



Removal of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) by coagulation: Influence of coagulant and dosing conditions

Pin Wang^{a,b}, Guangyu An^c, Irene Carra^a, Francis Hassard^a, Pablo Campo Moreno^a, Hacer Sakar^a, Monika Jodkowska^a, Dongsheng Wang^d, Bruce Jefferson^a, Wenhai Chu^b, Peter Jarvis^{a,*}

^a Cranfield University, College Road, Cranfield, Bedfordshire MK43 0AL, United Kingdom

^b State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China

^c State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

^d Department of Environmental Engineering, Zhejiang University, Hangzhou 310058, Zhejiang, China

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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) pose significant risks to the environment and human health. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are two of the most frequently detected PFAS in the environment. In most surface water drinking water treatment works (WTW), coagulation is the first processes exposed to a range of contaminants, including PFAS. While not designed to be a process for removal of micropollutants, it is important to understand the fate of PFAS in coagulation processes, intended or otherwise, to determine whether water treatment sludge can be a significant sink for this group of micropollutants. This work advances understanding of PFAS removal in coagulation processes by comparing the removal of PFOA and PFOS by four metal coagulants (Zr, Zn, Fe, and Al) from real water matrices. The coagulant performance followed the order Al > Fe > Zr > Zn. Al was taken forward for further evaluation, with significant removal of PFAS (>15 % for PFOA and > 30 % for PFOS) being observed when the pH<5.5 and the dose was > 5 mg Al·L⁻¹. The adsorption of PFOA and PFOS onto flocs through hydrophobic interaction was the primary removal route. The impacts of background matrix on the mechanisms of coagulation for PFAS were explored using five organic compounds. Macromolecular organic compounds contributed to an increase in removal due to the sorption of PFAS and subsequent removal of the organic-PFAS aggregate during coagulation. Low molecular weight organic matter inhibited the removal of PFAS due to the ineffective removal of these compounds during coagulation.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) have been commonly used in many commercial and industrial products over the past five decades, including in cookware, food packaging, firefighting foam, and waterproof fabrics [1–4]. Historically, Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) have been the most widely studied PFAS chemicals and they are still found in the environment as two of the most frequently detected compounds in source waters [5,6]. They are characterized as persistent organic pollutants in the environments due to their high chemical and thermal stability, poor biodegradability, potential for bioaccumulation and their ability to persist and mobilise in the environment [7]. The identification of PFAS in finished drinking water at a few ng·L⁻¹ has been reported across the globe [8,9].

The consumption of PFAS-contaminated water is recognized as one of the main exposure pathways for humans to PFAS [10], which has been associated with numerous health endpoints, for example, decreased immunity, thyroid function disease and cancer [11–14]. Advanced water treatment technologies for removal of PFAS, such as granular activated carbon, ion exchange treatment, dense membrane processes, and advanced oxidation/reduction process have high potential for removal of PFAS from water [15–20]. However, in many locations, these processes are not feasible due to their high operational and capital costs. In these cases, understanding how existing conventional treatment processes can be enhanced for PFAS removal is required.

Coagulation is among the most commonly applied processes for water treatment due to its effectiveness in removing colloids, particles and dissolved organic matter, and its lower cost [21–24]. Multivalent

* Corresponding author.

E-mail address: p.jarvis@cranfield.ac.uk (P. Jarvis).

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metal salts such as $\text{Al}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3$, and ZrOCl_2 have been used as coagulants [24–26]. The removal of organic matter using these metal salts largely depended on coagulation parameters, including the dose used and pH conditions [27,28]. Highly charged coagulants such as those based around zirconium (Zr^{4+}) have been shown to be highly effective for bulk removal of natural organic matter and turbidity, but less evidence is available on the removal of micropollutants [26].

While coagulation is not designed to be a process for significant removal of micropollutants, the concomitant removal of trace organic compounds has been reported previously in this process [29–31]. It is therefore important to understand the fate of micropollutants such as PFAS across the coagulation processes through unintended removal to determine whether such compounds may be found in WTWs sludge. Adsorption onto precipitated coagulant complexes is the main route by which organic micropollutants are removed in coagulation-flocculation processes [31]. However, many micropollutants are hydrophilic and hence have poor affinity for adsorbing onto hydrophobic floc aggregates. This is consistent with previous studies, where coagulation provided limited removal of chloro-triazine herbicides and a wide variety of pesticides when using alum or iron salts as coagulants [29,30]. Perfluoroalkyl acids consist of a hydrophobic perfluorinated carbon chain and a charged hydrophilic head group such as $-\text{COOH}$ and $-\text{SO}_3\text{H}$ [32]. As such, consideration of the charge of the coagulant and hydrophobicity of the precipitate formed was hypothesized to play a more important role in controlling PFAS removal than is seen for other micropollutants. This study therefore used a range of coagulants of varying charge and hydrophobicity (Zn^{2+} , Al^{3+} , Fe^{3+} and Zr^{4+}) to explore their impact on PFAS removal. There have only been a few reported studies on the efficacy of coagulation for removal of PFAS. In these studies, aluminum and ferric based coagulants were mostly used [33–35]. Inefficient removal of PFAS was reported in these studies. For example, less than 35 % PFAS was removed across a wide coagulant dose range ($\text{Al}_2(\text{SO}_4)_3$ 3–110 $\text{mg}\cdot\text{L}^{-1}$) [35]. Efficient removal of PFAS have been proposed using electrocoagulation with zinc anodes based on the premise that a more hydrophobic zinc oxide surface is available for PFAS adsorption [36,37]. Specially designed polymers have also been developed to target PFAS removal [38]. However, these studies have generally used high PFAS concentrations in the $\mu\text{g}\cdot\text{L}^{-1}$ and $\text{mg}\cdot\text{L}^{-1}$ ranges, while the concentrations of PFAS in the environment are routinely observed in the $\text{ng}\cdot\text{L}^{-1}$ range [8]. The removal of trace organic micropollutants by coagulation is different to that seen for the organic micropollutant in the $\text{mg}\cdot\text{L}^{-1}$ range because of the different interfacial concentration gradients between the pollutant in the bulk liquid and the flocs onto which they adsorb [39]. There is also a lack of understanding around the role background organic matter plays in removal of PFAS by coagulation. It has been demonstrated that PFAS will associate with dissolved organic matter (DOM) and increase the solubility of PFAS in liquid phase [40]. DOM may also interfere with the hydrolysis of metal salts through complexation [41–43]. Thus, there is a clear knowledge gap on the conditions which govern the removal of PFAS by coagulation using realistic concentrations of the pollutants, coagulants of different character, and in understanding the influence of background matrices on the partitioning of the pollutants.

The aim of this study was to therefore determine the role played by coagulants of different charge and hydrophobicity (ZrOCl_2 , ZnSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, and $\text{Al}_2(\text{SO}_4)_3$) in the removal of PFOA and PFOS (the two most widely reported PFAS compounds) at environmentally relevant concentrations from surface water. For the best performing coagulant, PFAS removal was assessed based on the coagulant speciation and an understanding of the potential for adsorption onto coagulant precipitates. In addition, the role of the interactions and competition between PFAS and background organic compounds on removal by coagulation mechanisms was explored by mixing PFOA and PFOS with model organic compounds of different physico-chemical characteristics (molecular size and hydrophobicity).

2. Materials and methods

2.1. Chemical and reagents

$\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3\cdot x\text{H}_2\text{O}$, $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$, $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$, sodium hydroxide, hydrogen chloride, HPLC-grade methanol and HPLC-grade ammonium acetate were purchased from Sigma-Aldrich (Merck, UK). PFOA and PFOS were used as model PFAS compounds due to their frequent occurrence in surface water and due to previously identified differences in their potential for removal by adsorption [8]. Pentadecafluorooctanoic acid ammonium salt (PFOA) was from Sigma Aldrich (Merck, UK) and perfluorooctanesulfonic acid potassium salt (PFOS) and mass-labelled internal standards were purchased from Wellington Laboratories (Ontario, Canada). All solutions were prepared with ultra-purified water (resistivity > 18.2 $\text{M}\Omega\cdot\text{cm}$). For real water tests, the surface water used in jar tests was collected from a river near Cranfield University as required (average water quality data for the source is presented in [Supporting Information, Table S1](#)).

2.2. Jar tests

Coagulation experiments were undertaken on a PB-900 jar tester (Phipps and Bird, VA, USA). The mixing process involved a 2 min rapid mix stage at 200 rpm, followed by 15 min flocculation at 30 rpm and a 20 min settlement period. All the coagulant salts were prepared at the concentration of 1 $\text{mol}\cdot\text{L}^{-1}$. The coagulation performance of different coagulants for PFAS removal was investigated under three scenarios, all using river water spiked with PFOA (0.002 $\mu\text{mol}\cdot\text{L}^{-1}$ equivalent to 1076 $\text{ng}\cdot\text{L}^{-1}$) and PFOS (0.0007 $\mu\text{mol}\cdot\text{L}^{-1}$, equivalent to 330 $\text{ng}\cdot\text{L}^{-1}$) as the test water. These concentrations were selected to represent the top end of realistic concentrations found in PFAS contaminated water sources [6]. **Scenario I** was performed under the pH conditions optimized for charge neutralization (pH 4.5 for iron and pH 5.5 for the other coagulants); **scenario II** was carried out without pH adjustment during coagulation; **scenario III** was conducted under the pH conditions optimized for sweep flocculation (pH 7.5 for iron and pH 6.5 for the rest of the coagulants). The dose was set based on the dissolved organic carbon (DOC) concentrations of the river water due to the fluctuation in river water quality in different seasons (see details in [Table S1](#) in [supporting information](#)). The ratios of metal ions [M] to DOC ($\text{mg [M]}/\text{mg [DOC]}$) were between 0.17–5.00, covering a range above and below optimum doses seen previously for the metal coagulants under test [26]. In the case of pH-controlled experiments, NaOH (0.1 $\text{mol}\cdot\text{L}^{-1}$) and HCl (0.1 $\text{mol}\cdot\text{L}^{-1}$) were used to adjust the conditions. NaOH (0.1 $\text{mol}\cdot\text{L}^{-1}$) was dosed after the addition of the coagulant to maintain the pH at the required values during the rapid mixing stage. Suspensions were analyzed for turbidity (Hach 2100 N turbidimeter, Manchester, UK) and zeta potential (Zetasizer 2000, Malvern Instruments, Malvern, UK). Further analysis was carried out after filtration through a 0.2 μm syringe filter (cellulose acetate membrane). Dissolved organic carbon (DOC) was measured by using a total organic carbon analyzer (Shimadzu TOC-VCPH, Kyoto, Japan). Procedural blanks (without coagulant addition) were processed along with every batch of coagulated water in triplicate.

Further tests were carried out using the best performing coagulant chemical, where the impact of alum dose on PFOA and PFOS removal was studied by spiking PFOS (0.002 $\mu\text{mol}\cdot\text{L}^{-1}$ equivalent to 1076 $\text{ng}\cdot\text{L}^{-1}$) and PFOA (0.002 $\mu\text{mol}\cdot\text{L}^{-1}$, equivalent to 862 $\text{ng}\cdot\text{L}^{-1}$) together into the river water. The coagulant dose ranged from 1.25 $\text{mg Al}\cdot\text{L}^{-1}$ to 15 $\text{mg Al}\cdot\text{L}^{-1}$.

The impact of pH on coagulation of PFAS was studied by spiking PFOA and PFOS (0.002 $\mu\text{mol}\cdot\text{L}^{-1}$ of each) together into the river water. The pH was adjusted to the required values (pH 4.5–6.5) and kept constant after coagulant addition by dosing NaOH during the rapid mixing stage.

The impact of initial concentration (C_0) of PFOA and PFOS was studied by spiking various amounts of PFOA and PFOS into the real

water. The jar tests were carried out with $\text{Al}_2(\text{SO}_4)_3$ at a dose of $11.5 \text{ mg Al-L}^{-1}$ at pH 4.5. The C_0 of PFOA and PFOS was in the range of $0.0005\text{--}0.02 \text{ }\mu\text{mol-L}^{-1}$. Additional samples were processed for the collection of the flocs to assess the amount of solid precipitate onto which the PFAS could adsorb. Here, a $0.45 \text{ }\mu\text{m}$ glass macrofibre filter paper was used to collect the flocs after the mixing process. The filter was dried at 45°C in a drying oven for 36 h before and after filtration. The mass difference of the membrane before and after drying was considered as the mass of the flocs formed during the coagulation process. Experiments were carried out in triplicate and an average mass reported.

2.3. Batch adsorption experiments

To determine the effect of water composition on removal of PFAS during coagulation tests, further experiments were carried out investigating the adsorption of PFAS onto the coagulant precipitates using the best performing coagulant chemical. All adsorption experiments were conducted on a PB-900 jar tester (Phipps and Bird, VA, USA), initially using DI water under ambient temperature (22°C). Floc precipitates were formed as before using the same mixing settings and pH control.

To determine whether pH played an important role on changing adsorption, subsequent tests explored how adjusting the pH during the coagulation process influenced PFAS removal. In these experiments, the pH of coagulation was initially set at 6.5 and then reduced to pH 4.5 after 10-minute slow stir at 30 rpm. Samples were collected before and after the pH change to determine whether this had an influence on PFAS adsorption onto the coagulant precipitates. Experiments were carried out using DI water spiked with PFOS ($0.002 \text{ }\mu\text{mol-L}^{-1}$) and PFOA ($0.002 \text{ }\mu\text{mol-L}^{-1}$). Kinetic experiments were carried out using coagulant conditions of optimal removal of PFAS ($\text{Al}_2(\text{SO}_4)_3$ dose of 20 mg Al-L^{-1} at pH 4.5). During the flocculation stage, 5 mL of sample was collected at time intervals of 1, 3, 5, 10, 15, and 20 min to determine how quickly PFAS was adsorbed and reached equilibrium.

Thermodynamic studies of adsorption of PFAS onto coagulant precipitates were carried out using DI water spiked with PFAS. The coagulant was dosed at 20 mg Al-L^{-1} at pH 4.5. This dosing condition enabled effective adsorption isotherms to be developed based on the amount of precipitates formed (providing measurable and different equilibrium concentrations). $\text{Al}_2(\text{SO}_4)_3$ was dosed into the water during the rapid mix stage, with precipitates being observed 3 min later during the slow stir period. Then, PFOS or PFOA was spiked into the water at concentrations between $0.0002\text{--}0.02 \text{ }\mu\text{mol-L}^{-1}$ (equivalent to $107.6\text{--}10,760 \text{ ng-L}^{-1}$ for PFOS and $86.2\text{--}8,620 \text{ ng-L}^{-1}$ for PFOA). After a slow-stir mixing period of 10 min, adsorption had stabilized and 5 mL of sample was collected and filtered. Additional jar tests were carried out for the collection of the precipitate. The mass of the precipitate formed in the DI water coagulation test was quantified in the same way as that for the real water coagulation tests.

The impact of organic matter on the removal of PFAS by coagulation was investigated by spiking different model compounds into the water (humic acid, resorcinol, vanillic acid, citric acid and tryptophan). Model compounds were selected based on differences in molecular weight (MW) and hydrophobicity (see supporting information Table S2). Initially, humic acid at various concentrations ($2\text{--}10 \text{ mg DOC-L}^{-1}$) was added to the water alongside PFOS and PFOA ($0.002 \text{ }\mu\text{mol-L}^{-1}$ of each) to be representative of organic matter concentrations found in surface waters. The additional four types of organic matter were then tested separately at concentrations of 10 mg DOC-L^{-1} , and spiked with PFOA and PFOS at a C_0 of $0.002 \text{ }\mu\text{mol-L}^{-1}$. The above test solutions were treated with a coagulant dose of 20 mg Al-L^{-1} at pH 4.5. The samples were collected and filtered for further analysis. Samples from control experiments were processed along with samples from coagulation tests. All experiments were carried out in triplicate.

2.4. Analytical methods and data analysis

The PFOA/PFOS concentrations were analyzed by using a SCIEX QTRAP 6500+ LC-MS/MS, which was operated in the negative electrospray ionization (ESI-) mode. The detailed LC-MS/MS and instrument parameters are provided in Text S2, and Tables S3 and S4 in supporting information.

The efficiency of PFOS and PFOA removal (in %) through coagulation was calculated from:

$$\text{Removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100$$

where C_0 is the concentration of PFOA and PFOS in procedural blank samples and C_t is the concentration of PFOA and PFOS samples collected after the mixing and filtration process.

The adsorption capacity of the floc precipitates was determined by:

$$q_t = \frac{(C_0 - C_t)V}{m}$$

where q_t (ng-g^{-1}) is the amount of PFOS/PFOA adsorbed per nanogram of the precipitate at time t (min). C_0 (ng-L^{-1}) is the concentration of PFOA and PFOS in procedural blank samples. C_t (ng-L^{-1}) is the concentration of PFOA and PFOS samples collected after the mixing process and filtration, and m (g) is the mass of floc/precipitates formed during coagulation process. Error bars in all figures represent the relative standard deviation of experiments carried out in triplicates.

3. Results and discussion

3.1. Impact of coagulant metal salt on removal of PFOA and PFOS removal

In the cases of scenario I and II, conditions of low pH, the removal of PFOA and PFOS was ranged between 2 % and 58 % for the four different coagulants. The highest removal was observed for Al, followed by Fe then Zr (Fig. 1). PFOS was more favorably removed than for PFOA for all of the coagulants tested. For the traditional metal salts, iron had lower removal of PFOS (15–20 %) compared to alum under the optimized pH conditions optimized for charge neutralization (scenario I), where removal was between 22 % and 27 % for PFOS as the Al coagulant dose increased. In the case of no pH adjustment (scenario II), the most significant removal of PFOA and PFOS (16 % for PFOA and 58 % for PFOS) was observed at the highest dose of alum (26 mg-L^{-1} as Al). This result implied that PFAS was being removed to some degree through conventional coagulation, particularly for the Al chemical. In comparison, the zirconium salt achieved the highest removal of DOC of the four coagulants under the pH condition that was optimized for charge neutralization (scenario I) (Fig. S1), but only 3–6 % of PFOA and 5–7 % of PFOS was removed (Fig. 1). These results implied that the charge driven interaction induced by the presence of highly charged species, for example Al^{3+} , Fe^{3+} , Zr^{4+} , were ineffective in removing PFAS. Previous studies have proposed that the removal of PFAS was attributed to the sorption of PFAS onto the metal hydroxide flocs in both coagulation and electrocoagulation process [35,36,44]. Therefore, the difference in PFAS sorption to metal hydroxide flocs was more associated with the various physical–chemical properties of the metal hydroxide, particularly in relation to its hydrophobicity. No removal of PFAS was observed for the Zn based salt. This was unexpected given that application of electrocoagulation using a zinc electrode showed up to 99 % of PFOA removed [36,45]. However, these previous studies all used high concentrations of PFOA in the mg-L^{-1} range in pure water matrices. The hemimicelle formation of PFAS in the mg-L^{-1} range is proposed to have enhanced the adsorption of PFOA onto the zinc hydroxide in these experiments [46,47]. For scenario III (pH optimized for sweep flocculation), no discernible PFAS removal was observed for any of the coagulants,

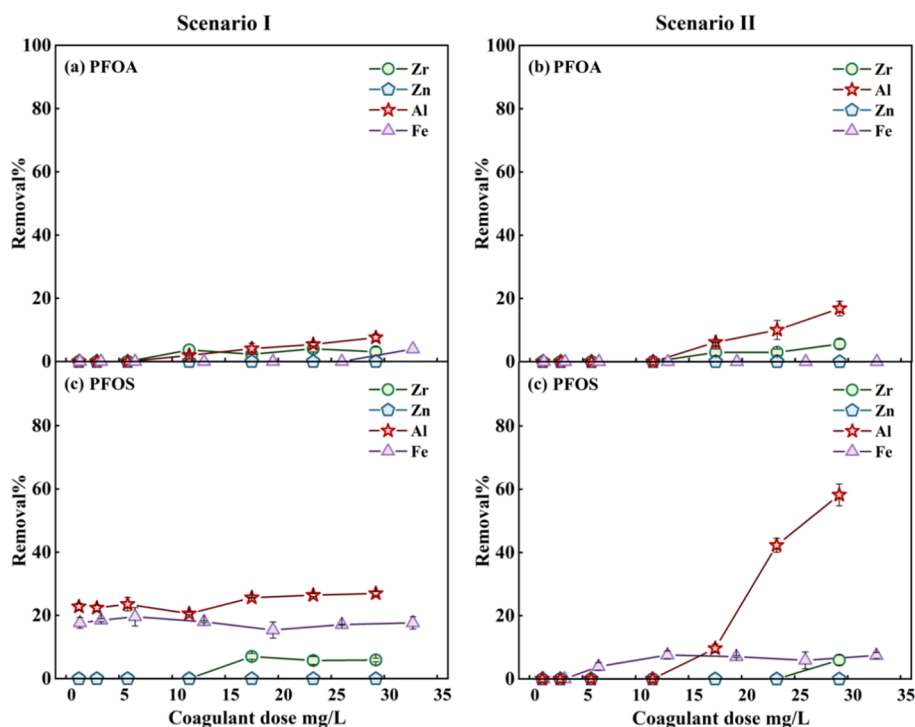


Fig. 1. Removal of PFOA (a) and PFOS (c) as a function of coagulant dose under pH conditions optimized for charge neutralization (Scenario I: pH 4.5 for Fe and pH 5.5 for Zr, Zn, Al); Removal of PFOA (b) and PFOS (d) as a function of coagulant dose without pH adjustment (Scenario II). $[PFOS]_0$ and $[PFOA]_0$ was $0.002 \mu\text{mol}\cdot\text{L}^{-1}$ and $0.0007 \mu\text{mol}\cdot\text{L}^{-1}$, respectively. Source water DOC was $6.9 \text{ mg}\cdot\text{L}^{-1}$ and turbidity was 7.19 NTU.

showing that flocs formed during sweep flocculation at elevated pH were unable to contribute to the removal of PFAS in coagulation.

3.2. Effect of coagulant dose on PFAS removal

Further experiments were carried out using the Al coagulant, given its superior performance in removing PFAS when compared to the three alternative coagulants under test. The removal of PFOA and PFOS

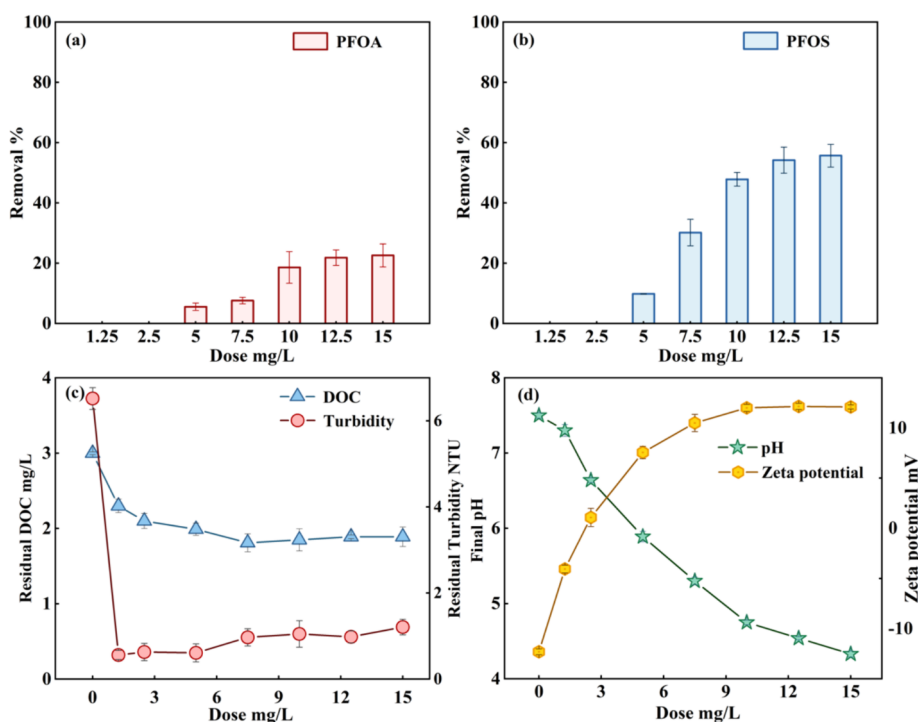


Fig. 2. Removal of PFOA (a), PFOS (b), DOC and turbidity (c) as a function of $\text{Al}_2(\text{SO}_4)_3$ dose; the changes in zeta potential and pH (d) with increasing $\text{Al}_2(\text{SO}_4)_3$ dose. $[PFOS]_0$ and $[PFOA]_0$ were $0.002 \mu\text{mol}\cdot\text{L}^{-1}$. Source water DOC was $3.0 \text{ mg}\cdot\text{L}^{-1}$ and turbidity was 6.52 NTU.

increased with the dose of $\text{Al}_2(\text{SO}_4)_3$ (Fig. 1b and 2a). At the lowest doses of $\text{Al}_2(\text{SO}_4)_3$ ($1.25 \text{ mg Al}\cdot\text{L}^{-1}$ and $2.5 \text{ mg Al}\cdot\text{L}^{-1}$), while no significant removal of PFOA and PFOS was observed, these conditions saw efficient removal of DOC and turbidity (Fig. 2c). It has previously been reported that PFOA adsorbs onto the suspended solids present in natural water and are hence removed along with the suspended solids during coagulation and clarification [34]. However, in this study, there was no evidence for this as there was no strong relationship between the removal of turbidity and PFAS removal during coagulation. To illustrate, as the dose increased from 5 to $15 \text{ mg Al}\cdot\text{L}^{-1}$, the removal of PFOA increased from 5.5 % to 22.83 %, while the residual turbidity increased slightly from 0.6 to 1.2 NTU across this range. It should be noted that the initial turbidity of the source water used in these studies was quite low (6.52 NTU) and hence the potential for partitioning of PFAS onto suspended solids was therefore low for this source.

Consistent with the data from the coagulant assessment and in previous studies, higher removal of PFOS was achieved in these experiments, increasing from 9.83 % to 55.7 % as the coagulant dose increased from 5 to $15 \text{ mg Al}\cdot\text{L}^{-1}$ [33–36]. However, in comparison to the results from the initial coagulant assessment, more efficient removal of PFOS was observed at lower alum doses. This was attributed to the lower levels of DOC and turbidity in the tested water (DOC of $3.0 \text{ mg}\cdot\text{L}^{-1}$ compared to $6.9 \text{ mg}\cdot\text{L}^{-1}$ in the first experiments; turbidity 6.52 NTU compared to 7.19 NTU). As such, the higher levels of DOC and turbidity in raw water consumed more coagulant. A higher dose of coagulant was required to neutralize the negative surface charge of the suspended particles and organic matter and induce the subsequent flocculation as it took more coagulant to bring about the formation of a floc onto which the PFAS could adsorb.

This was a result consistent with previous studies, which showed preferential removal of PFOS over PFOA [33,34,36]. When considering the hydrophobicity of the two PFASs under investigation, the $\log K_{\text{ow}}$ values for PFOA and PFOS were 4.3 and 5.25, respectively, indicating the higher hydrophobicity of PFOS [48]. Molecules of higher hydrophobicity are more conducive to removal during coagulation [31]. In addition, according to the Pearson's concept of hard and soft acids and bases, the $-\text{SO}_3^-$ group is a relatively hard base when compared to the $-\text{COO}^-$ group, and is hence more readily adsorbed onto oxide surfaces [49]. In these experiments, as the Al dose increased, the pH reduced from 7.5 to 4.2, hence the most efficient removal of PFOA/PFOS was observed under acidic conditions. This is in accordance with the adsorption performance of PFOA/PFOS onto alumina, in which the maximum adsorption capacities of solid alumina were achieved under acidic conditions at pH 4.3 [50]. As the dose increased from 0 to $10 \text{ mg Al}\cdot\text{L}^{-1}$, the zeta potential increased from -12.3 mV to 12.0 mV , with the PFOA and PFOS removal reaching 18.61 % and 47.85 %, respectively. The pKa values of PFOA and PFOS are -0.1 and -3.27 , respectively [51]. Under the pH conditions tested, PFOA and PFOS were therefore primarily anions. This indicates that as the coagulant dose increased, the negative surface charge of contaminants present in the water were neutralized and the extent of the net positive surface charge available was sufficient for charge driven mechanisms of adsorption to occur. As a small but highly charged species, Al^{3+} (high valency and small molecular diameter) has been shown to have a high affinity for binding to organic compounds, including bulk organic matter and PFAS, and this may assist in contaminant removal [52,53]. However, as the coagulant dose rose further to $15 \text{ mg Al}\cdot\text{L}^{-1}$, the zeta potential remained around 12.0 mV while there was a further increase in the removal of PFOA/PFOS, reaching 22.6 % and 55.70 % for PFOA and PFOS, respectively. This follows as a result of an increase in surface area available for adsorption as the coagulant dose increases, alongside the importance of non-charged mechanisms of interaction, such as hydrophobicity, between PFAS and coagulant precipitates.

3.3. Effect of coagulation pH

For the bulk parameters of DOC and turbidity, there was no significant difference in DOC removal for various pH conditions, while turbidity removal decreased at pH 4.5 when compared to that at pH 5.5 and 6.5 (Fig. 3). This was explained by the decreased formation of Al precipitates at the lower pH 4.5, and hence the reduced potential for removal of turbidity particles through enmeshment [31]. The removal of PFOA and PFOS was positively correlated with the proton concentration (acidic pH) and the $\text{Al}_2(\text{SO}_4)_3$ dose. Both PFOA and PFOS were not effectively removed at pH 6.5. The removal of PFOA and PFOS increased to 13.3 % and 22.23 % at pH 5.5 at the highest coagulant dose ($15 \text{ mg Al}\cdot\text{L}^{-1}$), respectively. The most effective removal of PFOA and PFOS was achieved at pH 4.5. For PFOA, the removal increased from 4.04 % to 20.52 % within the dose range. For PFOS, 20.6 % of PFOS was removed at the lowest dose of $\text{Al}_2(\text{SO}_4)_3$ ($1.25 \text{ mg Al}\cdot\text{L}^{-1}$), while the maximum removal of PFOS (45 %) was achieved as the dose rose to $12.5 \text{ mg Al}\cdot\text{L}^{-1}$. It should also be noted that under the acidic condition (pH 4.5), more than 20 % of PFOS could be removed at a low dose (e.g., $1.25 \text{ mg Al}\cdot\text{L}^{-1}$ and $2.5 \text{ mg Al}\cdot\text{L}^{-1}$), even though the flocs formed during coagulation were negatively charged. This further supported the view that non-charged based processes play an important role in the removal of PFAS during coagulation. Aluminum-based coagulants can remove organic matter and colloids through adsorption and enmeshment as aluminum hydroxide precipitates form [27] and hence provides a route by which PFAS may be removed. Using the theoretical aluminum solubility in equilibrium with amorphous $\text{Al}(\text{OH})_3$ some indication of the conditions under which PFAS was preferentially removed can be gleaned (Fig. 4). The interior portion marked with the blue dotted line in the alum coagulation diagrams refers to a region where the formation of amorphous $\text{Al}(\text{OH})_3$ is expected [54]. The amorphous $\text{Al}(\text{OH})_3$ should form under all conditions studied. When mapping the PFAS removal onto the phase diagram, it can be seen that the most efficient removal of PFAS (>15 % for PFOA and >30 % for PFOS) was observed in the area where the pH was lower than 5.5 and the dose was higher than $5 \text{ mg Al}\cdot\text{L}^{-1}$. Increasing the alum dose led to an increase in the surface area of fresh precipitates, which in turn contributed to an increase in the removal of PFOA and PFOS, supportive of the view that available adsorption area is important for enhancing PFAS removal.

3.4. Effect of initial concentration of PFOS and PFOA

The impact of the initial concentrations of PFOA/PFOS on coagulation performance from real water by coagulation was further studied for a constant coagulant dose (Fig. 5). As expected, the removal of turbidity and DOC was not affected by the increasing concentrations of the trace pollutants in the source water and the removal of PFOA and PFOS were between 15–18 % and 35–41 %, respectively. When considered on a mass basis, as the C_0 of PFOA and PFOS rose from $0.0005 \mu\text{mol}\cdot\text{L}^{-1}$ to $0.02 \mu\text{mol}\cdot\text{L}^{-1}$ (equivalent mass increase from 269 to $10,760 \text{ ng}\cdot\text{L}^{-1}$ for PFOS and 215.50 to $8,620 \text{ ng}\cdot\text{L}^{-1}$ for PFOA), the adsorption capacities of the floc precipitates increased almost linearly from $621 \text{ ng}\cdot\text{g}^{-1}$ to $23,564 \text{ ng}\cdot\text{g}^{-1}$ for PFOA and from $1797 \text{ ng}\cdot\text{g}^{-1}$ to $61,476 \text{ ng}\cdot\text{g}^{-1}$ for PFOS (see Fig. 5c and 5d). The overall increase in the adsorption capacity could be attributed to the fact that the higher concentration gradient led to a stronger driving force for adsorption [39]. This result is in line with findings that show that activated carbon and anion exchange achieved more efficient removal of PFAS from membrane concentrate than from raw water due to the higher concentration of PFAS in concentrated waste stream [55]. No adsorption saturation was observed, even though the highest concentrations of PFOA and PFOS applied here were 4 orders of magnitude higher than those typically found in the environment [56–58]. This implies that there was still available surface area for adsorption but that a suitable concentration gradient is needed to drive the adsorption process. Nevertheless, for typical coagulant doses in the range of $5\text{--}10 \text{ mg}\cdot\text{L}^{-1}$ as Al, there will be available surface area for

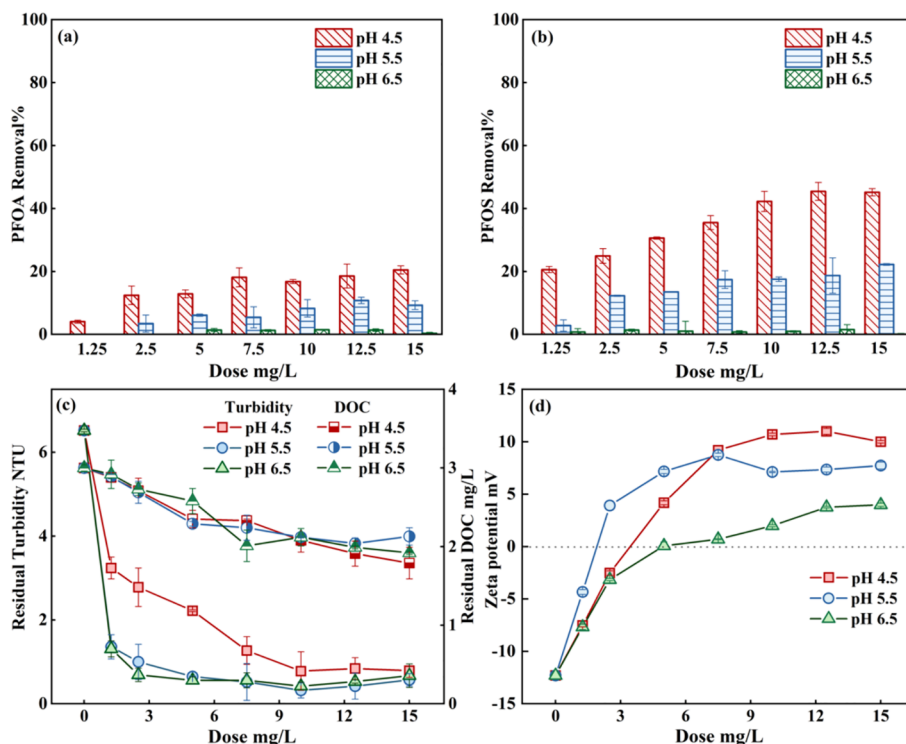


Fig. 3. Impacts of pH and Alum dose on removal of PFOA (a), PFOS (b), turbidity and DOC (c); the changes in zeta potential with an increasing $\text{Al}_2(\text{SO}_4)_3$ dose at different pH (d). $[\text{PFOS}]_0$ and $[\text{PFOA}]_0$ were $0.002 \mu\text{mol}\cdot\text{L}^{-1}$. Source water DOC was $3.0 \text{ mg}\cdot\text{L}^{-1}$ and turbidity was 6.52 NTU .

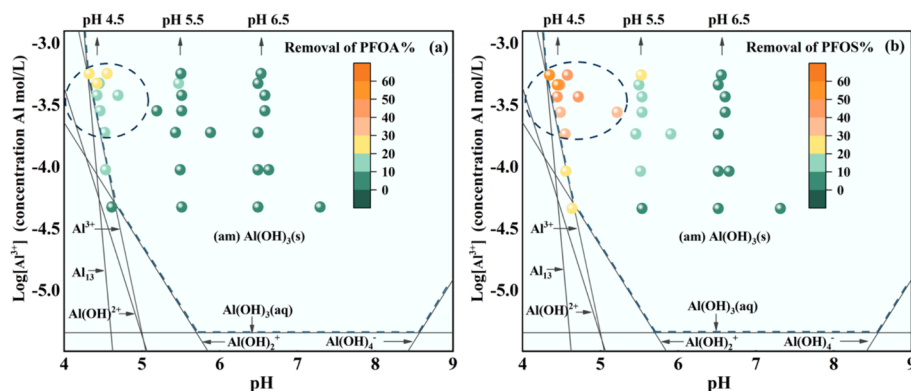


Fig. 4. Theoretical aluminum solubility diagram in equilibrium with amorphous $\text{Al}(\text{OH})_3$ with the removal of PFOA and PFOS presented.

PFAS adsorption primarily driven by hydrophobic interactions, aligning with the concept of accessible hydrophobic surface area.

3.5. Adsorption of PFOA and PFOS onto Al precipitates

To investigate the adsorption behaviour of Al precipitates for PFOA and PFOS, pre-formed Al precipitates were prepared by dosing alum into DI water at pH 4.5. PFOA and PFOS were then spiked into the system after the formation of amorphous Al precipitates. The adsorption of PFOA and PFOS reached an equilibrium within the first minute after spiking (see Fig. S2), indicating that the sorption sites on the Al precipitates were readily accessible. The impacts of changing pH on the adsorption of PFAS onto the fresh Al precipitates resulted in a significant increase in PFOA and PFOS removal as the pH decreased from 6.5 to 4.5 (Fig. 6a). Under these conditions, Al precipitates mainly consist of colloidal aluminium hydroxide with a small amount of hydrophobic hydrated aluminium ions [36,59]. As previously noted, the hydrophobic attraction between PFAS and the aluminium precipitates was considered

to be the main driving force behind the removal of the PFAS. However, the presence of hydrophobic hydrated aluminium ions could have played an important role in the PFAS adsorption process. It was therefore hypothesized that the content of hydrophobic hydrated aluminium ions in Al precipitates at pH 4.5 was higher than that at pH 6.5, conditions which resulted in more effective removal of PFAS at the lower pH.

The adsorption of PFOA and PFOS onto the Al precipitates followed the Freundlich isotherm model (Fig. 6c and 6d and Text S1). The Freundlich model considers that the adsorbate can accumulate on the surface of the adsorbent in multiple layers, using heterogeneous binding opportunities, and that the interactions are driven by physisorption processes [60,61].

The proportional removal of PFOA and PFOS from DI water by alum coagulation decreased from 39 % to 22 % for PFOS and from 11 % to 4 % for PFOA with an increase in the C_0 of PFOA and PFOS (Fig. 6b). This was different from the results observed for the real water, which stayed similar at around 38 % for PFOS and 17 % for PFOA (Fig. 5b). While the % removal decreased, the mass adsorbed onto the Al precipitates formed

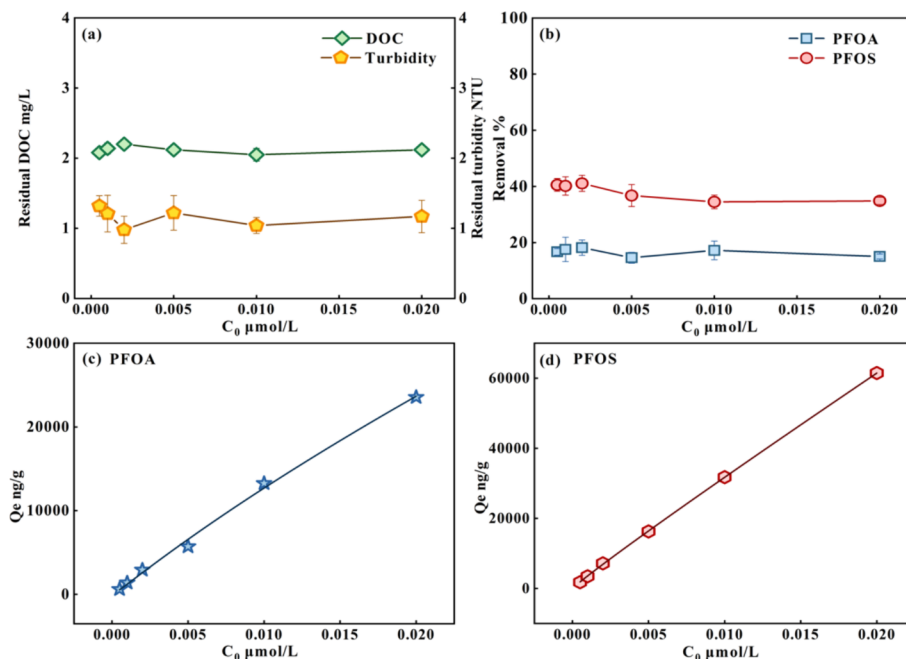


Fig. 5. Impacts of initial concentrations of PFOA and PFOS on DOC and turbidity (a), PFOA and PFOS (b) removal from river water at pH 4.5; Adsorption capacities of floes for PFOA (c) and PFOS (d) as functions of initial concentrations of PFOA and PFOS at pH 4.5 (The initial DOC and turbidity of the raw water were 3.5 $\text{mg}\cdot\text{L}^{-1}$ and 3.42 NTU, respectively. $[\text{PFOS}]_0$ and $[\text{PFOA}]_0$ were between 0.0005 and 0.02 $\mu\text{mol}\cdot\text{L}^{-1}$. The dose of $\text{Al}_2(\text{SO}_4)_3$ was 11.5 $\text{mg}\cdot\text{L}^{-1}$ as Al).

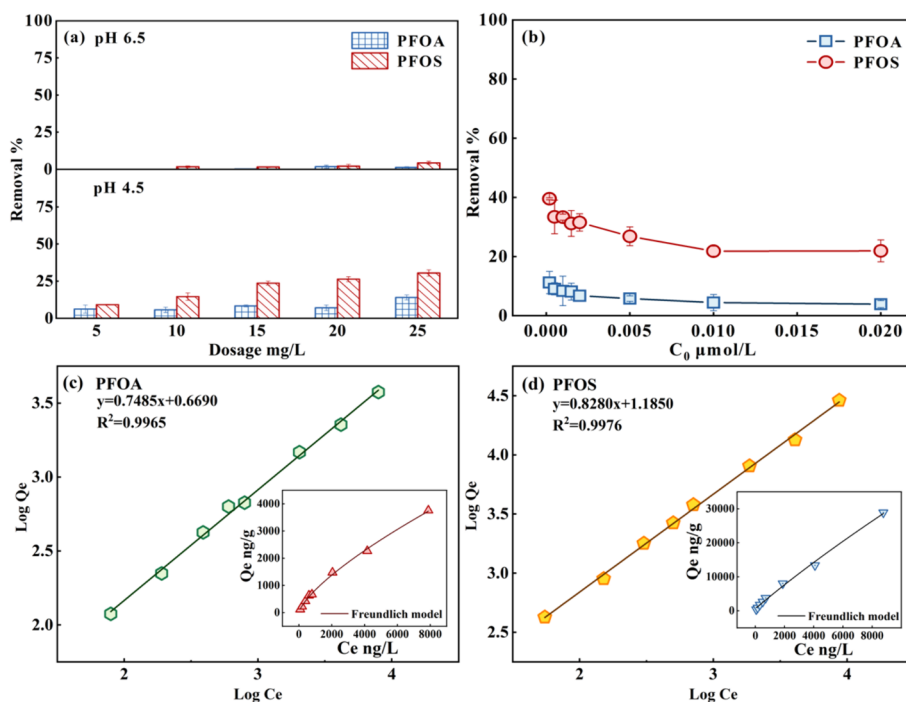


Fig. 6. Impacts of pH on the adsorption of PFOA and PFOS onto Al precipitates formed at a dose of 20 $\text{mg}\cdot\text{L}^{-1}$ as Al in DI water (The $[\text{PFOS}]_0$ and $[\text{PFOA}]_0$ were 0.002 $\mu\text{mol}\cdot\text{L}^{-1}$) (a); Removal of PFOA and PFOS as a function the initial concentrations of PFOA and PFOS (b); Adsorption isotherm of PFOA (c) and PFOS (d) onto the Al precipitates at pH 4.5 at a dose of 20 $\text{mg}\cdot\text{L}^{-1}$ as Al ($[\text{PFOS}]_0$ or $[\text{PFOA}]_0$ was between 0.0002 and 0.02 $\mu\text{mol}\cdot\text{L}^{-1}$).

increased from 223 $\text{ng}\cdot\text{g}^{-1}$ to 3759 $\text{ng}\cdot\text{g}^{-1}$ for PFOA and 898 $\text{ng}\cdot\text{g}^{-1}$ to 28,912 $\text{ng}\cdot\text{g}^{-1}$ for PFOS as the C_0 of PFOA and PFOS increased from 0.0005 $\mu\text{mol}\cdot\text{L}^{-1}$ to 0.02 $\mu\text{mol}\cdot\text{L}^{-1}$. However, this range is much lower than that seen for floes formed in the real water coagulation (Fig. 5c and 5d). This result implied that the original constituents in source water play a key role in the removal of PFAS by alum coagulation.

3.6. Effect of organic matter on PFOS/PFOA removal

DI water spiked with humic acid was used to determine whether the introduction of background organic matter influenced the coagulation efficacy for PFAS removal. Humic acid was effectively removed in all cases (see Fig. S3), implying that the dose of coagulants was sufficient for DOC removal. An overall increase in both PFOA and PFOS removal

was observed as the addition of humic acid rose from 0 to 10 mg DOC·L⁻¹, which increased from 7 % to 19 % for PFOA and 35 % to 55 % for PFOS. The maximum removal of PFOA and PFOS observed in humic acid-spiked water was very close to that achieved when coagulating the real water at the higher doses (see Figs. 2 and 3). Those results show that humic acid improved the removal of PFOA and PFOS from the water during alum coagulation. Previous research reported that the sediment organic carbon content was the dominant sediment-specific parameter affecting the sorption of anionic PFAS onto sediments due to the sorption of anionic PFAS to organic matter [62]. It was therefore postulated that in addition to the quick, direct adsorption onto the Al precipitates, PFOA and PFOS were adsorbed to humic acid through hydrophobic interaction, which was further removed as a result of the efficient humic acid removal by coagulation [63]. This is a result consistent with that seen for coagulation of wastewater, where a hydrophobic interaction pathway between long-chain PFAS and humic acid was posited to be the reason why significant micropollutant removal was observed alongside bulk removal of phosphorus [64].

To further confirm the impacts of organic matter on the removal of PFOA and PFOS through alum coagulation, four additional types of organic matter with different hydrophobicity were used as background organic matter (resorcinol, vanillic acid, tryptophan, and citric acid – for structure and MW characteristics see Table S2). Almost no DOC was removed from the test water spiked with resorcinol, vanillic acid, or tryptophan after coagulation (see Fig. S4). Generally, the dissolved organic matter with a low MW was ineffectively removed through conventional coagulation due to the weak association with the coagulants [31]. In the case of citric acid, the DOC decreased to 4 mg DOC·L⁻¹ after coagulation. This arose from the strong complexation between the citric acid and Al hydrolysis products, which led to a decrease in the DOC [43]. For PFAS removal, the results for the additional organic matter spikes were different to those seen for humic acid. When compared to the control water (no DOC spike), the presence of tryptophan had no impact on PFOA and PFOS removal, whereas it decreased by 4–7 % for PFOA and 13–24 % for PFOS when resorcinol, vanillic acid or citric acid was present (Fig. 7). Competition during the adsorption process between PFAS and small organic matter has been reported in previous studies using activated carbon [16]. When compared to PFAS, low MW organic matter typically has a higher affinity towards activated carbon resulting in a decrease in PFAS removal. A few studies have demonstrated the sorption of PFAS onto natural organic matter and macromolecular organic matter [46,62,63], while the association between organic compounds and PFAS has not been widely reported. In this study, different impacts of low MW organic matter on coagulation efficacy of PFAS removal were observed, suggesting different specific interactions between the small organic matter and PFAS. For resorcinol, vanillic acid and citric acid, there was

evidence for association between the organic matter and the PFAS that changed the ability of it being removed during coagulation. For resorcinol and vanillic acid, which was ineffectively removed by coagulation, the association with PFAS led to an inhibition in the removal of PFOA and PFOS. The slightly higher removal of PFAS in the presence of citric acid was related to the strong association between citric acid and the Al precipitates. In the case of tryptophan, it seems likely that there were no interactions between tryptophan and PFAS, and hence no influence on PFAS removal was observed.

3.7. Mechanism interpretation

The results put forward the position that the removal of PFOA and PFOS is driven by a coupled pathway consisting of hydrophobic and electrostatic interactions (Fig. 8). The most efficient removal of PFOA and PFOS was observed in the region of the logC_{Al}-pH diagram where the amorphous Al precipitates could form under acidic conditions (pH<5.5), enriching the proportion of available hydrophobic hydrated Al³⁺. This was further supported by the observation of enhanced removal of PFAS in the presence of humic acid (Fig. 8b). Conversely, the addition of small organic compounds impeded the uptake, or had no impact on removal (Fig. 8c and d). As hydrophobic and charge mechanisms were proposed to be the primary driving force for the interactions between organic matter and PFAS, it is postulated that humic acid readily associates with PFAS, which in turn influences the removal pathway of micropollutant. While there is no direct empirical evidence for NOM-PFAS complexes, indirect research outcomes strongly point towards this view. Density functional theory calculations have shown that divalent ions can bind PFAS with humic acid molecules by an ion-induced bridging mechanism, increasing the molecular size of the aggregate [65]. The proportion of undetected/unknown fluoride increased from 2.8 to 25.3 % when 15 mg L⁻¹ humic acid was added to a PFAS solution, hypothesized to have been caused by the formation of NOM-PFAS complexes that couldn't be detected by LC/MS/MS [66]. Finally, a range of PFAS compounds have been shown to associate with soil organic matter, which indicated that more hydrophobic long chain PFAS preferentially complexed with condensed regions or organic compounds, while shorter chain PFAS were primarily associated with organic matter through cationic effects [52].

Alum showed a potential for removal of PFOS during coagulation, while PFOA was removed by a more moderate degree. The adsorption of PFOS and PFOA onto the Al precipitates was the main route for removal of PFOS and PFOA in the coagulation process. The consequence being that PFAS in source water will end up in drinking water sludge when alum is used as the coagulant in drinking water treatment plants whether through intended or unintended removal. Most previous studies have reported that sewage sludge is a sink for long chain PFAS [67,68],

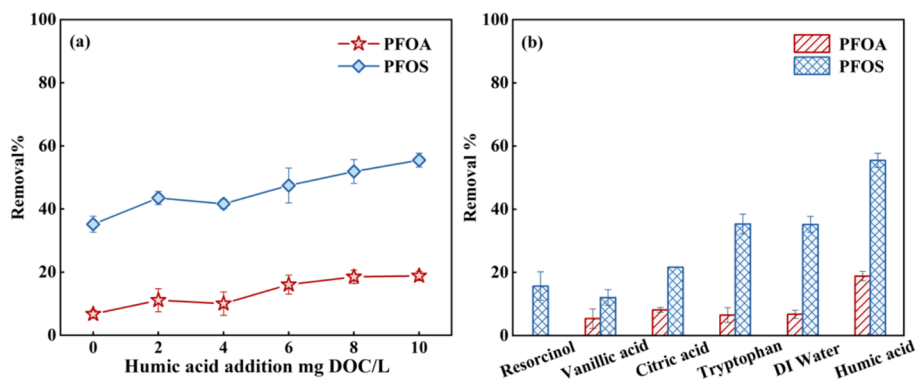


Fig. 7. Removal of PFOA and PFOS as functions of humic acid concentration at pH 4.5 at a dose of 20 mg·L⁻¹ (The DOC was between 2–10 mg·L⁻¹) (a); Impacts of five types of organic matter on PFOA and PFOS removal in coagulation at pH 4.5 at a dose of 20 mg·L⁻¹ (b) ([PFOS]₀ and [PFOA]₀ were 0.02 μmol·L⁻¹. The DOC was 10 mg·L⁻¹).

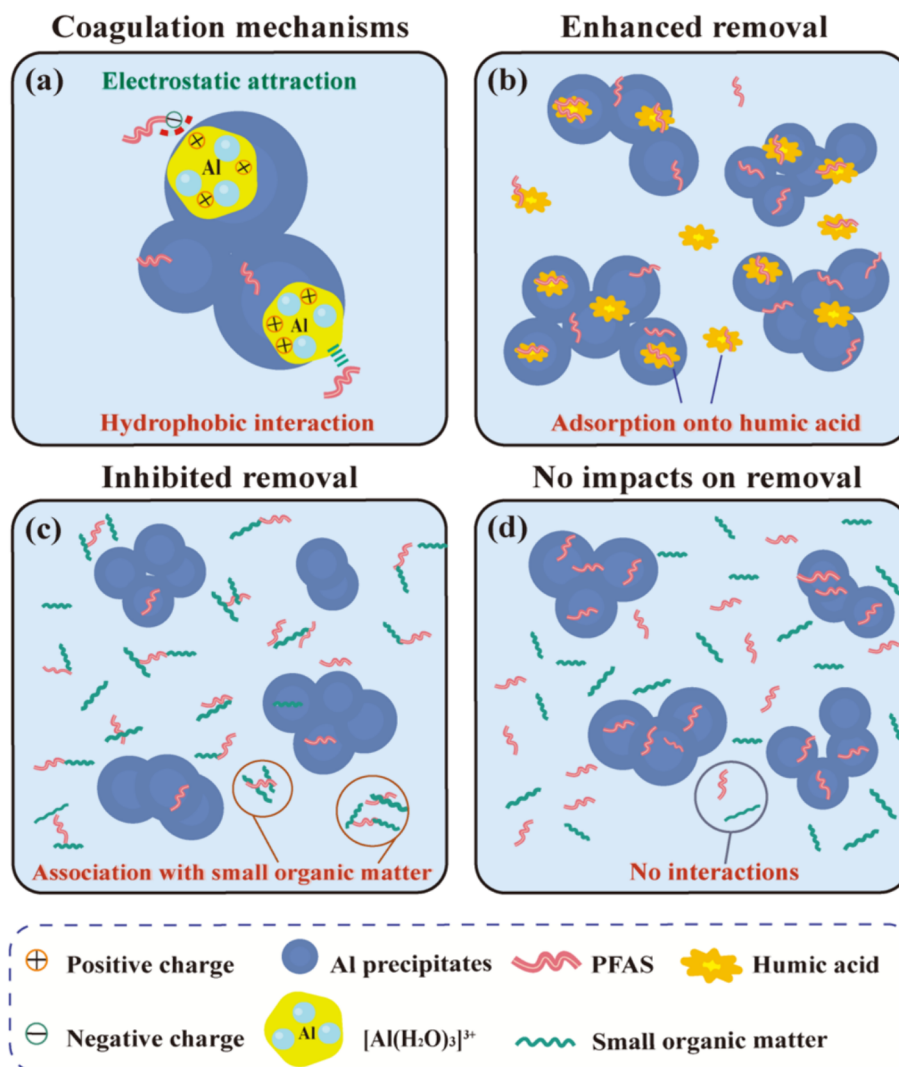


Fig. 8. Coagulation mechanisms for removal of PFAS (a); impacts of background matrices on removal of PFAS during coagulation (b-d).

however, few studies on drinking water sludge have been reported [69]. This research therefore provides some of the first evidence to show that drinking water sludge from coagulation will contain PFAS, particularly for WTWs employing alum coagulation. Hundreds of millions of tonnes of WTW sludge is generated across the globe each year. Should this sludge be considered hazardous waste, it is unlikely that there will be capacity to handle this waste [69]. Therefore, more consideration on the fate of PFAS during drinking water treatment along with the disposal routes for drinking water sludge are needed.

4. Conclusions

This is the first reported evaluation of a range of coagulants, selected based on their hydrophobicity and charge profiles, for the removal of PFAS from real water matrices under environmentally relevant conditions. Alum showed a high potential for removal of PFOS during coagulation, while PFOA had a more moderate removal profile. Other coagulants performed less well in the order: Fe > Zr > Zn. The removal of PFAS by alum coagulation was observed in a region where the amorphous Al precipitates could form under acidic conditions, with hydrophobic and charge interaction then being the primary driving force for adsorption. The interaction between organic matter and PFAS played an important role in how well the PFAS are removed during the coagulation process. Organic matter of high MW improved the removal of PFAS through co-association followed by concurrent removal of the

bulk organic matter alongside the PFAS. The association between lower MW organic matter and PFAS resulted in a decrease in removal of PFAS as the small organic matter was ineffectively removed by coagulation. The results provide important information on the fate of important PFAS compounds during the coagulation processes, such that source waters rich in low MW organic matter and more hydrophilic compounds are likely to inhibit removal of PFAS during coagulation.

Data Statement.

Data sets that contributed to this paper are at: <https://doi.org/10.17862/cranfield.rd.25608102>.

CRediT authorship contribution statement

Pin Wang: Investigation, Methodology, Data curation, Writing – original draft. **Guangyu An:** Supervision. **Irene Carra:** Writing – review & editing, Supervision. **Francis Hassard:** Writing – review & editing. **Pablo Campo Moreno:** Writing – review & editing. **Hacer Sakar:** Writing – review & editing. **Monika Jodkowska:** Methodology. **Dongsheng Wang:** Supervision. **Bruce Jefferson:** Writing – review & editing. **Wenhui Chu:** Supervision. **Peter Jarvis:** Writing – review & editing, Supervision.

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 sets that contributed to this paper are at: 10.17862/cranfield.rd.25608102

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2024.129562>.

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Wang, Pin; An, Guangyu; Carra, Irene; Hassard, Francis; Campo Moreno, Pablo ...

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