powdered activated carbon as pretreatment to ultrafiltration membrane system. Sci. Total Environ. 550, 1075–1083. https://doi.org/10.1016/j.scitotenv.2016.01.179.

Song, M., Chu, S., Letcher, R.J., Seth, R., 2006. Fate, partitioning, and mass loading of polybrominated diphenyl ethers (PBDEs) during the treatment processing of municipal sewage. Environ. Sci. Technol. 40, 6241–6246. https://doi.org/10.1021/es060570k.

Stackelberg, P.E., Gibs, J., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Lippincott, R.L., 2007. Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. Sci. Total Environ. 377, 255–272. https://doi.org/10.1016/J.SCITOTENV.2007.01.095.

UNEP, 2020. Stockholm Convention on Persistent Organic Pollutants. Text and Annexes (revised in 2019). [WWW Document]. URL http://www.pops.int/TheConvention/Overview/TextoftheConvention/tabid/2232/Default.aspx accessed 4.11.22.

Vieno, N., Tuhkanen, T., Kronberg, L., 2006. Removal of pharmaceuticals in drinking water treatment: effect of chemical coagulation. Environ. Technol. 27, 183–192. https://doi.org/10.1080/09593332708618632.

Wray, H.E., Andrews, R.C., 2014. Optimization of coagulant dose for biopolymer removal: impact on ultrafiltration fouling and retention of organic micropollutants. J. Water Process Eng. 1, 74–83. https://doi.org/10.1016/j.jwpe.2014.03.007.

Zhang, X., Graham, N., Xu, L., Yu, W., Gregory, J., 2021. The influence of small organic molecules on coagulation from the perspective of hydrolysis competition and crystallization. Environ. Sci. Technol. 55, 7456–7465. https://doi.org/10.1021/acs.est.1c00869.

Zheng, Z., Zhang, H., He, P.J., Shao, L.M., Chen, Y., Pang, L., 2009. Co-removal of phthalic acid esters with dissolved organic matter from landfill leachate by coagulation and flocculation process. Chemosphere 75, 180–186. https://doi.org/10.1016/j.chemosphere.2008.12.011.