

CRANFIELD UNIVERSITY

Sara Sánchez López

Metaldehyde Treatability by Dissolved Air Flotation Combined with
Powdered Activated Carbon Adsorption

School of Water, Energy and Environment

MSc by Research
Academic Year: 2016 – 2017

Supervisor: Prof. Peter Jarvis
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ABSTRACT

The removal of metaldehyde to meet pesticide compliance limits in drinking water remains a challenge for water companies. A combined treatment of dissolved air flotation (DAF) and powdered activated carbon (PAC) was investigated as a treatment process for metaldehyde removal. Four different water sources were spiked with metaldehyde and treated using PAC. A PAC dose of 100 mg/L using a contact time of 20 minutes was required in order to effectively remove metaldehyde to the compliance concentrations for all of the water sources. The water quality was shown to affect the removal of metaldehyde through competition with NOM. Moreover, the PAC dosing position relative to the coagulant was studied regarding its impact on the removal of NOM and metaldehyde, the floc formation and the clarification efficiency. The simultaneous addition of coagulant and PAC resulted in the lowest removal of metaldehyde. The best removal was seen for dosing sequences of PAC/Coagulant and Coagulant/PAC. However, there were no significant differences between these two approaches. The sequence of addition of PAC/Coagulant was selected due to its better clarification results.

Keywords:

Metaldehyde, Dissolved Air Flotation, Pesticide, Adsorption, Powdered Activated Carbon, Drinking Water.

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LIST OF ABBREVIATIONS

DAF	Dissolved Air Flotation
DI	Deionised Water
DOC	Dissolved Organic Carbon
GAC	Granular Activated Carbon
GCMS-SIM	Gas chromatography-mass spectrometry - Selective Ion Monitoring
NOM	Natural Organic Matter
NPOC	Non-Purgeable Organic Carbon
PAC	Powdered Activated Carbon
SUVA	Specific Ultraviolet Absorbance
UP	Ultra-Pure Water

1 Introduction

Metaldehyde is a pesticide that has been used since the 1940s, particularly in wet agricultural regions (Kay and Grayson, 2014). It is applied in agriculture and gardening, mostly as a pellet, for the control of snails and slugs causing their death by desiccation (Wilkinson, 2010; Tang *et al.*, 2016). Metaldehyde is relatively soluble, having a solubility of 200 mg/L at 20 °C (Busquets *et al.*, 2014) and is mobile in soil, having a low organic carbon sorption coefficient measured between 34 and 240 L/kg (Kegley *et al.* 2016). Metaldehyde is also very recalcitrant to treatment using conventional water treatment systems. As a result, metaldehyde has become a major issue for water companies as it is regularly found in source waters at concentrations above the EU statutory drinking limit of 0.1 µg/L for individual pesticides and 0.5 µg/L for total pesticides (Castle *et al.*, 2017).

Despite the difficulties that its removal entails, metaldehyde is widely used. In Great Britain, 1605 tonnes of metaldehyde were applied between 2000 and 2004. Ten years later between 2010-2014, the quantity applied was cut by 58% to 926 tonnes (FERA, 2016). This reduction has been promoted by a number of measures, including restricting the application period (Get Pelletwise!, 2012; AHDB Potatoes, 2014), or publishing information campaigns providing appropriate guidance for efficient pesticide application such as 'Get Pelletwise' (Get Pelletwise! 2012a). The longevity of metaldehyde in the environment is poorly understood. Its half-life in soil has been reported to be 67 days in aerobic conditions and 223 days under anaerobic conditions (Kegley *et al.* 2016). Furthermore, according to Tang *et al.* (2016) its half-life in water may reach 17 years. The continued widespread use of metaldehyde (although reduced) and its potential longevity in the environment means that metaldehyde remains an important issue to tackle.

The treatability of pesticides depends on their physical and chemical properties (Marshall, 2013). In the case of metaldehyde, traditional oxidation treatments such as chlorine and ozone cannot break down the structure of metaldehyde (Marshall 2013; Kay & Grayson 2014). Adsorption using granular activated

carbon (GAC) has been shown to remove metaldehyde (Salvestrini et al., 2016), however the costs associated with its maintenance can be prohibitive. This is because GAC is usually used in a fixed filter GAC bed. When used for metaldehyde adsorption the life of this bed is too short and the cost of regeneration is too high to make this treatment economically feasible (Tang et al. 2016).

In the recent past, new technologies have been investigated in order to more effectively degrade metaldehyde. For example, this includes using ultraviolet light (UV) irradiation combined with TiO_2 or H_2O_2 (Autin *et al.*, 2012), a dual-stage method of catalyst and ion-exchange resin as an adsorbent (Tao and Fletcher 2016), nanoparticle catalysts, and powdered activated carbon (PAC) (Li *et al.*, 2017). Adsorption processes using PAC have been shown to be able to reduce metaldehyde to below the limits set by regulators (Nabeerasool *et al.*, 2015) and is one of the most promising technologies. Besides, it presents the advantage of being able to be integrated to treatments where DAF is being used without major change. In addition, it can be easily adapted to seasonal peaks of metaldehyde concentration. This is because of its relatively low cost, the simplicity in operation, the flexibility of dosage and its widespread use in the water industry. Being easily adapted to the different conditions is a big advantage for the removal of target chemicals like metaldehyde that vary through the year. Li et al. (2017) conducted research comparing three nanoparticle catalysts as well as PAC for the removal of metaldehyde from water, and reported that PAC was found to be the most efficient material achieving 90% removal.

Despite PAC and GAC both being made from the same types of material, PAC has a smaller average particle diameter, typically <0.1 mm, compared to GAC which is usually a granule around 1 mm in diameter (Parsons & Jefferson 2006). The smaller particle size of PAC gives it the advantage of having relatively more accessible micropores located near to the surface compared to GAC. This leads to shorter diffusion pathways and consequently to more rapid adsorption (Busquets *et al.*, 2014). Furthermore, PAC is usually dosed in a

virgin state such that fresh adsorption sites are always available in the system. GAC is typically only regenerated after periods of 1 year or more meaning that the number of potential adsorption sites available is typically much less than for PAC. PAC is a well-known technology for the removal of organic compounds from drinking water. Generally used in tandem with coagulants, it is commonly used to remove taste and odour compounds, natural organic matter (NOM), and pesticides (Uyak *et al.*, 2007). Because PAC has the potential to adsorb NOM, it is expected that competition will occur between NOM and pollutants such as metaldehyde that are usually at much lower concentration than NOM, reducing the adsorption of the target pesticide.

NOM characteristics are related to the biogeochemical cycles of the surrounding environment. As a result NOM varies substantially in character and concentration (Fabris *et al.* 2008; Matilainen *et al.* 2010). Therefore, in order to study how the treatment of metaldehyde by PAC may be influenced by different water sources, this research will determine the PAC doses required to remove metaldehyde concentrations to under compliance limits, and analyse the kinetics of adsorption for four different waters from different types of sources.

There are other practical aspects of adsorption by PAC that require more attention. Although, PAC is traditionally dosed before or with a coagulant, the studies regarding the optimum dosing position of PAC are contradictory. Kouras *et al.* (1995) argued that the best removal efficiency of the fungicide dodine by PAC addition was obtained when the PAC was dosed at least 30 minutes after the coagulant. Their following research on lindane removal supported the previous conclusion, when they reported an increase of adsorption rate when PAC was dosed in the same way (Kouras *et al.*, 1998). On the contrary, Cook *et al.* (2001) showed that PAC should be dosed at least 30 minutes before the coagulant addition for MIB and geosmin removal. Other authors suggest that the addition of PAC one minute before the coagulant leads to the best removal of contaminants such as humic acids (Duan *et al.*, 2001). Therefore, further research is needed to understand the influence of the dosing position of PAC

for adsorption, and also the implications that it might have on the floc formation and thus on the clarification.

In this research, the clarification process investigated is dissolved air flotation (DAF). DAF is a technology that has been used for more than 50 years in Europe (Edzwald *et al.*, 1992) and is currently well established and implemented worldwide. Since it was introduced in UK by Doosan Enpure in 1972 its usage has been extended through the country becoming a usual technology in water treatment (Dissolved Air Flotation (DAF), 2018). The power used to generate the bubbles for flotation increases its operational cost. However, compared to conventional sedimentation based clarification, DAF presents the advantage of lower constructions cost due to the need of smaller flocculation tanks and also lower coagulant dosages (Edzwald *et al.*, 1992; Crossley and Valade, 2006). DAF is also very efficient for separating low-density particles from waters (Edzwald, 2010; Shutova *et al.*, 2016). It is therefore widely employed for the treatment of algae (Edzwald *et al.*, 1992; Henderson, Parsons and Jefferson, 2008; Henderson *et al.*, 2010). Furthermore, DAF has been shown to be efficient for an increasing number of applications, including: removing emulsified oils from aqueous mediums (Etchepare *et al.*, 2017), removing organic matter from fresh water (Shutova *et al.*, 2016), and reducing oxygen demand, phosphorus, and suspended solids from municipal wastewater (Edzwald, 2010). Recent studies have been carried for the treatment of pathogens such as *Giardia* (Ribeiro and Daniel, 2016).

Due to its advantages and potential, the implementation of DAF has therefore been expanding. Therefore, this research aimed to study its combination with PAC for the treatment of metaldehyde. The results were expected to provide practical data for the implementation of PAC-DAF as a treatment for the removal of metaldehyde.

This thesis is structured in the form of two research papers. In Chapter 1, the introduction provides the context of this study. The objectives of this research are described in Chapter 2. Chapter 3 and 4 consist of two research papers. The first paper (Chapter 3) determined the kinetics and the required PAC doses

to remove the metaldehyde below the compliance limit for four waters. The second paper (Chapter 4) assessed the impact of the dosing position of PAC on the metaldehyde and NOM removal. The effect of the PAC on floc formation and on clarification by dissolved air flotation (DAF) was also investigated. Finally, a general discussion is presented in chapter 5 followed by the conclusions in Chapter 6.

2 Aim and Objectives

The aim of the project was to study the efficacy of PAC/Coagulant treatment for removal of metaldehyde and its potential for combination with DAF. This was achieved through the following objectives:

1. Analyse the impact that different water sources have on metaldehyde removal using PAC.
2. Determine the PAC doses required to achieve effective metaldehyde removal and investigate the kinetics of metaldehyde adsorption using PAC to understand the contact time needed for metaldehyde removal.
3. Assess how the sequence of PAC and coagulant addition affects the removal of metaldehyde.
4. Analyse the capacity of the DAF to cope with the PAC doses required to fulfil the pesticide regulations.

3 PAC doses and kinetics of adsorption in PAC/Coagulant treatment for metaldehyde removal from four raw waters

Abstract

Metaldehyde is a recalcitrant pesticide to remove from water and water companies are investigating technology that is able to economically reduce its concentration to meet the prescribed drinking water quality regulations. Here, adsorption by PAC was investigated as a metaldehyde removal treatment for drinking water. The required PAC dose and the kinetics of adsorption were analysed. Four water sources were used during this investigation to analyse the impact that different water qualities have on the metaldehyde removal. Water quality was shown to affect the removal of metaldehyde by competition of NOM. A contact time of 60 minutes was required using a PAC dose of 50 mg/L. However, it was recommended that a dose of 100 mg/L PAC was needed over a shorter contact time of 20 minutes in order to achieve the compliance concentration of metaldehyde in drinking water.

Keywords:

Metaldehyde, DAF, Dissolved Air Flotation, Pesticide, Adsorption, Powdered Activated Carbon, Drinking Water, Raw Water, Kinetics.

Introduction

Metaldehyde is a pesticide used in agriculture and gardening applied as a pellet for the control of snails and slugs causing their death by desiccation (Wilkinson, 2010; Tang *et al.*, 2016). This pesticide started receiving increased attention in 2008, when the English Environmental Agency reported that, in some areas, the metaldehyde levels in source waters used for drinking water were over the European and UK drinking water quality standards. Ever since, it has been the subject of extensive investigation by both industry and the scientific community to find an efficient and economic treatment to remove it from drinking water.

As a pesticide, metaldehyde must meet the prescribed drinking water quality regulations: 0.1 µg/L for individual pesticides and 0.5 µg/L for total pesticides. However, some water companies are failing to consistently meet the pesticide compliance required for drinking water, and metaldehyde has been the pesticide which has caused most of the problems.

There are a number of ways by which metaldehyde can be removed from water (Autin *et al.*, 2012; Tao and Fletcher, 2016; Li *et al.*, 2017). However, adsorption processes using powdered activated carbon (PAC) has been demonstrated to be one of the most promising technologies to reduce metaldehyde below the prescribed limits (Nabeerasool *et al.*, 2015; Li *et al.*, 2017). Li *et al.* (2017) compared the performance of three nanoparticle catalysts with PAC for metaldehyde removal and reported that PAC was found to be the most efficient material with removal of >90%. This was 71% more than the catalyst materials.

PAC is usually dosed in a virgin (unused) state such that fresh adsorption sites are always available in the system. As a result of its small particle size, micropores have high accessibility since they are located close to the surface of the particle. This leads to shorter diffusion pathways and consequently to a more rapid adsorption when compared to GAC (Busquets *et al.*, 2014).

Several studies have shown that water quality affects the removal of targeted micropollutant compounds (Ho & Newcombe 2005; Matilainen *et al.* 2010; Amosa 2016; Jefferson *et al.* 2016; Bhatnagar & Sillanpää 2017). For example, it has been widely reported how NOM significantly reduces the adsorption capacity of PAC for targeted micropollutants as a result of competition. NOM characteristics are related to the biogeochemical cycles of the surrounding environment, therefore, NOM varies substantially in character and concentration (Fabris *et al.* 2008; Matilainen *et al.* 2010). Consequently, it is expected that NOM will be preferentially removed by PAC, thus affecting the adsorption of micropollutants by competition.

In this research, four different source waters were selected to investigate the effect that different water qualities have on the removal of metaldehyde. For this purpose, the PAC dose required to reach the compliance metaldehyde

concentration was determined for each water and the kinetics of adsorption were analysed.

Materials and Methods

Materials and Equipment

Experiments were conducted using four different source waters: Water A (Groundwater), Water B (River water), Water C (River water), and Water D (Reservoir water). Water was stored at 4°C and taken out to reach room temperature (21 ± 2 °C) prior to the experiments.

A stock solution of metaldehyde was prepared by dissolving 10 mg of metaldehyde (Sigma Aldrich, Germany) in 1 L of deionised water (DI) (15 MΩ, Pure Lab Option. Elga, UK) and mixed for 36 h. A stock solution of PAC was prepared by suspending 10 g of PAC Norit SA-Super (Cabot, USA) dried overnight at 105 °C, into 500 mL of DI water and mixing overnight. Both stock solutions were prepared weekly.

When required, the samples were filtered through a 0.45 µm filter, by using either Cellulose Nitrate Membrane Filters (Whatman, Germany) or syringe-driven filters (Milex, UK).

All the metaldehyde analyses were conducted in an external laboratory (ALS Environmental, UK). 250 mL of samples were extracted onto a pre-rinsed Strata-X cartridge. The compound was eluted using ethyl acetate/acetone mixture, followed by iso-octane. Metaldehyde is analysed by gas chromatography-mass spectrograph - selective ion monitoring (GCMS-SIM) (Full method statement in Appendix A). The experiments were conducted using a standard 6 paddle jar tester, model PB-900 (Phipps and Bird, USA).

Experimental Methods

Water Characterisation

All waters were characterised measuring pH, conductivity (pH meter Hanna Instruments, UK), UV₄₀₀, and UV₂₅₄ (Spectroquant Pharo 300, Germany), residual turbidity (2100N Turbidimeter HACH, USA), zeta potential (Zeta Sizer

Nano series Malvern, UK), suspended solids (0.5L following the standard method 2450-D (APHA, 1992)), alkalinity (HCl titrimetric method 2320B (APHA, 1992)), non-purgeable organic carbon (NPOC) (TOC-V CSH Total Organic Carbon Analyzer, Shimadzu, UK), and the concentrations of iron, and manganese (Perkin Elmer NexION 350D ICP-MS, UK), and metaldehyde. Specific UV absorbance (SUVA) was calculated by dividing UV_{254} with NPOC.

Zeta potential, turbidity, UV_{400} , UV_{254} , pH, conductivity, and alkalinity values were calculated as the average of three different measurements with the standard deviation reported. NPOC was the average result from two measurements, whilst suspended solids, iron concentrations, and manganese concentrations were the results of a single analysis.

Determination of PAC doses and kinetics of adsorption

Metaldehyde was spiked to achieve a concentration of 2 µg/L in a 20 L vessel from a stock solution of 10 mg/L. This water was used for both adsorption and kinetics experiments.

To investigate the required PAC dose, a range of PAC doses (0-200 mg/L) were added and 1 L of water was mixed at 100 rpm for 20 min. To study the adsorption kinetics, 50 mg/L of PAC was dosed and 500 mL of water was mixed at 100 rpm over a range of different contact times (0-120 min). At the end of each experiment, samples were filtered (0.45 µm) and analysed for metaldehyde concentration, NPOC, and UV_{254} .

Results

Water Characterisation

Water A is a ground water that is highly influenced by karstic geology. It, therefore, contains higher background NOM concentrations than would be expected for most ground waters as a result of significant impacts from surface water (4.9 mg/L of NPOC and 13.2 abs/m UV_{254}) and a turbidity of 11.4 NTU. Water B is a river water impacted by upland moorland. It has a high UV_{254} (20.3 abs/m), a high NPOC (5.8 mg/L), and a high turbidity (11.1 NTU). Water C is a

river water of high quality with a low NPOC (2.63 mg/L), low UV₂₅₄ (1.7 abs/m) and low turbidity (2.5 NTU). Water D has a low turbidity (1.3 NTU) because is a reservoir water, and a high NPOC concentration of 6.54 mg L⁻¹. Therefore, in general terms, Water B and D were the most laden water sources in terms of NPOC levels.

The SUVA in all waters varied from 2.1 to 3.5 L mg⁻¹ cm⁻¹. Water B had the highest SUVA of 3.5 L mg⁻¹ cm⁻¹. Typically water with a SUVA values >4 are considered hydrophobic and water with a SUVA <2 are considered hydrophilic (Zazouli *et al.*, 2007; Ghernaout, 2014). In his study, the SUVA values indicated that the waters were not dominated by either hydrophobic or hydrophilic NOM. The pH in all the waters ranged from 7.6 in Water A to 8.6 in Water C. Finally, background metaldehyde was detected only in Water D at 0.119 µg/L (Table 1).

Table 1. Water quality parameters of the four different water sources used in this research.

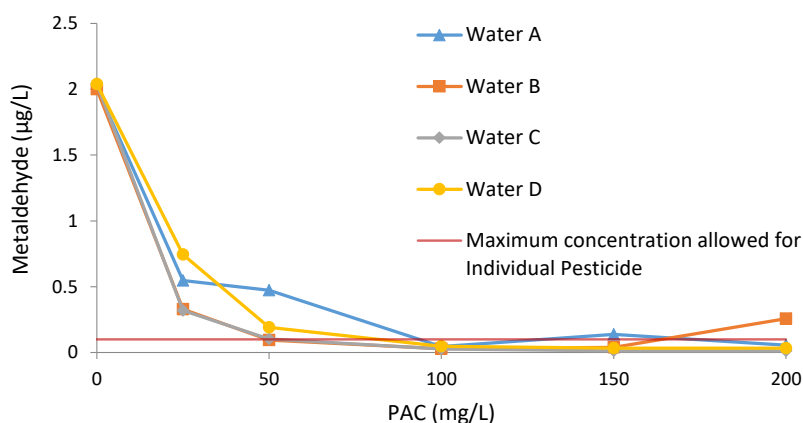
	Water A	Water B	Water C	Water D
pH	7.6 ± 0.0	8.3 ± 0.0	8.6 ± 0.0	8.3 ± 0.0
Turbidity (NTU)	11.4 ± 1.4	11.1 ± 0.3	2.5 ± 0.2	1.3 ± 0.1
UV400 (abs/m)	1.0 ± 1	1.3 ± 0.1	1.7 ± 0.2	2.1 ± 0.1
UV254 (abs/m)	13.2 ± 0.7	20.3 ± 0.2	5.43 ± 1	13.6 ± 0.9
SUVA (L/mg cm)	2.7	3.5	2.1	2.1
Conductivity (mS)	0.9 ± 0	0.5 ± 0	0.6 ± 0	0.7 ± 0
Zeta Potential (mV)	-13.3 ± 0.9	-13.6 ± 0.2	-10.7 ± 1.1	-12.2 ± 1.1
Suspended Solids (mg/L)	13.6	16.6	0.8	0.2
Alkalinity (mg CaCO ₃ /L)	250 ± 0	163 ± 2	245 ± 4	160 ± 0
Iron (mg Fe/L)	0	0,6	0	0
Mn (mg Fe/L)	0	0	0	0
NPOC (mg/L)	4.86	5.83	2.63	6.54
Metaldehyde (µg/L)	<0.005	<0.005	<0.005	0.119

Determination of PAC dose

The four waters were studied separately and the PAC dose was determined for each of them. A dose of 100 mg/L of PAC was needed to remove the metaldehyde concentration from 2 µg/L to below the compliance limit of 0.1 µg/L in the four waters (Water A: 0.045 µg/L and Water D: 0.046 µg/L). However, a PAC dose of 50 mg/L was just able to achieve compliance limits in Water B and C (0.094 µg/L for Water B and 0.10 µg/L for Water C) (Figure 1 a). As the PAC dose increased, the NPOC concentration decreased for all of the waters. Water C, which had the lowest initial NPOC concentration, also saw the lowest residual NPOC of 1.0 mg/L (Figure 1 b). On the other hand, the highest removal of NPOC, was seen in Water D (3.3 mg/L). A total of 1.2 mg/L of NPOC was removed from Water C, lower than the removals of 2.9 mg/L in Water A and of 3.3 mg/L in Water B and D.

Kinetics of adsorption

The kinetics of adsorption were investigated for the four waters for a dose of 50 mg/L of PAC. After the first 5 minutes, 85.2% metaldehyde removal was seen from Water A, 85.5% from Water B, 92.7% from water C, and 80.7% from Water D. During the following 55 minutes the metaldehyde removal achieved was: Water A: 9.9%, Water B: 12.2%, Water C: 4.4%, and Water D: 14.2%. This shows that higher mass adsorption of the metaldehyde took place at the beginning of the contact time. Regarding the NPOC, during the first 5 minutes of contact time, 31.9% NPOC removal was seen from Water A, 28.6% from Water B, 24.1% from Water C, and 30.1 % from water D. Only Water B showed a removal of 2% from the initial NPOC concentration from 60 minutes to 120 minutes of contact time. Consequently, it can be seen that most of the adsorption happened during the first minutes of contact for both NPOC and metaldehyde (Figure 2). It was also shown that the adsorption of NPOC occurred during a longer period of time.



a

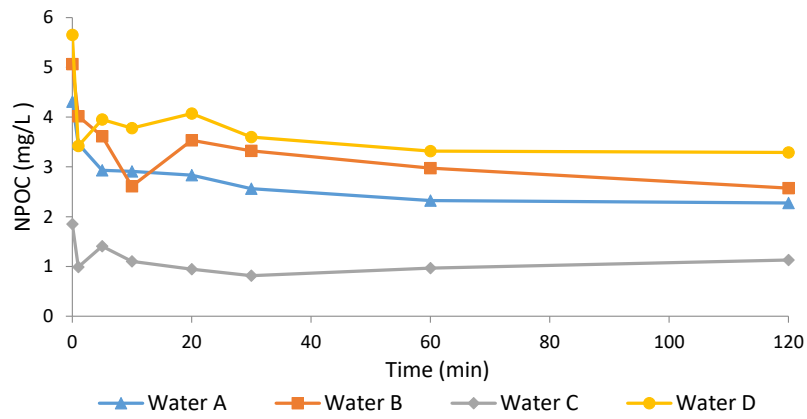
b

Figure 1 The removal of (a) metaldehyde and (b) NPOC with increasing PAC doses for the four water sources. The contact time was 20 minutes.

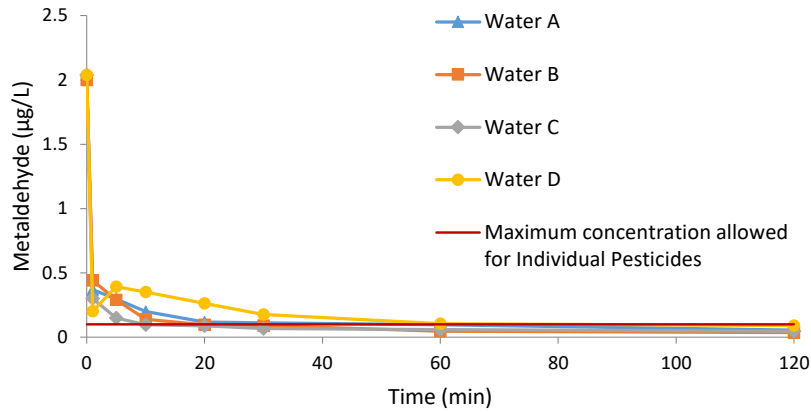
Each water required a different contact time to bring the metaldehyde concentration to below 0.1 µg/L. In water B, 0.091 µg/L was achieved after 20 minutes whereas after only 10 minutes the concentration was reduced to 0.098 µg/L in Water C. On the contrary, Water A needed 60 minutes to reduce the metaldehyde concentration to 0.097 µg/L, and Water D 120 minutes to achieve a concentration of 0.091 µg/L.

The final metaldehyde concentration achieved after 20 minutes of contact time was: Water A: 0.47 µg/L, Water B: 0.09 µg/L, Water C: 0.82 µg/L, and Water D: 0.19 µg/L. These results were compared with the final concentrations of metaldehyde achieved after the same contact time of 20 minutes but using a

higher PAC dose of 100 mg/L to show the effect of increasing concentration on removal of the pesticide (Figure 1). Water A: 0.04 $\mu\text{g/L}$, Water B: 0.03 $\mu\text{g/L}$, Water C: 0.03 $\mu\text{g/L}$, and Water D: 0.05 $\mu\text{g/L}$. The removal was clearly better with the same contact time but a higher PAC dose. In addition, these removals were also higher than those seen for longer contact times up to 120 minutes for the lower PAC dose of 50mg/L. This suggests that by increasing the PAC dose the amount of adsorption time required will decreased.



a



b

Figure 2 The removal of (a) NPOC and (b) metaldehyde with contact time using a dose of 50 mg/L PAC for the four water sources.

The data from the kinetics of adsorption were fitted to the pseudo-second-order model. The linear forms of this model were used before by Li et al. (2017) who

reported a good fit for the kinetics of metaldehyde adsorption using PAC. The four linear forms of the model were tested and the best fit to the data was selected and adopted for this research. The fits of the linearised models are shown in Appendix B.

Ho & McKay (1999) proposed Equation 1 from which the adsorption capacity of the adsorbent at a given time, Q_t , was calculated.

$$Q_t = \frac{C_0 - C_t}{PAC} \quad \text{Equation 1}$$

where C_0 is the initial concentration of metaldehyde in $\mu\text{g/L}$, C_t is the concentration of metaldehyde after removal at a given time, and PAC is the dose of PAC added (mg/L).

Equation 2 was given by Ho & McKay (1999) which was integrated and transferred into Equation 3

$$\frac{dQ_t}{dt} = k(Q_e - Q_t)^2 \quad \text{Equation 2}$$

$$\frac{t}{Q_t} = \frac{1}{kQ_e^2} + \left(\frac{1}{Q_e}\right)t \quad \text{Equation 3}$$

Based in Equation 3, a plot of t/Q_t against t to enable Q_e and k to be calculated. t was the time in minutes, Q_t ($\mu\text{g/mg}$) was the adsorption capacity of the adsorbent at a given time and was calculated according to Equation 1. Q_e ($\mu\text{g/mg}$) was the adsorption capacity at the equilibrium ($\mu\text{g/mg}$). The slope of the t/Q_t line corresponded to $\left(\frac{1}{Q_e}\right)$ from which Q_e was calculated. k was the adsorption rate constant and was calculated from equation $\left(\frac{1}{kQ_e^2}\right)$ that corresponds to the intercept value of the fitting line (Li *et al.*, 2017). For each water, k was calculated for the metaldehyde (k_{met}) and the NOM (k_{NOM}) adsorption, as well as their theoretical equilibrium adsorption capacity ($Q_{e_{met}}$ and $Q_{e_{NOM}}$). For example, for water A, the slope of $1/Q_e$ was 25.52 from which

Q_e was calculated to be 0.039 mg/g. The independent value gives the theoretical k_{met} of 28.83 g mg⁻¹ min⁻¹ (Table 2).

The obtained R^2 values varied from 0.9998 to 1, suggesting a very good fit of the data to the pseudo-second order rate model (Figure 3 and Figure 4).

The obtained adsorption capacity for metaldehyde was consistent for the four different waters with values that barely changed from 0.039 to 0.040 mg/g. On the contrary, the adsorption rate constant k , shows bigger differences, with a maximum of 79.4 g mg⁻¹min⁻¹ in Water C and a minimum of 20.99 g mg⁻¹min⁻¹ in Water D.

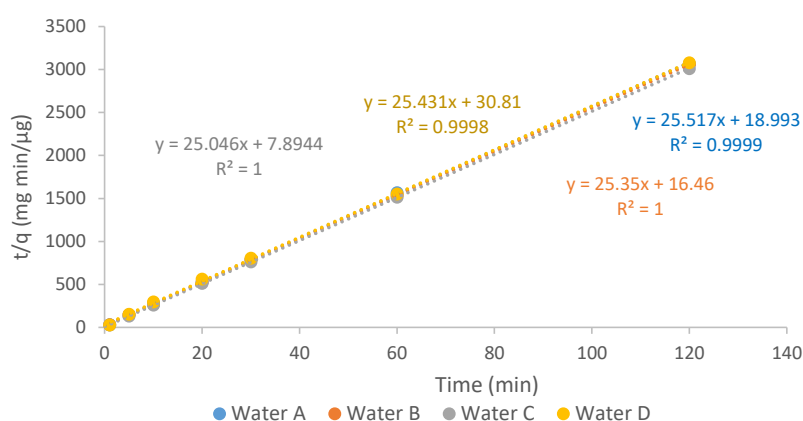


Figure 3 Metaldehyde adsorption fitted to a pseudo-second order kinetic model.

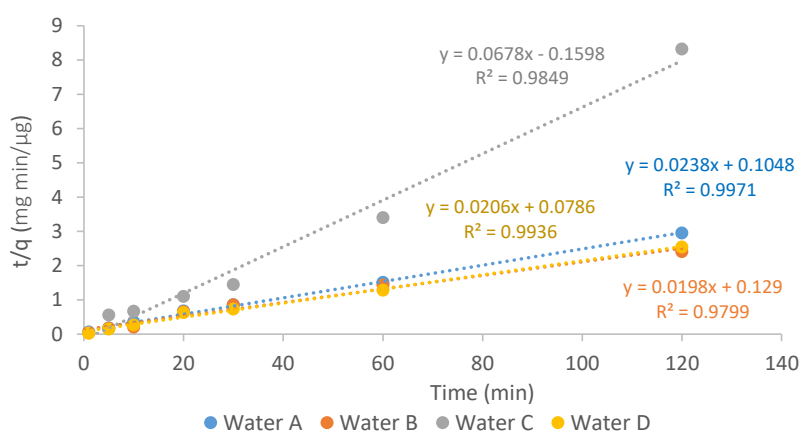
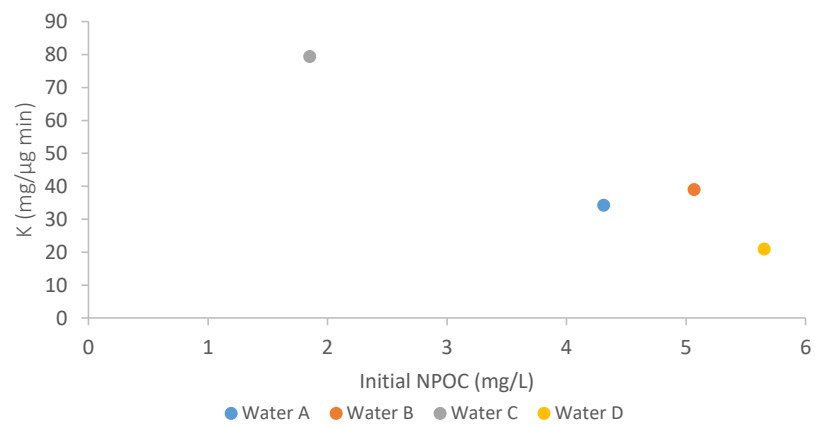


Figure 4 NPOC adsorption fitted to pseudo-second order kinetic model.

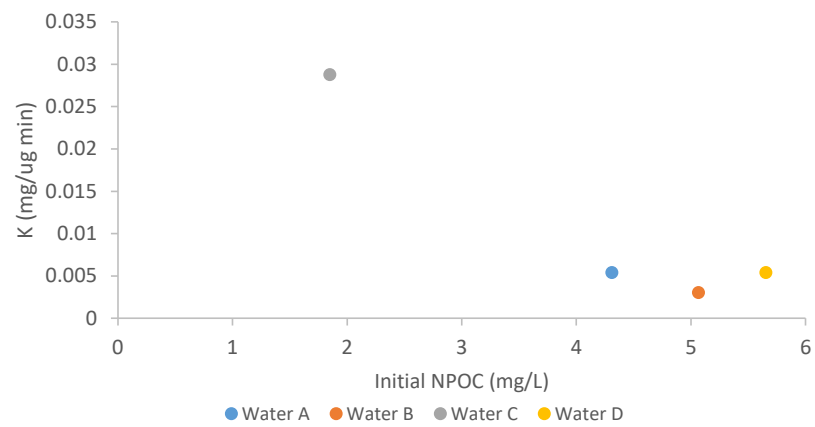
The data from the adsorption of NOM by PAC shows also a good fit with the pseudo-second-order kinetic model with R^2 ranging from 0.98 to 0.99.

In order to analyse the impact of the NOM on the kinetics and the adsorption capacity, k_{met} and k_{NOM} were plotted against the initial NPOC of the waters (Figure 5). Similarly the $Q_{e_{met}}$ and $Q_{e_{NOM}}$ were plotted against the initial NPOC (Figure 6). Regarding metaldehyde removal, the results suggest that K_{met} was inverse to the initial NPOC, so the removal of metaldehyde was more efficient when there was less NPOC present. The $Q_{e_{met}}$ was stable independently of the initial NPOC concentration. According to this, the initial concentration of NPOC did not affect the adsorption capacity of metaldehyde but it made the adsorption process slower. The K_{NOM} was higher at lower initial NPOC concentrations indicating that the adsorption of NPOC was faster at lower initial NPOC concentrations. The $Q_{e_{NOM}}$, on the contrary, shows higher values at higher NPOC concentrations.

On the other hand, according to the adsorption rate constants k_{met} and k_{NOM} , the metaldehyde adsorption was faster than the adsorption of NOM (Table 2). It should be noted that the mass adsorbed of NPOC was greater than of metaldehyde. The initial NPOC concentrations were around 3-6 mg/L whereas the initial metaldehyde concentrations were around 2 μ g/L. Therefore, when the majority of the metaldehyde was adsorbed, the NPOC removal carried on over a longer period of time.

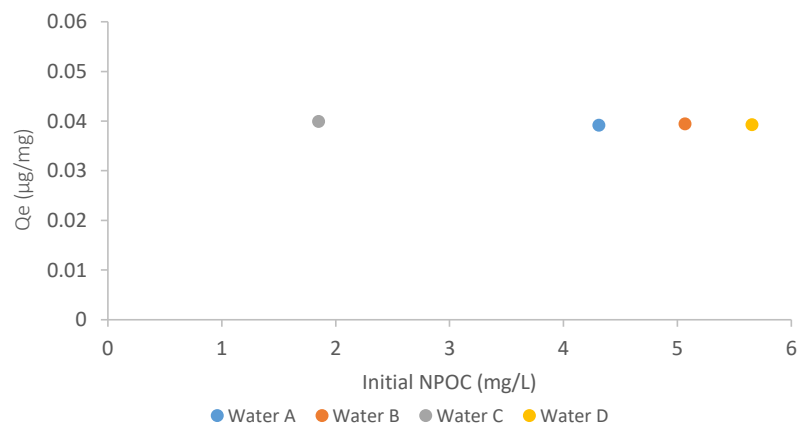


a. K_{met}

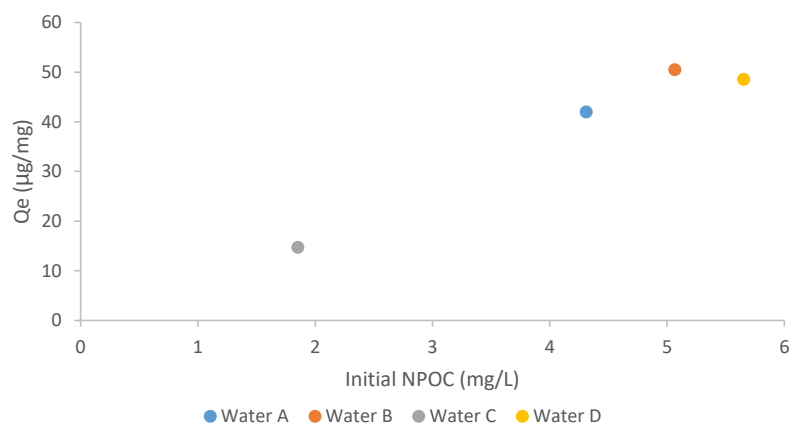


b. K_{NOM}

Figure 5 Adsorption rate constant (k) for metaldehyde (a) and NOM adsorption (b) against the initial NPOC for the four water sources.



a. $Q_{e_{\text{met}}}$



b. $Q_{e_{\text{NOM}}}$

Figure 6 Adsorption capacity (Q_e) for metaldehyde (a) and NOM adsorption (b) against the initial NPOC for the four water sources.

Table 2 Adsorption capacity and adsorption rate constant of metaldehyde and NOM for the four waters.

	Metaldehyde			NOM		
	$Q_{e_{met}}$ ($\mu\text{g mg}^{-1}$)	$Q_{e_{met}}$ ($\mu\text{g g}^{-1}$)	K_{met} ($\text{mg } \mu\text{g}^{-1}\text{min}^{-1}$)	$Q_{e_{NOM}}$ ($\mu\text{g mg}^{-1}$)	$Q_{e_{NOM}}$ ($\mu\text{g g}^{-1}$)	K_{NOM} ($\text{mg } \mu\text{g}^{-1}\text{min}^{-1}$)
Water A	0.039	39.19	34.28	42.02	42016.81	0.0054
Water B	0.039	39.45	39.04	50.5	50505.05	0.00304
Water C	0.04	39.93	79.46	14.75	14749.26	0.02877
Water D	0.039	39.32	20.99	48.54	48543.69	0.0054

Further data analysis

In order to obtain a better understanding about the mass transfer during the adsorption of metaldehyde, further analysis was conducted calculating the film diffusion coefficient, K_f (m s^{-1}) and the intra-particle diffusion coefficient, D ($\text{m}^2 \text{s}^{-1}$) (Equation 4 and Equation 5) (Urano et al., 1991; Khraisheh et al., 2002; Martin *et al.*, 2017):

$$\text{Intra-particle} \quad - \left[\log \left(1 - \left\{ \frac{Q_t}{Q_e} \right\}^2 \right) \right] = \frac{4\pi^2 D t}{2.3 d^2} \quad \text{Equation 4}$$

$$\text{Film diffusion} \quad \ln \left(\frac{C_t}{C_0} \right) = -k_f \frac{A}{V} t \quad \text{Equation 5}$$

Where Q_t and Q_e are the adsorbed amounts at time t and at equilibrium ($\mu\text{g mg}^{-1}$), the Q_e used are described in Table 2; d is the media diameter (m), C_0 is the initial concentration and C_t is the concentration at time t . A is the media area (m^2) and V is the solution volume (m^3).

The Biot number (Bi) is a dimensionless parameter usually used for investigating the rate-limiting step of adsorption. Bi relates the external mass transfer resistance with the internal mass transfer resistance and is calculated according to Equation 6 (Girish and Murty, 2016); Martin *et al.*, 2017).

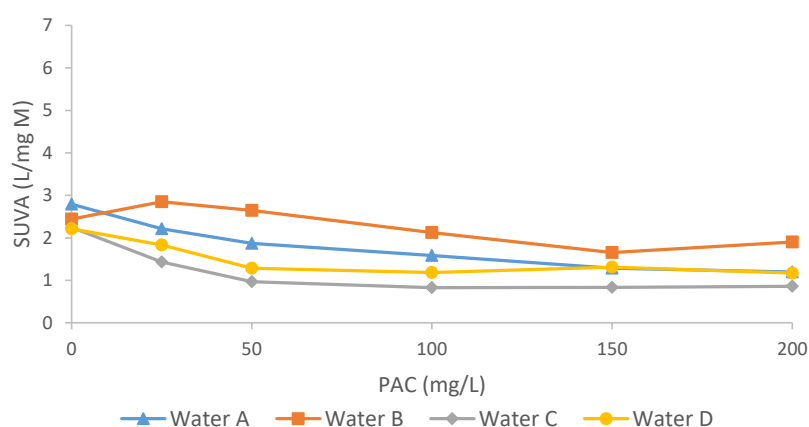
$$\text{Biot Number} \quad Bi = \frac{k_f d}{D} \quad \text{Equation 6}$$

A Bi greater than 100 indicates that the adsorption process is mainly controlled by film transfer. On the contrary, the adsorption process is mostly controlled by the internal diffusion mechanism if Bi is smaller than 100 (Baup *et al.*, 2000; Krishna Prasad and Srivastava, 2009; Girish and Murty, 2016). Since $K_f \gg D_s$, the obtained Biot numbers were very high (Table 3). All values were $\gg 100$ suggesting that the rate limiting step is strongly dependent on intra-particle diffusion (Girish and Murty, 2016). One of the main factors that influence intra-particle diffusion is the size and distribution of pores in the adsorbent. Therefore, in order to improve an adsorption process controlled by intra-particle diffusion, it may be possible to select a carbon with a different pore size distribution.

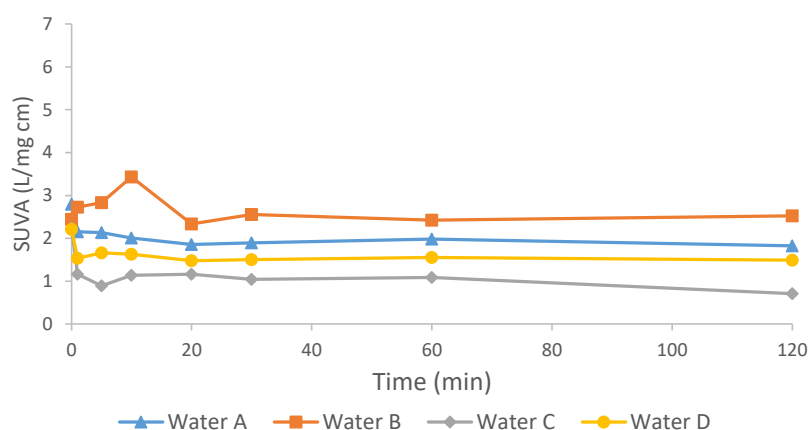
The range of SUVA in the water sources was from 2.1 to 3.5 L mg⁻¹ cm⁻¹. Because this presented a narrow band of hydrophobicities, no relationship was seen between SUVA and the capacity of adsorption or the k value. This effect was more obvious when plotting SUVA directly against PAC doses (Figure 7). The SUVA of the water decreased with an increase in the PAC dose for three out of four waters indicating that the hydrophobic compounds were removed in higher proportion than the hydrophilic compounds. Conversely, Water B showed an increase of SUVA after the first PAC doses of 25 and 50 mg/L. However, this was likely to be due to an uncertainty in the measurement of the initial NPOC as the SUVA reduced after this dose.

Table 3 Biot Number for the metaldehyde adsorption in the four waters.

	Contact time (min)	Metaldehyde concentration ($\mu\text{g L}^{-1}$)	K_f (m s^{-1})	D_s ($\text{m}^2 \text{s}^{-1}$)	$Bi \times 10^{12}$
Water A	0	2.01			
	1	0.371	39840.23	1.1E-13	5.2
	5	0.297	9017.15	2.7E-14	4.9
	10	0.199	5452.72	1.8E-14	4.5
	20	0.119	3332.54	1.39E-14	3.9
	30	0.111	2276.39	8.8E-15	3.9
	60	0.097	1191.18	4.8E-15	3.7
	120	0.056	703.53	4.1E-15	2.6
Water B	0	2			
	1	0.442	35711.46	9.3E-14	5.8
	5	0.291	9113.39	2.6E-14	5.2
	10	0.139	6298.79	2.1E-14	4.5
	20	0.098	3561.43	1.3E-14	4.2
	30	0.091	2432.53	8.7E-15	4.2
	60	0.047	1475.91	6.2E-15	3.6
	120	0.037	784.96	3.7E-15	3.2
Water C	0	2.04			
	1	0.3	44848.76	1.3E-13	5.0
	5	0.149	12269.96	4.3E-14	4.3
	10	0.098	7122.87	2.8E-14	3.8
	20	0.088	3688.32	1.5E-14	3.7
	30	0.067	2673.17	1.2E-14	3.4
	60	0.06	1379.95	6.5E-15	3.2
	120	0.047	737.96	4.5E-15	2.5
Water D	0	2			
	1	0.442	54174.38	2.0E-13	4.1
	5	0.291	7684.40	2.3E-14	5.0
	10	0.139	4114.69	1.3E-14	4.9
	20	0.098	2402.11	8.1E-15	4.5
	30	0.091	1909.65	7.2E-15	4.0
	60	0.047	1160.03	5.5E-15	3.2
	120	0.037	608.13	3.2E-15	2.8



a.



b.

Figure 7 The change in SUVA for the four waters against PAC doses (a) and time (b).

Discussion

PAC Doses and contact time determination

The PAC dose required to effectively reduce the pesticide to below regulatory standards for the four waters was determined to be 100 mg/L for an initial metaldehyde concentration of 2 μ g/L and a contact time of 20 minutes. However, some of the waters, such as Water C, might reach the compliance levels at a lower concentration of 50 mg/L of PAC. Therefore an individual adjustment is always required on a site-by-site basis to save avoidable costs of

dosing extra PAC as well as the additional resources required during the clarification.

One way to decrease the contact time is to increase the PAC doses. This allows the treatment to be adjusted according to the plant needs, enabling the possibility of increasing the PAC doses if shorter contact time is required or reduce it if a longer contact time is preferred. However, the impact of an increase of PAC dose on the clarification must be taken into account.

Since the required PAC dose was determined to be 100 mg/L for most of the water sources, it is expected that the contact time needed to achieve metaldehyde concentrations less than 0.1 µg/L will be reduced. Results indicated that after 20 minutes of contact time, the metaldehyde concentrations were under the pesticide compliance limits (Figure 1). However further research would be needed to confirm and determine the required contact time for a PAC doses of 100 mg/L.

Kinetics of adsorption

In terms of kinetics, the R^2 values obtained were very high (0.99-1), indicating that the data were well fitted to the pseudo-second-order model, confirming the results seen in previous studies for metaldehyde and phosphorus removal (Luo *et al.*, 2010; Martin *et al.*, 2017). Moreover, higher NPOC concentrations resulted in lower k for NOM and metaldehyde, indicating that longer contact times will be required in waters with high NPOC concentrations (Figure 5). Therefore, as expected the kinetics of metaldehyde adsorption were influenced by the water quality.

The results did not show any relationship between the adsorption capacity at equilibrium, Q_e , and the adsorption rate, which is in agreement with the observations made by Li *et al.* (2017) who saw that high adsorption capacities does not lead to high adsorption rates. The adsorption capacity for NOM was much higher than for metaldehyde. The adsorption capacity does not consider the variables that influence the adsorption rate such as the distribution of the

adsorption sites and pores. Therefore, a low adsorption capacity could present high adsorption rates if the adsorbate is rapidly adsorbed in the pores.

The adsorption capacities (Q_e) for metaldehyde obtained in this study (39.19 to 39.93 $\mu\text{g g}^{-1}$) were approximately 500 times smaller than the 23.04 mg g^{-1} reported by Li et al. (2017) for PAC adsorption of metaldehyde from deionised water. It is not surprising that there was a difference between the metaldehyde adsorption achieved in pure water and in raw waters where NOM or even other pesticides may be present and interfere on the efficiency of adsorption. However, the difference between the adsorption capacities reported by Li et al. (2017) and this study were bigger than expected showing the big influence background organic compounds have on removal of micropollutants. In addition, the starting concentration of metaldehyde were very different between these two investigations. Li et al. (2017) studied metaldehyde concentrations from 0.1 mg/L to 15 mg/L.

In this study the calculated values of k_{met} were much higher than those reported by Li et al. (2017) from their study in pure water (Table 2). Water D had the lowest adsorption rate constant of 20.99 $\text{mg } \mu\text{g}^{-1}\text{min}^{-1}$ obtained for metaldehyde. This is more than 900 times higher than the 0.023 $\text{mg } \mu\text{g}^{-1}\text{min}^{-1}$ reported by their study and it is also higher compared to the $8 \times 10^{-5} \text{ mg } \mu\text{g}^{-1}\text{min}^{-1}$ obtained for GAC by Salvestrini et al. (2016). These differences between the characterisation of the adsorption of metaldehyde from different studies are probably due to the different starting concentrations of metaldehyde used. As noted above Li et al. (2017) used higher initial metaldehyde concentrations. Similarly, Salvestrini et al. (2016) used metaldehyde concentrations between 1 and 30 mg/L. In this study, the starting metaldehyde concentrations was always around 2 $\mu\text{g L}^{-1}$. The adsorption of the metaldehyde is particularly challenging at lower concentrations, particularly in the presence of higher background NOM concentrations.

Although the obtained k_{met} were higher than k_{NOM} , the mass being reviewed was considerably higher for NOM than for metaldehyde. Regarding NOM, the K_{NOM} for the different waters were lower than those obtained for the adsorption of

metaldehyde with values from 0.00304 to 0.028 mg $\mu\text{g}^{-1}\text{min}^{-1}$. Therefore, despite the fact that the adsorption capacity of the NOM was much higher than for metaldehyde, the amount of metaldehyde that was removed was adsorbed faster than the NOM. This supports the previous discussion about the lack of relationship between the adsorption capacity and the adsorption rate.

In adsorption, it is generally accepted that the most important steps in the adsorption process and thus, those which determine the kinetics, are the mass transfer through the liquid film at the adsorbent surface, and the diffusion of the adsorbate within the adsorbent, in this case the activated carbon (Díaz Delgado, 2003). The results support such affirmation, since the calculated Biot number for the different waters indicate that the adsorption kinetics are strongly dependent on surface diffusion, hence, this was the rate limiting mechanism.

The influence of different water sources on metaldehyde adsorption

The biggest difference in adsorption was seen for river Water C, whose UV_{254} (5.43 m^{-1}) and NPOC (2.63 mg/L) were significantly lower than for the other waters. For this water, the highest rates of metaldehyde adsorption were seen. As previously discussed, the calculated adsorption capacity for metaldehyde was almost identical for all of the waters. However, the adsorption capacity for NOM was much more variable for the different water sources. The Q_{eNOM} in Water C was 14.75 $\mu\text{g mg}^{-1}$ whereas in Water A, B and D it ranged from 42.02 to 50.50 $\mu\text{g mg}^{-1}$. This is a big difference in the adsorption capacity associated with this water. Conversely, Water C presented the highest rate of adsorption for NOM, 0.29 mg $\mu\text{g}^{-1}\text{min}^{-1}$, against values from 0.003 and 0.005 mg $\mu\text{g}^{-1}\text{min}^{-1}$ showing the most rapid adsorption of NOM in all waters. It is possible that this efficiency was due to the lower starting concentration of NPOC in this water, but it could also be related to the compounds that characterised the NOM. This would require further characterisation of the NOM to confirm the impact of NOM characteristics on adsorption.

Other factors that influence the adsorption

In a process where kinetics are controlled by intra-particle diffusion such as the adsorption of metaldehyde by PAC, one option to increase the velocity of adsorption is to change the type of carbon. The type of carbon selected affects the adsorption since different activated carbons have different pore size distributions and surface properties. The importance of the type of carbon has been previously highlighted. Busquets et al. (2014) reported that the type of carbon significantly affected the uptake of metaldehyde whereas the type of water did not.

One of the characteristics of the activated carbon that is important is the selectivity of adsorption for target contaminants. In general, activated carbon shows greater affinity for molecules that have certain characteristics. For instance, the adsorption of larger molecules over smaller molecules, and non-polar molecules over polar molecules is favoured and slightly soluble molecules adsorb more than highly soluble molecules (Parsons and Jefferson, 2006).

The results indicate that the adsorption of NPOC was faster at lower NPOC concentrations. It may be that at lower NOM concentrations there was less obstruction of pores and thus more efficient adsorption. In addition, the rate of the adsorption could also be affected by the composition of the NOM. Moreover, it was found that at lower concentrations of NPOC, the adsorption of metaldehyde was faster. Similarly, the adsorption capacity was higher for metaldehyde when the NPOC was lower suggesting less competition between NOM and metaldehyde under these conditions. It would therefore be interesting to see if the competition between NOM and metaldehyde is always to the detriment of metaldehyde adsorption, or if the adsorption of metaldehyde also produces a decrease on the NOM adsorbed.

Further investigation would be required for a better understanding of these processes, particularly, the characterisation of the organic matter present in each water.

Conclusions

- The PAC dose required to remove the metaldehyde to under 0.1 µg/L for all of the four water sources was 100 mg/L with a contact time of 20 minutes.
- The pseudo-second-order model provided the best fit for modelling the kinetics of metaldehyde adsorption by PAC.
- The water quality influenced the adsorption rate. Both, the removal of metaldehyde and NOM were more efficient when there was less NOM present. PAC showed a better adsorption capacity for metaldehyde when NPOC was reduced. Conversely, $Q_{e,NOM}$, showed higher values at higher NPOC concentrations.
- The adsorption rate of metaldehyde was strongly dependent on intra-particle diffusion.
- The treatment should be adjusted to the particular conditions of each water to optimise the efficiency and avoid overdosing or longer contact time than needed.

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References

AHDB Potatoes (2014) *Appeal to adhere to metaldehyde stewardship*. Available at: <https://potatoes.ahdb.org.uk/news/appeal-adhere-metaldehyde-stewardship> (Accessed: 8 December 2017).

Amosa, M. K. (2016) 'Sorption of water alkalinity and hardness from high-strength wastewater on bifunctional activated carbon: process optimization, kinetics and equilibrium studies', *Environmental Technology*. Taylor & Francis, 37(16), pp. 2016–2039.

Autin, O., Hart, J., Jarvis, P., MacAdam, J., Parsons, S. A. and Jefferson, B. (2012) 'Comparison of UV/H₂O₂ and UV/TiO₂ for the degradation of

metaldehyde: Kinetics and the impact of background organics', *Water Research*, 46(17), pp. 5655–5662. doi: 10.1016/j.watres.2012.07.057.

Baup, S., Jaffre, C., Wolbert, D. and Laplanche, A. (2000) 'Adsorption of pesticides onto granular activated carbon: Determination of surface diffusivities using simple batch experiments', *Adsorption*, 6(3), pp. 219–228.

Bhatnagar, A. and Sillanpää, M. (2017) 'Removal of natural organic matter (NOM) and its constituents from water by adsorption – A review', *Chemosphere*, 166, pp. 497–510.

Busquets, R., Kozynchenko, O. P., Whitby, R. L. D., Tennison, S. R. and Cundy, A. B. (2014) 'Phenolic carbon tailored for the removal of polar organic contaminants from water: A solution to the metaldehyde problem?', *Water Research*, 61(0), pp. 46–56.

Castle, G. D., Mills, G. A., Gravell, A., Jones, L., Townsend, I., Cameron, D. G. and Fones, G. R. (2017) 'Review of the molluscicide metaldehyde in the environment', *Environ. Sci.: Water Res. Technol.*, 3(3), pp. 381–574.

Cook, D., Newcombe, G. and Sztajn bok, P. (2001) 'The application of powdered activated carbon for MIB and geosmin removal: Predicting PAC doses in four raw waters', *Water Research*, 35(5), pp. 1325–1333.

Crossley, I. A. and Valade, M. T. (2006) 'A review of the technological developments of dissolved air flotation', *Journal of Water Supply: Research and Technology—AQUA*, 55(7–8), pp. 479–491. doi: 10.2166/aqua.2006.057.

Díaz Delgado, C. (2003) *Agua potable para comunidades rurales, reuso y tratamientos avanzados de aguas residuales domésticas*, RIPDA-CYTED. Buenos Aires.

Duan, J., Wilson, F., Graham, N. and Tay, J. . (2001) 'Adsorption of humic acid by powdered activated carbon in saline water conditions', *Desalination*, 151, pp. 53–66.

Edzwald, J. K. (2010) 'Dissolved air flotation and me', *Water Research*, 44(7),

pp. 2077–2106. doi: 10.1016/j.watres.2009.12.040.

Edzwald, J. K., Walsh, J. P., Kaminski, G. S., Dunn, H. J., Journal, S., Water, A., Association, W., March, R. U., Edzwald, J. K., Walsh, J. P., Kaminski, G. S. and Dunn, H. J. (1992) 'Flocculation and Air requirements for dissolved air flotation', *American Water Works Association*, 84(3), pp. 92–100.

Etchepare, R., Oliveira, H., Azevedo, A. and Rubio, J. (2017) 'Separation of emulsified crude oil in saline water by dissolved air flotation with micro and nanobubbles', *Separation and Purification Technology*, 186, pp. 326–332. doi: 10.1016/j.seppur.2017.06.007.

Fabris, R., Chow, C. W. K., Drikas, M. and Eikebrokk, B. (2008) 'Comparison of NOM character in selected Australian and Norwegian drinking waters', *Water Research*, 42(15), pp. 4188–4196. doi: 10.1016/j.watres.2008.06.023.

FERA (2016) *PUS Stats*. Available at: <https://secure.fera.defra.gov.uk/pusstats/> (Accessed: 10 September 2016).

Get Pelletwise! (2012) *Restriction period for metaldehyde begins*. Available at: http://www.getpelletwise.co.uk/news/restriction_period_for_metaldehyde_begin_s/ (Accessed: 11 August 2016).

Gheraout, D. (2014) 'The hydrophilic/hydrophobic ratio vs. dissolved organics removal by coagulation - A review', *Journal of King Saud University - Science*. King Saud University, 26(3), pp. 169–180.

Girish, C. R. and Murty, V. R. (2016) 'Mass Transfer Studies on Adsorption of Phenol from Wastewater Using Lantana camara, Forest Waste', *International Journal of Chemical Engineering*, 2016.

Han, M. Y. (2002) 'Modeling of DAF: The effect of particle and bubble characteristics', *Journal of Water Supply: Research and Technology - AQUA*, 51(1), pp. 27–34.

Henderson, R. K., Parsons, S. A. and Jefferson, B. (2008) 'Surfactants as Bubble Surface Modifiers in the Flotation of Algae : Dissolved Air Flotation That

Utilizes a Chemically Modified Bubble Surface', 42(13), pp. 4883–4888.

Henderson, R. K., Parsons, S. A., Jefferson, B., Henderson, R. K., Parsons, S. A. and Jefferson, B. (2010) 'Polymers as bubble surface modifiers in the flotation of algae', 31(January).

Ho, L. and Newcombe, G. (2005) 'Effect of NOM, turbidity and floc size on the PAC adsorption of MIB during alum coagulation', *Water Research*, 39(15), pp. 3668–3674. doi: 10.1016/j.watres.2005.06.028.

Ho, Y. S. and McKay, G. (1999) 'Pseudo-second order model for sorption processes', *Process Biochemistry*, 34(5), pp. 451–465.

Jarvis, P., Jefferson, B., Gregory, J. and Parsons, S. A. (2005) 'A review of floc strength and breakage', *Water Research*, 39(14), pp. 3121–3137.

Jefferson, B., Jarvis, P., Bhagyanathan, G. K., Smith, H., Autin, O., Goslan, E. H., MacAdam, J. and Carra, I. (2016) 'Effect of elevated UV dose and alkalinity on metaldehyde removal and THM formation with UV/TiO₂ and UV/H₂O₂', *Chemical Engineering Journal*, 288.

Kay, P. and Grayson, R. (2014) 'Using water industry data to assess the metaldehyde pollution problem', *Water and Environment Journal*, 28(3), pp. 410–417.

Kegley, S.E., Hill, B.R., Orme S., Choi A.H. (2016) *Pesticides Database-Chemicals - Metaldehyde*, PAN - Pesticide Action Network. Available at: http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC32878 (Accessed: 11 August 2016).

Khraisheh MAM, Al-Degs YS, Allen SJ, and Ahmad M.N.. *Elucidation of controlling steps of reactive dye adsorption on activated carbon*. Ind Eng Chem Res. 2002;41:1651–1657.

Kouras, A., Zouboulis, A., Samara, C. and Kouimtzis, T. (1995) 'Removal of pesticides from surface waters by combined physicochemical processes. Part I: Dodine', *Chemosphere*, 30(12), pp. 2307–2315.

Kouras, A., Zouboulis, A., Samara, C. and Kouimtzis, T. (1998) 'Removal of pesticides from aqueous solutions by combined physicochemical processes - The behaviour of lindane', *Environmental Pollution*, 103(2–3), pp. 193–202.

Krishna Prasad, R. and Srivastava, S. N. (2009) 'Sorption of distillery spent wash onto fly ash: Kinetics and mass transfer studies', *Chemical Engineering Journal*, 146(1), pp. 90–97.

Li, Z., Kim, J. K., Chaudhari, V., Mayadevi, S. and Campos, L. C. (2017) 'Degradation of metaldehyde in water by nanoparticle catalysts and powdered activated carbon', *Environmental Science and Pollution Research*. *Environmental Science and Pollution Research*, 24(21), pp. 17861–17873.

Luo, T., Cui, J., Hu, S., Huang, Y. and Jing, C. (2010) 'Arsenic removal and recovery from copper smelting wastewater using TiO₂', *Environ Sci Technol*, 44(23), pp. 9094–9098.

Marshal, J. (2013) *Briefing paper on , Water UK, Water UK*. Available at: [https://www.water.org.uk/sites/default/files/documents/Policy-Briefings/Water UK Policy briefing Metaldehyde 13 Aug 2013_0.pdf](https://www.water.org.uk/sites/default/files/documents/Policy-Briefings/Water%20UK%20Policy%20briefing%20Metaldehyde%2013%20Aug%202013_0.pdf).

Martin, B. D., De Kock, L., Gallot, M., Guery, E., Stanowski, S., MacAdam, J., McAdam, E. J., Parsons, S. A. and Jefferson, B. (2017) 'Quantifying the performance of a hybrid anion exchanger/adsorbent for phosphorus removal using mass spectrometry coupled with batch kinetic trials', *Environmental Technology (United Kingdom)*. Taylor & Francis, 0(0), pp. 1–11.

Matilainen, A., Vepsäläinen, M. and Sillanpää, M. (2010) 'Natural organic matter removal by coagulation during drinking water treatment: A review', *Advances in Colloid and Interface Science*, 159(2), pp. 189–197.

Matsui, Y., Fukuda, Y., Inoue, T. and Matsushita, T. (2003) 'Effect of natural organic matter on powdered activated carbon adsorption of trace contaminants: Characteristics and mechanism of competitive adsorption', *Water Research*, 37(18), pp. 4413–4424.

Nabeerasool, M. A., Campen, A. K., Polya, D. A., Brown, N. W. and van

Dongen, B. E. (2015) 'Removal of metaldehyde from water using a novel coupled adsorption and electrochemical destruction technique', *Water (Switzerland)*, 7(6), pp. 3057–3071. doi: 10.3390/w7063057.

Parsons, S. A. and Jefferson, B. (2006) *Potable Water Treatment Processes*. Oxford: Blackwell Publishing.

Ribeiro, P. and Daniel, L. A. (2016) 'Dissolved air flotation as a potential treatment process to remove Giardia cysts from anaerobically treated sewage', *Environmental Technology*. Taylor & Francis, 38:19(November), pp. 2392–2399.

Salvestrini, S., Vanore, P., Bogush, A., Mayadevi, S. and Campos, L. C. (2016) 'Sorption of metaldehyde using granular activated carbon', *Journal of Water Reuse and Desalination*, (1), p. jwrd2016074.

Shutova, Y., Karna, B. L., Hambly, A. C., Lau, B., Henderson, R. K. and Le-Clech, P. (2016) 'Enhancing organic matter removal in desalination pretreatment systems by application of dissolved air flotation', *Desalination*, 383, pp. 12–21.

Tang, L. L., DeNardo, M. A., Gayathri, C., Gil, R. R., Kanda, R. and Collins, T. J. (2016) 'TAML/H₂O₂ Oxidative Degradation of Metaldehyde: Pursuing Better Water Treatment for the Most Persistent Pollutants', *Environmental Science & Technology*, 50, p. acs.est.5b05518.

Tao, B. and Fletcher, A. (2016) 'Development of a novel dual-stage method for metaldehyde removal from water', *Chemical Engineering Journal*, 284, pp. 741–749.

Tomaszewska, M., Mozia, S. and Morawski, A. W. (2004) 'Removal of organic matter by coagulation enhanced with adsorption on PAC', *Desalination*, 161(1), pp. 79–87.

Urano K, Tachikawa H. *Process development for removal and recovery of phosphorus from wastewater by a new adsorbent. Adsorption rates and breakthrough curves*. Ind Eng Chem Res. 1991;30:1897–1899.

- Uyak, V., Yavuz, S., Toroz, I., Ozaydin, S. and Genceli, E. A. (2007) 'Disinfection by-products precursors removal by enhanced coagulation and PAC adsorption', *Desalination*, 216(1–3), pp. 334–344.
- Wang, Y.-J., Wu, C.-D., Duan, Y. and Zhang, Z.-L. (2016) 'Removal of pollutants by enhanced coagulation combined PAC with variable charge soils: flocs' properties and effect of pH', *Environmental Technology*, 33(30)(March), pp. 1–8.
- Wilkinson, P. G. (2010) *Characterisation of the bacterial flora associated with the grey field slug Deroceras reticulatum and assessment of its suitability as a target for biological control*. Available at: <http://hdl.handle.net/1842/5276>.
- Yu, W., Gregory, J. and Campos, L. C. (2011) 'Breakage and re-growth of flocs: Effect of additional doses of coagulant species', *Water Research*, 45(20), pp. 6718–6724.
- Yukselen, M. A. and Gregory, J. (2004) 'The reversibility of floc breakage', *International Journal of Mineral Processing*, 73(2–4), pp. 251–259.
- Zazouli, M. A., Nasser, S., Mahvi, A.H., Mesdaghinia A.R., Younecian, M., and Gholami M. (2007) 'Determination of Hydrophobic and Hydrophilic Fractions of Natural Organic matter.pdf', *Journal of Applied Sciences*, 7(18), pp. 2651–2655. Available at: <http://www.sid.ir/FileServer/JE/1044620120103>.
- Zhao, Y. X., Gao, B. Y., Shon, H. K., Cao, B. C. and Kim, J. H. (2011) 'Coagulation characteristics of titanium (Ti) salt coagulant compared with aluminum (Al) and iron (Fe) salts', *Journal of Hazardous Materials*, 185(2–3), pp. 1536–1542. doi: 10.1016/j.jhazmat.2010.10.084.

4 The impact of dosing sequence on metaldehyde removal and floc properties in a combined PAC/DAF process.

Abstract

The removal of metaldehyde from drinking water to below the pesticide compliance limit has been a problem for some water companies. A combined treatment of dissolved air flotation (DAF) and powdered activated carbon (PAC) was investigated as a treatment process for metaldehyde removal. The PAC dosing position relative to the coagulant was studied regarding its impact on the removal of NOM and metaldehyde, the floc formation and the clarification efficiency. The simultaneous addition of coagulant and PAC resulted in the lowest removal of metaldehyde. PAC dosed alone achieved the best metaldehyde removal but it was poorly clarified. It was also shown that clarification by DAF was compromised as the PAC dose increased due to ineffective incorporation of PAC into the floc.

Keywords:

Metaldehyde, Dissolved Air Flotation, Pesticide, Adsorption, Powdered Activated Carbon, Drinking Water.

Introduction

Metaldehyde is a pesticide that has been used since the 1940s, particularly in wet regions (Kay and Grayson, 2014). It is applied in agriculture and gardening, mostly as a pellet, for the control of snails and slugs causing their death by desiccation (Wilkinson, 2010; Tang *et al.*, 2016). Metaldehyde is particularly difficult to remove from water by treatment processes. It started receiving increased attention in 2008, when the UK Environment Agency reported that, in some areas, the metaldehyde levels in water sources used for drinking water and in drinking water itself were over the European and UK drinking standards (0.1 µg/L for individual pesticides and 0.5 µg/L for total pesticides) (Water UK, 2013). Since then, it has been the subject of extensive investigation by both

industry and the scientific community to find an efficient and economic treatment to remove it from drinking water.

New technologies have been investigated for this purpose such as advanced oxidation processes (Autin *et al.*, 2012), ion-exchange resins (Tao and Fletcher 2016), and powdered activated carbon (PAC) (Li *et al.*, 2017). Adsorption processes using PAC have been shown to be able to reduce metaldehyde to below the limits set by the regulation if dosed at high enough concentration (Nabeerasool *et al.*, 2015). Li *et al.* (2017) reported that PAC achieved almost 90% removal. PAC is usually dosed into the contaminated water as a fine powder (diameter smaller than 45 μm), prior to, or with, the coagulant. The PAC is then agglomerated into the flocs by coagulation and removed from the water by clarification processes. The clarification can be achieved using sedimentation or flotation processes. This research has focussed on combining PAC with dissolved air flotation (DAF).

The combination of PAC and DAF needs to consider the most appropriate dosing position of the adsorbent. This is a balance between allowing sufficient adsorption time and the ability to remove the PAC from the water. Despite the fact that PAC is commonly dosed prior to the coagulant, the studies regarding the optimum dosing position of PAC are contradictory. Kouras *et al.* (1995) argued that the best removal efficiency of the fungicide dodine by PAC addition was obtained when the PAC was dosed at least 30 minutes after the coagulant. Their following research on lindane removal, supported the previous conclusion when they reported an increase in adsorption rate when PAC was dosed in the same way (Kouras *et al.*, 1998). On the contrary, Cook *et al.* (2001) showed that PAC should be dosed at least 30 min before the coagulant addition for (Methyl-Isoborneol (MIB) and geosmin removal. Other authors suggest that the addition of PAC one minute before the coagulant leads to the best removal of contaminants such as humic acids (Duan *et al.*, 2001). There is therefore a need to better understand how PAC should be dosed into water when used in combination with DAF, particularly for removal of recalcitrant compounds such as metaldehyde. The sequence of addition also has an impact not only on the

adsorption capacity but also on the floc formation and thus, on the clarification efficiency. This study therefore investigated three different dosing scenarios:

1. ***Dosing PAC first then the coagulant.*** When dosing PAC first, it was hypothesised that there would be more time to adsorb metaldehyde before being incorporated into the floc where its adsorption capacity is potentially reduced. However, in this case there is also opportunity for competition between NOM and the targeted contaminant for adsorption sites.
2. ***Dosing PAC with the coagulant.*** When coagulant and PAC are dosed together, PAC may be better incorporated in to the floc but its adsorption capacity may decrease when it is contained in a floc.
3. ***Dosing coagulant first then the PAC.*** It was hypothesised that when dosing coagulant first, the coagulant removes NOM, reducing the competition between metaldehyde and NOM. However, there may be ineffective clarification in such a dosing scenario.

A balance between the PAC dosed and the clarification needs to be reached for efficient treatment. Consequently, the specific objectives of this study were to (1) analyse the effect that the dosing position of PAC has on the removal of metaldehyde; (2) study how PAC affects floc formation; and (3) determine the parameters that lead to effective clarification by DAF. The results were expected to provide useful data for the implementation of PAC-DAF as a treatment for the removal of metaldehyde.

Materials and Methods

4.1.1 Materials and Equipment

The raw water used in these experiments was collected from a reservoir receiving water from both upland and lowland sources (See Table 1, Water D). Water samples were collected three times during the study to account for potential variations in water quality. Water was stored at 4°C and then allowed to equilibrate to room temperature (21 ± 2 °C) prior to the experiments.

A stock solution of metaldehyde was prepared by dissolving 10 mg of metaldehyde (Sigma Aldrich, Germany) in 1 L of deionised water (DI) (15 MΩ, Pure Lab Option. Elga, UK) and mixed for 36 h. A stock solution of PAC was prepared by suspending 10 g of PAC Norit SA-Super (Cabot, USA) dried overnight at 105 °C, into 500 mL of DI water and mixed overnight. Stock solutions were freshly prepared each week. All chemicals used were of analytical grade or above. Ferric sulphate (Ferrisol xl, EA, West) was used as the coagulant, while HCl (1M, Fisher Scientific, UK), and NaOH (Fisher Scientific, UK) were added to adjust pH. When required, the samples were filtered through a 0.45 µm filter, by using either Cellulose Nitrate Membrane Filters (Whatman, Germany) or syringe-driven filters (Milex, UK).

UV₂₅₄ and turbidity were measured in some experiments using respectively a Spectroquant Pharo 300 (Germany); and a 2100N Turbidimeter (HACH, USA). Metaldehyde analyses were conducted in an external laboratory (ALS Environmental, UK). 250 mL of samples were extracted onto a pre-rinsed Strata-X cartridge. The compound was eluted using ethyl acetate/acetone mixture, followed by iso-octane and metaldehyde was then analysed by gas chromatography-mass spectrograph - selective ion monitoring (GCMS-SIM) (Full method statement in Appendix A).

The experiments were conducted using a standard 6 paddle jar tester, model PB-900 (Phipps and Bird, USA) and a DAF saturator Platypus 4G DAF System (Platypus, USA) that aims to simulate coagulation/flocculation and clarification processes used at a full-scale water treatment plant. In this system, pressurised air-saturated water is released into the water to produce bubbles that attach to floc. When DAF is implemented in water treatment plants, part of the clarified water is saturated with air and used as the flow that is released for the clarification of the next water to treat. However, it is not possible to use directly recycled water with the equipment used for this study. Therefore, when the term 'recycle ratio' is used here, it refers to the equivalent flow that would be released if recycling was possible.

4.1.2 Experimental Methods

Coagulant dose determination and the impact of different parameters on effective clarification

During 1 min of rapid mixing (300 rpm), ferric sulphate and PAC were added to 1 L of raw water, and adjusted to pH 4.5. These conditions were identified as being optimum from preliminary experiments (Appendix C). The mixing speed was then reduced to 55 rpm for 10 mins. At the end of the slow mixing period, a flow of air-saturated water was injected into the sample followed by 10 minutes of clarification by flotation (0 rpm). Samples were analysed for residual turbidity and, after filtration (0.45 µm), for UV₂₅₄.

Optimum coagulant dose determination

In order to determine the optimum coagulation doses, coagulant addition from 4 to 9 mg/L as Fe were tested with and without PAC in a set of experiments where pH (4.5), recycling ratio (10%), and PAC dose (0 or 50 mg/L) were fixed.

PAC dosing conditions and flotation recycle ratio

In order to study the influence of different parameters on clarification, the same experiments were repeated focusing on the recycle ratio, and then on the PAC dose. The standard conditions used during these tests were: pH 4.5 and coagulant dose: 7 mg/L as Fe of Fe₂(SO₄)₃ (Figure 9). These conditions were maintained while testing the other parameters.

Two different sets of experiments were then carried out. Firstly the recycle flow rate was tested at 5, 10, 15, and 20 %. Here the PAC dose was kept at 50 mg/L. Secondly, different PAC doses were applied (25, 50, 100, 150, 200 mg/L) using a 10 % recycle ratio. Residual turbidity and UV₂₅₄ were used as indicators to assess the degree of clarification achieved after DAF and the air-solid ratio (a_s) was calculated for each of these experiments, using the following formula from Parsons & Jefferson (2006):

$$a_s = \frac{(19.5P)R}{C_{feed}} \quad \text{Equation 7}$$

where P is the pressure in atmospheres (5.92 atm for this research), R is the recycle ratio, and C_{feed} is the influent solids concentration. To calculate the C_{feed} , an estimation of suspended solids was calculated based on the following expression from Parsons & Jefferson (2006):

$$\begin{aligned} \text{Suspended solids } \left(\frac{\text{mg}}{\text{l}} \right) = & \quad \text{Equation 8} \\ 2 \times \text{turbidity (NTU)} + 1.9 \times \text{iron precipitated } \left(\frac{\text{mg}}{\text{l}} \text{Fe} \right) + \\ \text{NPOC } \left(\frac{\text{mg}}{\text{l}} \right) + \text{PAC dosed } \left(\frac{\text{mg}}{\text{l}} \right) \end{aligned}$$

NPOC was derived from the relationship between NPOC and UV_{254} for this water as the NPOC was not directly measured in these tests (Appendix D).

The effect of PAC dosing on floc formation during the removal of pesticides

These experiments focused on studying the impact of PAC concentration on floc formation by measuring the floc strength and recoverability. Five different doses of PAC were tested (0, 25, 50, 100, and 200 mg/L). The coagulant dose was 7 mg/L as Fe as obtained from previous experiments. A laser diffraction particle sizing instrument (Mastersizer 3000, Malvern, UK) was used to monitor the floc size during a standard jar test using samples of 1L of raw water spiked with 2 $\mu\text{g/L}$ of metaldehyde. The suspension was continuously extracted from the jar to the particle sizer by an inflow tube and guided through the optical unit of the Mastersizer for analysis and returned to the cylindrical jar through an outflow tube. The tubes were of 5 mm internal diameter. Flow was pumped through the particle sizer by a peristaltic pump powered by a pump at a flow rate of 30 rpm. The tubes were secured to the sides of the jar, opposite one another at a depth of approximately 2.5 cm to avoid the intrusion of bubbles at high shear rates. In these test the following protocol was used: PAC dose (0-200 mg/L) was added followed by 2 mins of rapid mixing at 200 rpm to disperse the PAC. During the following minute (200 rpm), coagulant was dosed (7 mg/L as Fe) and the pH adjusted to 4.5. Slow mixing (55 rpm) was applied for 10 mins followed by 10 mins of rapid mixing at 200 rpm to determine the impact of high shear rates on floc size and breakage. Finally 10 minutes of slow stirring at

55 rpm was applied to determine whether flocs could regrow after breakage. During these experiments, flocs were carefully withdrawn from the jar during the slow mixing phase of the jar test and observed under a light microscope from where images were taken (Infinity 3 camera, Lumenera, Canada) to visually observe PAC incorporation into the floc.

Floc strength and regrowth factors were calculated using the following formula from Wang et al. (2016)

$$\textbf{Strength Factor} = \frac{F_2}{F_1} \times 100 \quad \textbf{Equation 9}$$

$$\textbf{Regrowth Factor} = \frac{F_2}{F_3} \times 100 \quad \textbf{Equation 10}$$

where F_1 is the average size of flocs before breakage, F_2 is the size of flocs after breakage, and F_3 is the size of flocs after regrowth. To ensure reproducibility, the last 5 stabilised measurements before the breakage, during the breakage, and during the re-growth were averaged and used for F_1 , F_2 , and F_3 respectively.

Dosing position of PAC relative to coagulant addition

Three different experiments were conducted to study the influence of the dosing position of PAC on metaldehyde removal and clarification. A PAC dose of 100 mg/L was selected based on previous experiments (see chapter 3). Similarly a coagulant dose of 7 mg/L as Fe was used (Figure 9). Each experiment was performed with 1 L of raw water spiked with 2 µg/L of metaldehyde and the pH was adjusted to 4.5 when coagulant was dosed. A control experiment was conducted for each sequence where PAC was dosed alone without coagulant addition. The experiments were undertaken using three different dosing position of PAC: PAC followed by coagulant (PAC-Coag), PAC and coagulant dosed simultaneously (Simult), and coagulant dosed before PAC (Coag-PAC) (Figure 8). After the 20 min of flocculation, 10% recycle flow volume was injected to the sample, followed by 10 min of clarification. Then, samples were taken from the

sampling points at the bottom of the jars to measure residual turbidity and zeta potential. 500 mL of sample was filtered (0.45 µm) and analysed for metaldehyde, dissolved iron and aluminium concentrations, NPOC, and UV₂₅₄. The filters were weighed after drying overnight at 105 °C to calculate suspended solids.

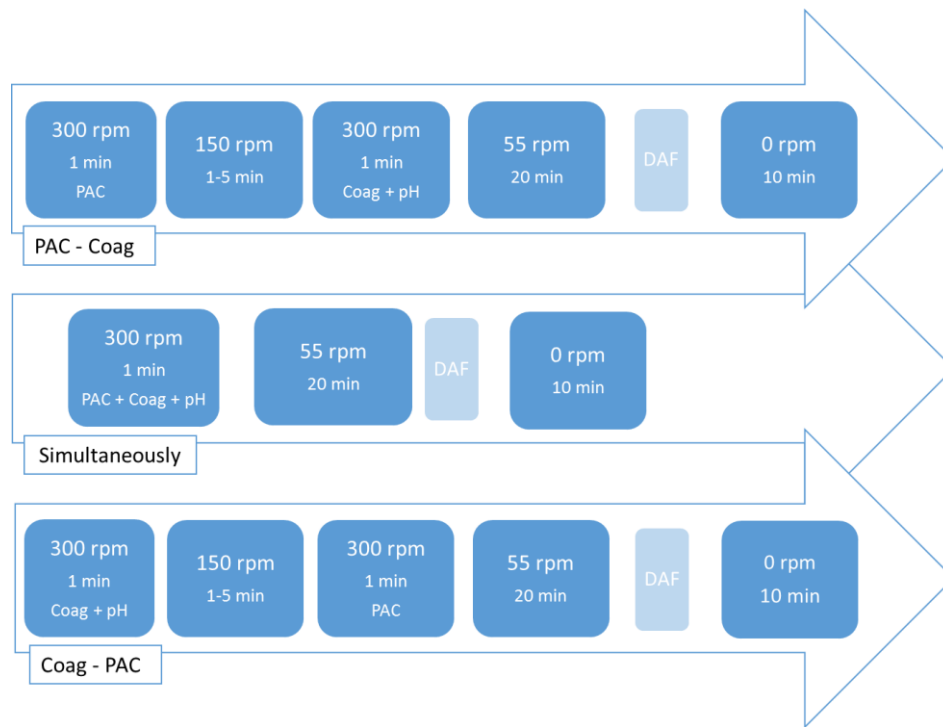


Figure 8. Description of the protocols used during the experiments to study the dosing position of PAC.

Floc properties for dosing sequence

These experiments were carried out to study the impact that the different dosing sequence may have on the floc formation. For this purpose, the particle sizing instrument was used in combination with the jar tester as described previously for the different dosing sequences as shown in (Figure 8). A control was made with only PAC for set of experiments, being a total of three experiments run only with PAC experiments.

Results

Determination of the coagulant dose

In the absence of PAC, the lowest UV_{254} (4.4 abs/m) was achieved at coagulant doses of 7 mg/L of Fe. Further increase in coagulant dose did not improve UV_{254} removal, which increased slightly to 5.7 abs/m at a dose of 8 mg/L of coagulant. The coagulant dose at 7 mg/L as Fe achieved the lowest turbidity (1.2 NTU). Higher coagulant doses caused a slight increase in turbidity values. When a dose of 50 mg/L PAC was added, the turbidity ranged from 1.5 (6.5 mg/L of Fe) to 0.7 NTU (9 mg/L as Fe). The variation in turbidity was not different for coagulant doses between 6.5 (1.2 NTU) and 8.5 mg/L of Fe (1.1 NTU). The UV_{254} was also stable with a maximum variation of 0.4 abs/m. Therefore, the recommended coagulant dose to be used in the remainder of the experiments was determined to be 7 mg/L of Fe (Figure 3).

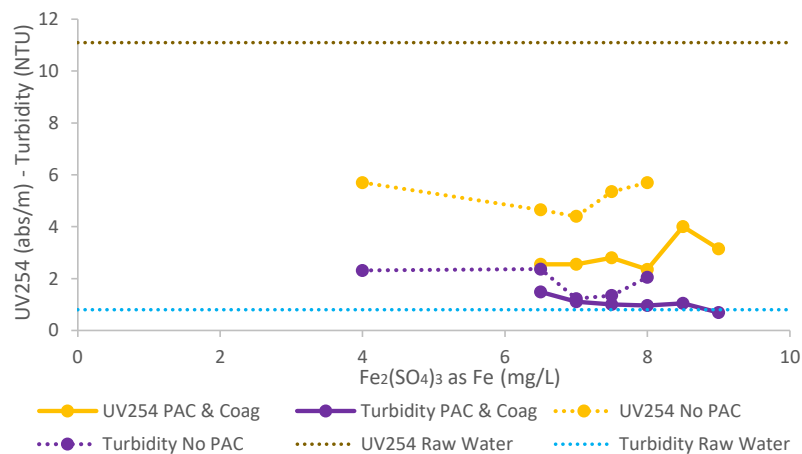


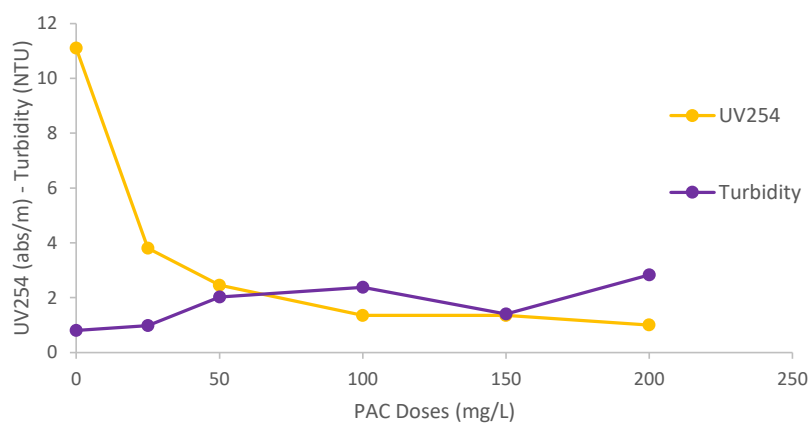
Figure 9 Residual turbidity and UV_{254} at different coagulant doses with and without PAC addition (7 mg/L as Fe, 50 mg/L of PAC, 10% Recycle Ratio).

The impact of different parameters on effective clarification

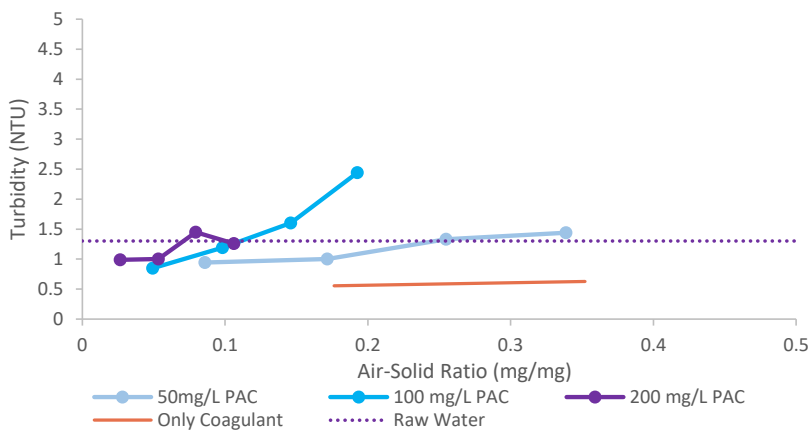
Residual turbidity and UV_{254} were used as indicators to assess the clarification reached after DAF. The UV_{254} decreased from 4.9 to 2.1 m^{-1} as the PAC dose increased from 25 to 200 mg/L. On the contrary, residual turbidity was higher (0.98 to 2.83 NTU) as the PAC dose was increased from 25 to 200 mg/L (Figure 10). These results should be compared with the metaldehyde removal data seen in chapter 3 where it was seen that a dose of 100 mg/L was needed to

remove the pesticide to below 0.1 µg/L. For this PAC dose (100 mg/L) the turbidity increased by 1.58 NTU compared to the control.

The results show that an increase in the air-solid ratio did not give any improvement in the clarification. In contrast, a small increase in turbidity was seen when the air-solid ratio increased (Figure 10 b). For instance, for a PAC dose of 100 mg/L, the turbidity increased by 0.4 NTU from 0.098 to 0.146 air-solid ratio (mg mg⁻¹).



a.



b.

Figure 10 Results of clarification. (a) UV_{254} and residual turbidity at different PAC doses (7 mg/L as Fe, 10% Recycle Ratio) (b) Residual turbidity at different air-solid ratios for different PAC doses (7 mg/L of Fe)

The effect of PAC on floc formation during the removal of pesticides

These experiments focused on the growth, breakage, and regrowth of flocs at different PAC doses. During the first minutes of slow mixing, the particles present in the water, the precipitated coagulant and the PAC aggregated into larger flocs that reached median sizes of between 338-538 μm after 4 minutes of flocculation. With an increase in the mixing speed (200 rpm) there was breakage of flocs, and the average size of the flocs decreased instantly to sizes between 275-430 μm during the first 2 minutes after applying the higher shear rate. As soon as the flocs stopped being exposed to the high shear rate, some floc growth was observed again. Flocs grew to between 67-116 μm during the two first minutes after stopping the rapid shear rate and returning to the normal flocculation conditions (30 rpm) (Figure 12, Replicate data in Appendix E).

Strength and regrowth factors were calculated using Equation 9 and Equation 10 (Table 4). Floc sizes after the growth ranged from 671 to 1200 μm while after regrowth they varied from 411 to 607 μm . In the absence of PAC, the flocs grew to an average median size of 666 μm after 10 minutes of flocculation. However when PAC was dosed, flocs reached a larger floc size between 800 and 1000 μm . The breakage factors varied from 18.0 (50 mg/L of PAC) to 48.3 (only coagulant). The regrowth factors ranged from 49.7 (50 mg/L of PAC) to 73.6 (25 mg/L of PAC). The evolution of the flocs' average size before breakage (Figure 11) compared to the average floc size after the second flocculation phase shows that although the flocs grew again during the second flocculation phase, they did not reach the size that they had prior to the breakage. When only the coagulant was present, the flocs had better recovery, reaching 68% of the initial size (454 μm during regrowth). The flocs formed with a dose of 25 mg/L PAC broke less and regrew better than with the other PAC doses (Growth: 865 μm , Regrowth: 607 μm).

Table 4 Breakage and regrowth factor of the flocs growth for different PAC doses

PAC Dose (mg/L)	Strength Factor	Regrowth Factor
0	48.3	73.6
25	42.6	60.5
50	18.0	49.7
100	29.6	57.2
200	30.2	58.3

Previous experiments (Chapter 3) indicated that 100 mg/L PAC was the required dose to remove metaldehyde to under 0.1 $\mu\text{g/L}$ for this water from an initial concentration of 2 $\mu\text{g/L}$. The addition of 50 mg/L of PAC resulted in a metaldehyde final concentration of 0.191 $\mu\text{g/L}$ compared to 0.046 $\mu\text{g/L}$ obtained using 100 mg/L of PAC (Figure 2). Therefore, considering the floc properties for this required dose of PAC (100 mg/L), the flocs reached a size of 858 μm during the growth phase, decreased to 252 $\mu\text{g/L}$, and regrew again to approximately half the size of the initial flocs, 437 μm . Compared to the other PAC doses, the strength factor was one of the lowest seen (strength factor = 29.6). This means that the flocs had a lower resistance to high shear rates compared with some of the other PAC doses. Moreover, despite the regrowth factor being similar to the others, this dose resulted in the second largest floc size achieved by the different doses after regrowth.

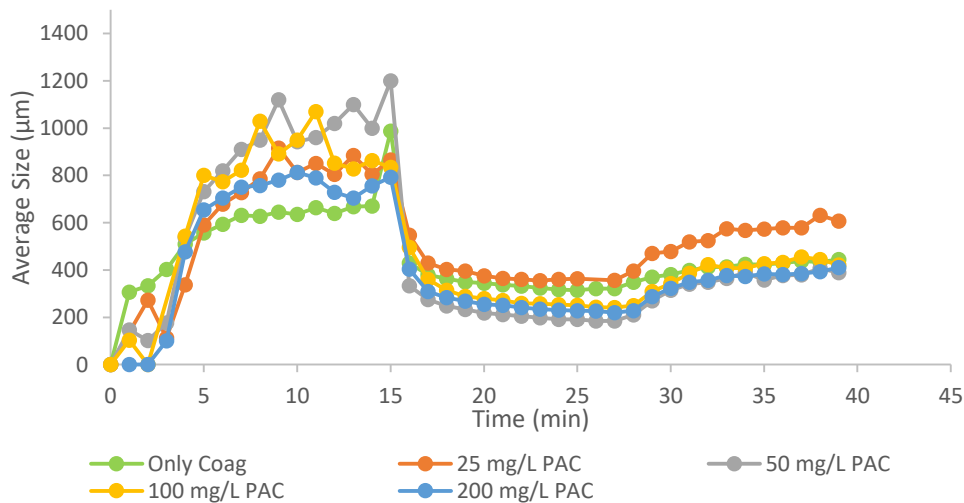


Figure 11 Results of floc's growth, breakage, and regrowth. Average size affected by different PAC doses

The floc sizing measurements are based on the distribution of the total particle volume and therefore this does not provide information on the frequency of the particles in each size range. This can mean that small particles are under-represented in the distribution, for example particles that are of a similar size to PAC (around 10-30 μm). Therefore, an inset figure has been given that zooms in on the small particles to observe the changes of those flocs/particles (Figure 12, Repetition in Appendix E).

In general, after breakage there was an increase in the particles between 20-60 μm . This size range is similar to the average size of the PAC particles (23.7 μm). Therefore, the increase of small particles could correspond to PAC particles or small floc pieces containing PAC that were released during the breakage but were not incorporated back into the flocs during regrowth.

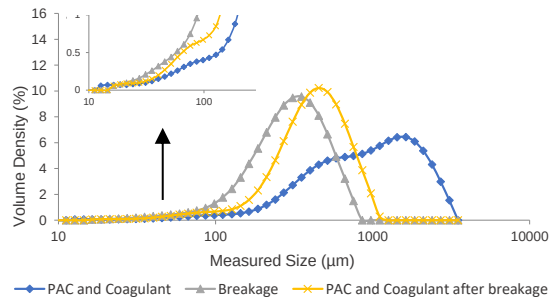
As an example, the flocs formed with a 50 mg/L dose of PAC resulted in a breakage distribution curve that went from 19 to 666 μm . There was a small increase in the particles between 21 and 45 μm , likely due to released PAC particles. During the initial growth phase, the distribution went from 52 to 3500 μm , whereas after regrowth the distribution was between 24.1 and 1110 μm . There was also an increase of particles between 24.1 to 98.1 μm that could be attributed to the PAC particles, and small pieces of flocs that were not

incorporated back into the new flocs after the breakage. After breakage, the distribution moved to the left of the graph indicating that the flocs were smaller and more tightly distributed.

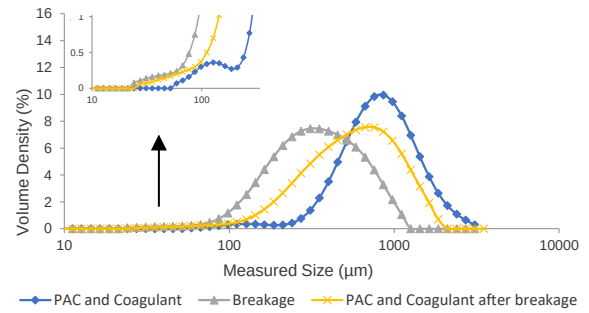
A similar observation could be made for the other PAC doses applied. The PAC dose of 100 mg/L, which was the dose determined as required for the metaldehyde removal resulted in flocs between 52 and 3500 μm during the growth phase. During the breakage phase the distribution was between 27 and 859 μm . However, there was a small increase in particles between 27-58 μm , likely due to released PAC particles. Lastly, after the regrowth phase the floc sizes were mainly between 35 and 1110 μm , but there was also an increase of particles with sizes between 35 and 98 μm , probably the result of incomplete incorporation of broken particles back into the flocs during regrowth.

The highest PAC dose of 200 mg/L resulted in a similar pattern, and despite having doubled the dose of PAC, the size of the flocs did not increase compared to the flocs formed at lower PAC doses.

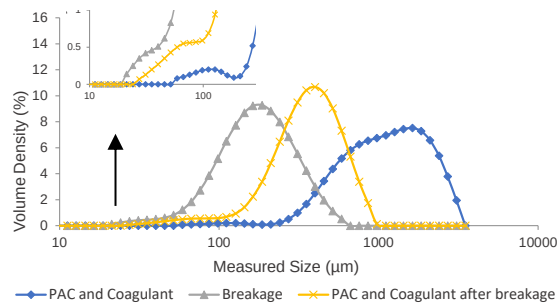
Visual images of the flocs taken under a microscope show how PAC was incorporated into the floc (Figure 13). There was a clear increase in the amount of PAC incorporated when the doses were higher. At a dose of 200 mg/L of PAC, the bulk of the floc appeared to be black, suggesting the PAC accounts for a large fraction of the floc mass, while as lower PAC doses were applied the proportion of PAC particles in the floc is substantially lower.



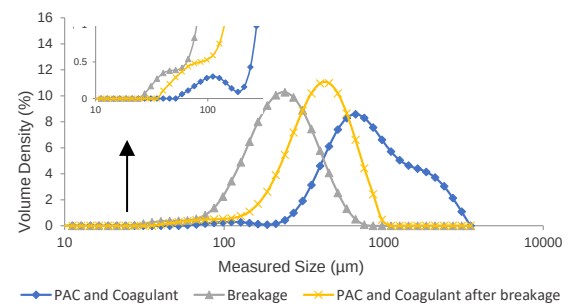
a. Only coagulant



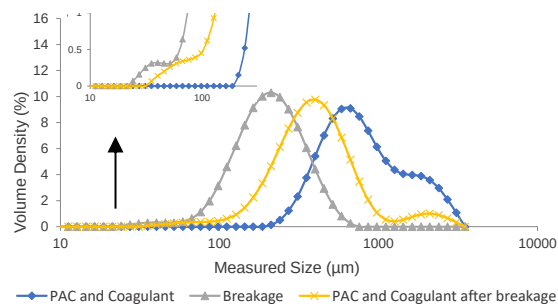
b. 25 mg/L PAC



c. 50 mg/L PAC



d. 100 mg/L PAC



e. 200 mg/L PAC

Figure 12 Results of floc growth, breakage, and regrowth for systems with and without PAC. Volume density of flocs affected by different PAC doses. The inset figure shows a zoomed in graph of the small flocs present in the system.



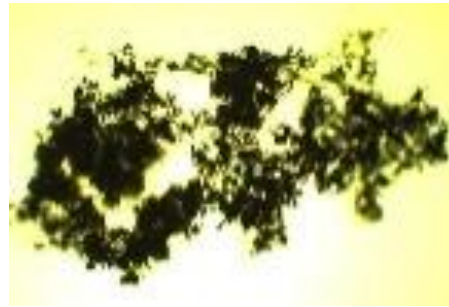
a. Only coagulant



b. 25 mg/L PAC



c. 50 mg/L PAC



d. 100 mg/L PAC



e. 200 mg/L PAC

Figure 13. Images of flocs with different PAC doses: (a) 0 mg/L PAC, (b) 25 mg/L, (c) 50 mg/L, (d) 100 mg/L, and (e) 200 mg/L.

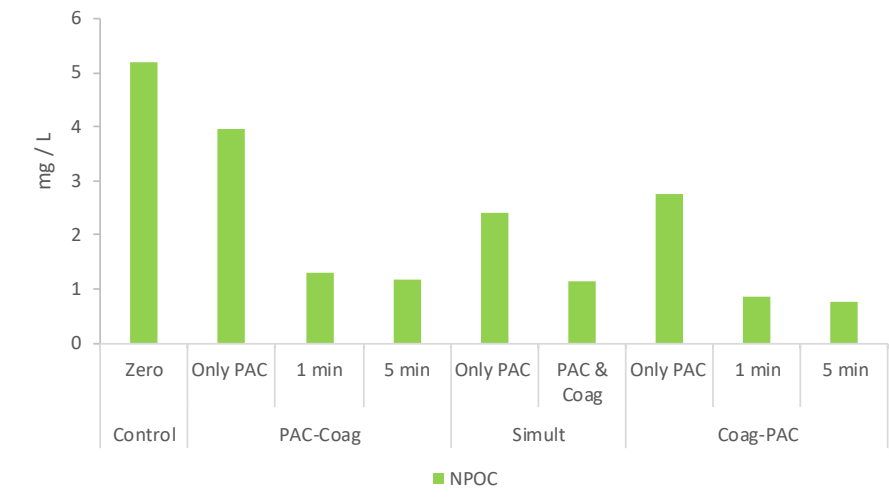
Dosing position of PAC

The results showed a very small difference in NPOC levels achieved after 1 and 5 minutes of contact time using both the following sequences: PAC-Coag (1 min: 1.30 mg/L, 5 min: 1.17 mg/L), and Coag-PAC (1 min: 0.87 mg/L, 5 min: 0.75 mg/L) (Figure 15). This suggests that the majority of NOM removal happens quickly during the first minute of contact with either PAC or coagulant. When comparing the different sequences of addition of PAC and coagulant using 1 minute of contact time before the following addition, data shows that the sequence of Coag-PAC achieved better NOM removal (0.87 mg/L NPOC, 0.65 m⁻¹ UV₂₅₄) than PAC-Coag (1.30 mg/L NPOC, 1.55 m⁻¹ UV₂₅₄) and Simultaneously (1.15 mg/L NPOC, 1.5 m⁻¹ UV₂₅₄). When the time applied between dosing PAC then Coag or Coag then PAC was 5 minutes, the results were similar and Coag-PAC achieved better NOM removal (0.75 mg/L, 0.65 m⁻¹) than PAC-Coag (1.17 mg/L, 1.05 m⁻¹) (Repetition in Appendix H and Raw Data in Appendix I)

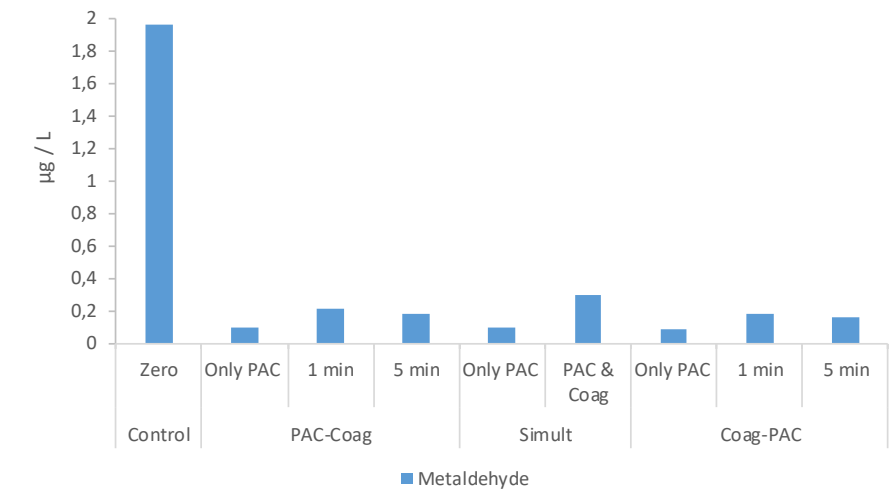
The lowest metaldehyde removal was obtained by simultaneous addition of PAC and coagulant, resulting in the highest residual metaldehyde concentration (0.3 µg/L). There was no significant difference between the metaldehyde removal of PAC-Coag (0.18 µg/L) and Coag-PAC (0.16 µg/L). The best metaldehyde removal was achieved when only PAC was dosed: 0.09 µg/L; which also efficiently removed NPOC (2.7 mg/L removed on average) and UV₂₅₄ (8.8 abs/m removed on average). This suggests that there is some interference in removal of micropollutants when PAC is coagulated into a floc. However, the experiments with only PAC also resulted in the highest turbidity (28.7 NTU) and suspended solids (55 mg/L) as there was no coagulant added to the system.

The amount of suspended solids was lower for PAC-Coag (2 mg/L) than for Coag-PAC experiments (7 mg/L) after 1 min of contact. Also the turbidity was higher for Coag-PAC (1.2 NTU) than for PAC-Coag (0.9 NTU). The difference is more significant in the suspended solids than in the turbidities. It should be

noted that 500 mL of clarified water was filtered for the measurement of the suspended solids while the turbidity was analysed from a small sample (50 mL) and was therefore more sensitive to error or fluctuations.

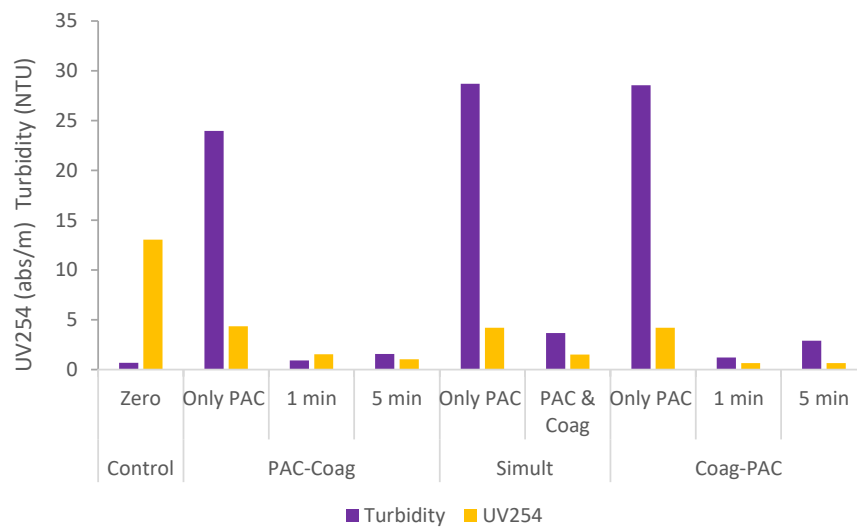


a. NPOC

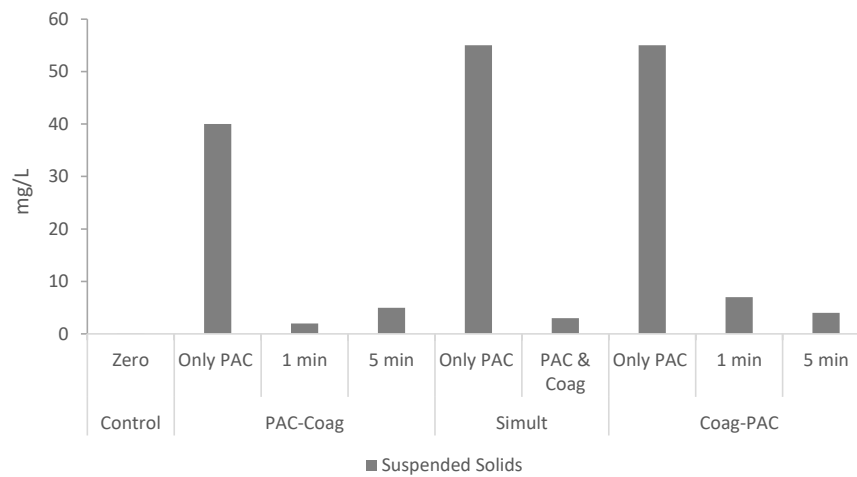


b. Metaldehyde

Figure 14 Results of (a) NPOC and (b) metaldehyde from the study of dosing position of PAC. In these experiments 100 mg/L of PAC, 7 mg/L as Fe of coagulant, and 20 minutes of contact time after PAC and coagulant were dosed.



a. Turbidity / UV254



b. Suspended Solids

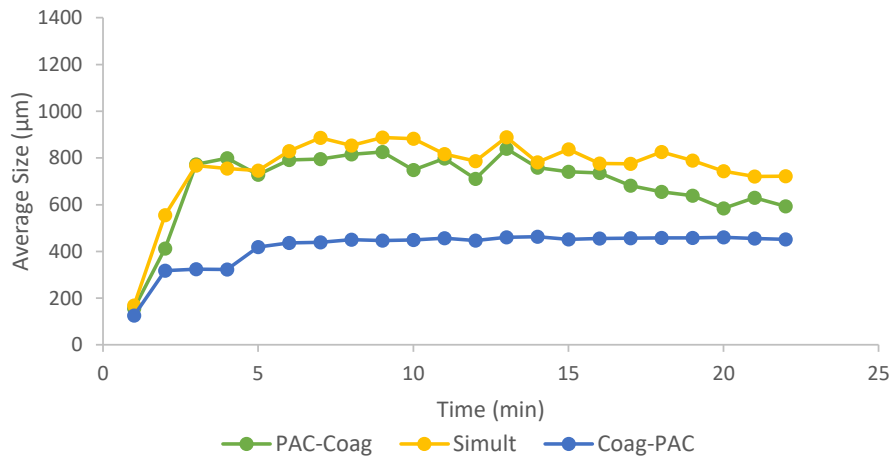
Figure 15 Results of (a) turbidity and (b) suspended solids from the study of dosing position of PAC. In these experiments 100 mg/L of PAC, 7 mg/L as Fe of coagulant, and 20 minutes of contact time after PAC and coagulant were dosed.

Floc properties for dosing position of PAC

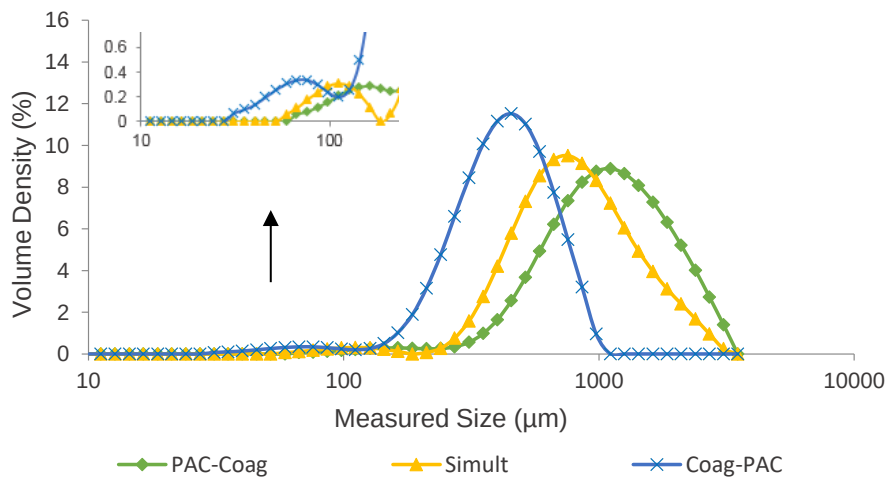
The data obtained from monitoring the particle size in the different dosing sequence experiments shows that after a few minutes of growth, the flocs reached a plateau region and stabilised for all dosing sequences investigated (Figure 16, Replicate in appendix J).

All the flocs were fully formed after the first 5 minutes of flocculation for all the dosing sequences. Whereas PAC-Coag and Simultaneously reached a similar floc size in the range of 700–900 μm , Coag-PAC floc size were significantly smaller at 300-500 μm . This occurred because the flocs were effectively being broken soon after they were formed. The flocs were first formed when the coagulant was dosed, they grew and then, when the rapid shear was applied in order to dose the PAC, the flocs were broken. As the previous results show, the regrowth capacity of these flocs is low, therefore they were not able to grow to large sizes as seen for PAC-Coag or Simultaneously which did not suffer high shear rates after floc formation.

The median floc size from the volume weighted distribution of Coag-PAC was 352 μm , which was clearly smaller than that seen for Simultaneously (666 μm) or PAC-Coag (756 μm) (Figure 16). There was an increase in the amount of particles with sizes between 27 and 98 μm when the coagulant was dosed first (Coag-PAC) suggesting that some of the PAC particles were not incorporated into the floc (Figure 16).



a.



b.

Figure 16 Results of the monitoring of flocs for the study of PAC dosing position.
a. Average size of flocs for different sequences of addition. b. Particle size distribution for flocs after 15 minutes of flocculating.

Discussion

Dosing position of PAC

There is some uncertainty in the literature regarding the most appropriate dosing position of PAC that enables the best removal of pesticides by PAC and effective removal of PAC from the water.

The results from this study show that PAC adsorbs both NOM and metaldehyde. Thus, NOM and metaldehyde could compete for adsorption sites. Therefore, the presence of NOM could potentially reduce the removal of metaldehyde as it has been documented that background organic compounds can interfere in the removal of other components, particularly at trace concentrations (Matsui *et al.*, 2003; Ho and Newcombe, 2005; Autin *et al.*, 2012). In this case, the competition between NOM and metaldehyde differs depending on the dosing position of PAC.

The results show no difference in metaldehyde removal between dosing PAC or coagulant first. It is possible that these experiments do not show more significant differences between the PAC-Coag and Coag-PAC because the PAC dose used was high enough to adsorb both metaldehyde and NOM. The results might change if PAC was less available and metaldehyde and NOM had to compete for the adsorbent. In that case, dosing the coagulant first might be an advantage, since part of the NOM would be removed by the time that PAC was dosed reducing the competition. Therefore, it is possible that with a smaller PAC dose, the competition with NOM could have had a greater impact.

Tomaszewska *et al.* (2004) reported that the simultaneous addition of PAC and coagulant resulted in lower removal of phenol compared to when coagulant and PAC were dosed separately. This is in agreement with the findings here since simultaneous addition resulted in the lowest removal of metaldehyde. As shown, when the PAC was dosed alone, it adsorbed pesticide and NOM (up to 2.8 µg/L of metaldehyde and 8.8 abs/m). Results showed that coagulant alone also removed NOM before the PAC was incorporated into the flocs. However, when dosed together, this pre-removal phase does not seem to occur, and part

of the removal capacity is lost. It is possible that when dosed simultaneously, PAC and coagulant immediately interact, and the coagulant occupied part of the adsorption sites of PAC that otherwise would be available for metaldehyde or NOM. It is also possible that part of the surface of the coagulant precipitate is used in the attachment with the PAC particles losing part of its capacity to adsorb as well.

The PAC dosed alone clearly showed the best removal of metaldehyde. However, the results indicate that metaldehyde could also be adsorbed when PAC was incorporated into flocs. According to this, although the adsorption capacity of PAC was lower when it was incorporated into the floc, the PAC maintains part of its adsorption capacity even as part of the floc.

There was an increase in the amount of particles with sizes between 27 and 98 μm when coagulant was dosed first (Coag-PAC). This could be attributed to PAC particles that were not incorporated into the flocs. When PAC was dosed after the coagulant, the PAC particles were incorporated into the already formed flocs, and the adsorption of metaldehyde happened while PAC was in the floc. The metaldehyde removal results obtained from the sequence of addition of Coag-PAC experiments (Figure 14) indicate that metaldehyde was still adsorbed when PAC particles were incorporated into the floc. However, when PAC particles were in a floc, their adsorption capacity was reduced when compared with the system in the absence of coagulant. This is in agreement with other research. For example, Kouras *et al.* (1998) reported that the removal of lindane by PAC decreased by up to 20% when coagulant was added. This was likely explained by competition. When PAC was dosed alone, all of the adsorption sites were available for metaldehyde adsorption and the pesticide was able to more easily access the pores. On the contrary, when the coagulant was present, some of the adsorption sites of the PAC may have been occupied by coagulant, so those sites were not able to adsorb metaldehyde, reducing the PAC adsorption capacity. In addition, when PAC was incorporated into a floc the pesticide had to access through the floc to get to the pores which were no longer as easily accessible.

PAC particles were poorly clarified by DAF when they were not attached or incorporated into a floc. The concentration of suspended solids in the supernatant after clarification could be taken as an indicator of the PAC being incorporated to a floc. However, it should be noted that the suspended solids could include a weak or smaller flocs and therefore this assumption is an approximation. The results show that when 1 minute of contact time was applied before dosing the following material (PAC or Coag) the amount of suspended solids in PAC-Coag (2 mg/L) was lower than in Coag-PAC (7 mg/L). This suggests that the PAC was better incorporated to the flocs when PAC was dosed first than when it was dosed after the coagulant.

In light of the results, the following revised hypotheses are proposed to explain what occurs for the different dosing positions of PAC (

Figure 17).

1. When dosing PAC first, it has more time to adsorb metaldehyde before being incorporated into the floc where its adsorption capacity is reduced. Once the coagulant is added to the sample, flocs grow quickly incorporating most of the PAC particles into the floc.
2. When the coagulant and PAC were dosed together, the floc is formed immediately, reducing its adsorption capacity which is lower than when dosed separately. PAC particles are incorporated into the floc and the clarification is efficient.
3. When dosing the coagulant first, the coagulant removes part of the NOM, reducing the competition for PAC which has then more available sites to adsorb metaldehyde. However, the addition of PAC after the flocs are formed resulted into an incomplete incorporation of the PAC into the floc and therefore, less efficient clarification.

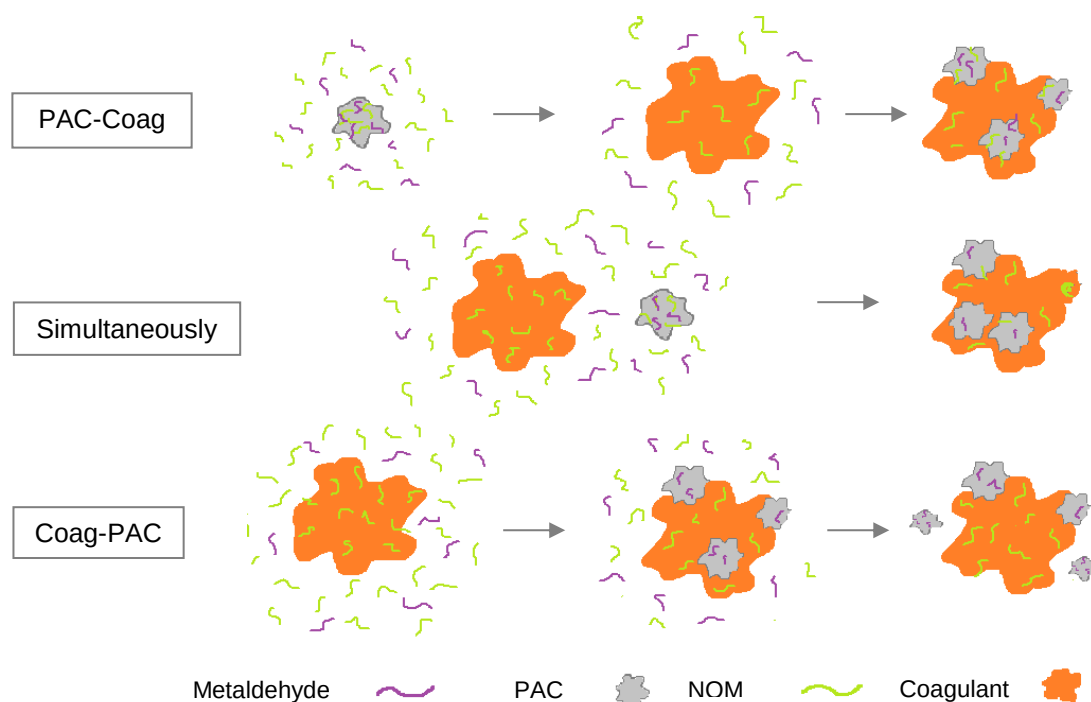


Figure 17. Revised hypotheses for metaldehyde removal depending on sequence of dosing of PAC and coagulant.

At a high PAC dose, such as 100 mg/L the impact of the competition between NOM and metaldehyde on the adsorption of metaldehyde was not big enough to be able to choose a sequence of addition. Considering this, and the advantage in terms of clarification that was shown by dosing PAC before the coagulant, PAC-Coag would be the preferred sequence of addition for the conditions examined in this work. For other water where metaldehyde removal was more efficient and the PAC dose needed was smaller, further studies would be recommended for a better understanding of the impact of NOM presence.

The influence of PAC on floc formation during the removal of pesticides

Coagulant neutralises the charge on particles and colloids present in water, including PAC when it is dosed, facilitating the formation of flocs (Zhao *et al.*, 2011; Wang *et al.*, 2016). During water treatment, flocs may be exposed to high rates of shear which can then cause inefficient clarification as a result of floc breakage. Therefore, floc strength and recovery are important operational parameters. The higher the value of the strength factor, the stronger the floc is

considered, and the less sensitive it is to break under shear conditions (Jarvis *et al.*, 2005). Similarly, high values for the regrowth factor indicate a better capacity of flocs to reform, so high values of strength and regrowth factor are desirable.. The dose of 25 mg/L of PAC resulted in flocs that grew flocs to the highest average value for both strength and regrowth factors. This suggests that there may be an optimum PAC dose to promote strong flocs. However, in this case, this did not coincide with the PAC dose necessary to achieve effective metaldehyde removal. At 100 mg/L, the strength factor of the flocs was lower (29.56) than for the doses of 25 mg/L of PAC (42.63), but the flocs regrew to achieve more than the half of their initial size (57.2). The flocs grew larger (844.5 μm), broke more (249.6 μm) and regrew better (436.2 μm) than those formed only with coagulant (Growth: 660.75 μm , Breakage: 319.4 μm , Regrowth: 434 μm). This suggests that there may be an impact on clarification following dosing of the required PAC dose.

Overall, however, the flocs were observed to grow larger in the presence of PAC, indicating that the PAC particles act as a support framework for the floc to grow around. Nevertheless, once a minimum of PAC is dosed, the size of the flocs seems to be insensitive to further increases in the amount of PAC dosed.

During this study, with or without PAC, flocs had limited re-growth capacity. Some studies have shown that the flocs formed when using hydrolysing coagulants are often seen to have irreversible breakage, so the regrowth of the flocs is limited (Yukselen and Gregory, 2004; Yu, Gregory and Campos, 2011). It is likely that the surface properties of the flocs may change during the breakage. Yu *et al.* (2011) suggest that after breakage of hydroxide flocs, the areas of the floc that were attached before forming the floc are unable to form new attachments. Therefore, the flocs will be getting smaller after each breakage unless new coagulant is dosed again. However, while the precise mechanism for this behaviour is not yet clear, the presence of PAC does not offer any benefits with respect to floc regrowth.

Clarification

Efficient clarification is important to ensure that PAC is effectively removed from treated water preventing it from continuing downstream where it could potentially interfere and reduce the efficacy of other water treatment processes.

The turbidity increased as the PAC doses increased. This was expected as the amount of particles was increasing. In contrast, UV_{254} decreased when PAC doses increased, which was also expected as more adsorbent was available to adsorb NOM. It was found that the PAC doses needed to treat the water were associated with higher turbidities in the clarified water. In an attempt to remedy this, higher coagulant doses were applied as well as different air-solid ratios. The increase of coagulant dose did not show any improvement on clarification. Similarly, the bench scale results showed no benefit to clarification in increasing the air-solid ratio, and there was a tendency to increase the turbidity when the air-solid ratio was increased. This could be due to the higher concentration of bubbles breaking the flocs apart as the ratio was increased. Higher doses of PAC were more sensitive to higher air-solids ratios resulting in higher residual turbidities. This would support the hypothesis of bubbles as the cause, since bigger flocs are more vulnerable to potential breakage.

Therefore, the PAC dose required for the removal of metaldehyde (100 mg/L) produced high levels of turbidity that the DAF was not able to clarify to the same level as for water with no PAC dosing. According to this, when using the treatment of PAC-DAF for the removal of metaldehyde, the downstream process will need to cope with a higher amount of particles. Typically, this will mean that filtration processes will be required to remove higher levels of turbidity.

Alternatively, modifications of the DAF process may enable better removal of the PAC. PAC particles were poorly removed by flotation when dosed alone. The size of PAC particles is within the recommended range suitable for flotation according to previous studies, 10-30 μm (Edzwald *et al.*, 1992). However, it is known that the electrostatic interactions between the bubble and the particle control the adhesion. Both influent PAC particles and air bubbles formed by

DAF (-25 mV) are negatively charged, leading to repulsion between them (Han, 2002; Henderson et al, 2008). In the absence of coagulant, the charges are not neutralised. Thus, PAC particles do not get attached to the bubbles. The use of bubble surface modifiers such as those used in the PosiDAF process, could be used as an alternative to pre-treatment in determined situations, or to increase the removal rate. In PosiDAF, bubble surface modification can be achieved by adding a chemical surfactant or polymer to the saturator of a DAF unit (Henderson et al., 2008; Henderson *et al.*, 2010). Similarly polymer could be used as a flocculation aid to help increase the capture of PAC particles during the coagulation/flocculation process.

The use of bubble modification in the removal of metaldehyde by PAC and DAF could contribute to better PAC attachment to the bubbles, improving its clarification. This not only could lead to the potential reduction of upstream coagulant addition but it would be also interesting to study its effect when used in addition to conventional coagulation. Possible setbacks of this treatment would be to ensure that no surfactant is present in the final drinking water, or the additional cost incurred in terms of energy or surfactant dose.

Conclusions

- PAC can adsorb metaldehyde when it is incorporated into a floc, but its adsorption capacity is reduced compared to when in the absence of coagulant.
- Simultaneous addition of PAC and coagulant resulted in lower removal rates of metaldehyde compared to when they were dosed separately.
- Coagulant dosed before the PAC achieved better NOM removal compared to dosing PAC first or following simultaneous addition.
- After the application of the PAC dose of 100 mg/L required to remove metaldehyde, the results indicated that the DAF system was not able to effectively clarify the suspension as well as for a non-PAC dosed system. Therefore, the downstream process will need to cope with a higher amount of particles when a high PAC dose is prescribed.

- An increase in the air-solid ratio did not show any improvement in the clarification.
- Further research is required to investigate if the sequence of addition effect is the same at lower PAC doses, or if the coagulant removes NOM before applying the PAC, reducing the competition and its effect on metaldehyde removal.

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References

AHDB Potatoes (2014) *Appeal to adhere to metaldehyde stewardship*. Available at: <https://potatoes.ahdb.org.uk/news/appeal-adhere-metaldehyde-stewardship> (Accessed: 8 December 2017).

Amosa, M. K. (2016) 'Sorption of water alkalinity and hardness from high-strength wastewater on bifunctional activated carbon: process optimization, kinetics and equilibrium studies', *Environmental Technology*. Taylor & Francis, 37(16), pp. 2016–2039.

Autin, O., Hart, J., Jarvis, P., MacAdam, J., Parsons, S. A. and Jefferson, B. (2012) 'Comparison of UV/H₂O₂ and UV/TiO₂ for the degradation of metaldehyde: Kinetics and the impact of background organics', *Water Research*, 46(17), pp. 5655–5662.

Baup, S., Jaffre, C., Wolbert, D. and Laplanche, A. (2000) 'Adsorption of pesticides onto granular activated carbon: Determination of surface diffusivities using simple batch experiments', *Adsorption*, 6(3), pp. 219–228.

Bhatnagar, A. and Sillanpää, M. (2017) 'Removal of natural organic matter (NOM) and its constituents from water by adsorption – A review', *Chemosphere*, 166, pp. 497–510.

Busquets, R., Kozynchenko, O. P., Whitby, R. L. D., Tennison, S. R. and

Cundy, A. B. (2014) 'Phenolic carbon tailored for the removal of polar organic contaminants from water: A solution to the metaldehyde problem?', *Water Research*, 61(0), pp. 46–56.

Castle, G. D., Mills, G. A., Gravell, A., Jones, L., Townsend, I., Cameron, D. G. and Fones, G. R. (2017) 'Review of the molluscicide metaldehyde in the environment', *Environ. Sci.: Water Res. Technol.*, 3(3), pp. 381–574.

Cook, D., Newcombe, G. and Sztajn bok, P. (2001) 'The application of powdered activated carbon for MIB and geosmin removal: Predicting PAC doses in four raw waters', *Water Research*, 35(5), pp. 1325–1333.

Crossley, I. A. and Valade, M. T. (2006) 'A review of the technological developments of dissolved air flotation', *Journal of Water Supply: Research and Technology—AQUA*, 55(7–8), pp. 479–491.

Díaz Delgado, C. (2003) *Agua potable para comunidades rurales, reuso y tratamientos avanzados de aguas residuales domésticas*, RIPDA-CYTED. Buenos Aires.

Duan, J., Wilson, F., Graham, N. and Tay, J. . (2001) 'Adsorption of humic acid by powdered activated carbon in saline water conditions', *Desalination*, 151, pp. 53–66.

Edzwald, J. K. (2010) 'Dissolved air flotation and me', *Water Research*, 44(7), pp. 2077–2106.

Edzwald, J. K., Walsh, J. P., Kaminski, G. S., Dunn, H. J., Journal, S., Water, A., Association, W., March, R. U., Edzwald, J. K., Walsh, J. P., Kaminski, G. S. and Dunn, H. J. (1992) 'Flocculation and Air requirements for dissolved air flotation', *American Water Works Association*, 84(3), pp. 92–100.

Etchepare, R., Oliveira, H., Azevedo, A. and Rubio, J. (2017) 'Separation of emulsified crude oil in saline water by dissolved air flotation with micro and nanobubbles', *Separation and Purification Technology*, 186, pp. 326–332.

Fabris, R., Chow, C. W. K., Drikas, M. and Eikebrokk, B. (2008) 'Comparison of

NOM character in selected Australian and Norwegian drinking waters', *Water Research*, 42(15), pp. 4188–4196.

FERA (2016) *PUS Stats*. Available at: <https://secure.fera.defra.gov.uk/pusstats/> (Accessed: 10 September 2016).

Get Pelletwise! (2012) *Restriction period for metaldehyde begins*. Available at: http://www.getpelletwise.co.uk/news/restriction_period_for_metaldehyde_begin_s/ (Accessed: 11 August 2016).

Gheraout, D. (2014) 'The hydrophilic/hydrophobic ratio vs. dissolved organics removal by coagulation - A review', *Journal of King Saud University - Science*. King Saud University, 26(3), pp. 169–180.

Girish, C. R. and Murty, V. R. (2016) 'Mass Transfer Studies on Adsorption of Phenol from Wastewater Using Lantana camara, Forest Waste', *International Journal of Chemical Engineering*, 2016.

Han, M. Y. (2002) 'Modeling of DAF: The effect of particle and bubble characteristics', *Journal of Water Supply: Research and Technology - AQUA*, 51(1), pp. 27–34.

Henderson, R. K., Parsons, S. A. and Jefferson, B. (2008) 'Surfactants as Bubble Surface Modifiers in the Flotation of Algae : Dissolved Air Flotation That Utilizes a Chemically Modified Bubble Surface', 42(13), pp. 4883–4888.

Henderson, R. K., Parsons, S. A., Jefferson, B., Henderson, R. K., Parsons, S. A. and Jefferson, B. (2010) 'Polymers as bubble surface modifiers in the flotation of algae', 31(January).

Ho, L. and Newcombe, G. (2005) 'Effect of NOM, turbidity and floc size on the PAC adsorption of MIB during alum coagulation', *Water Research*, 39(15), pp. 3668–3674.

Ho, Y. S. and McKay, G. (1999) 'Pseudo-second order model for sorption processes', *Process Biochemistry*, 34(5), pp. 451–465.

Jarvis, P., Jefferson, B., Gregory, J. and Parsons, S. A. (2005) 'A review of floc

strength and breakage', *Water Research*, 39(14), pp. 3121–3137.

Jefferson, B., Jarvis, P., Bhagianathan, G. K., Smith, H., Autin, O., Goslan, E. H., MacAdam, J. and Carra, I. (2016) 'Effect of elevated UV dose and alkalinity on metaldehyde removal and THM formation with UV/TiO₂ and UV/H₂O₂', *Chemical Engineering Journal*, 288.

Kay, P. and Grayson, R. (2014) 'Using water industry data to assess the metaldehyde pollution problem', *Water and Environment Journal*, 28(3), pp. 410–417.

Kegley, S.E., Hill, B.R., Orme S., Choi A.H. (2016) *Pesticides Database-Chemicals - Metaldehyde*, PAN - Pesticide Action Network. Available at: http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC32878 (Accessed: 11 August 2016).

Kouras, A., Zouboulis, A., Samara, C. and Kouimtzis, T. (1995) 'Removal of pesticides from surface waters by combined physicochemical processes. Part I: Dodine', *Chemosphere*, 30(12), pp. 2307–2315.

Kouras, A., Zouboulis, A., Samara, C. and Kouimtzis, T. (1998) 'Removal of pesticides from aqueous solutions by combined physicochemical processes - The behaviour of lindane', *Environmental Pollution*, 103(2–3), pp. 193–202.

Krishna Prasad, R. and Srivastava, S. N. (2009) 'Sorption of distillery spent wash onto fly ash: Kinetics and mass transfer studies', *Chemical Engineering Journal*, 146(1), pp. 90–97.

Li, Z., Kim, J. K., Chaudhari, V., Mayadevi, S. and Campos, L. C. (2017) 'Degradation of metaldehyde in water by nanoparticle catalysts and powdered activated carbon', *Environmental Science and Pollution Research*. *Environmental Science and Pollution Research*, 24(21), pp. 17861–17873.

Luo, T., Cui, J., Hu, S., Huang, Y. and Jing, C. (2010) 'Arsenic removal and recovery from copper smelting wastewater using TiO₂', *Environ Sci Technol*, 44(23), pp. 9094–9098.

Marshal, J. (2013) *Briefing paper on , Water UK, Water UK*. Available at: https://www.water.org.uk/sites/default/files/documents/Policy-Briefings/Water UK Policy briefing Metaldehyde 13 Aug 2013_0.pdf.

Martin, B. D., De Kock, L., Gallot, M., Guery, E., Stanowski, S., MacAdam, J., McAdam, E. J., Parsons, S. A. and Jefferson, B. (2017) 'Quantifying the performance of a hybrid anion exchanger/adsorbent for phosphorus removal using mass spectrometry coupled with batch kinetic trials', *Environmental Technology (United Kingdom)*. Taylor & Francis, 0(0), pp. 1–11.

Matilainen, A., Vepsäläinen, M. and Sillanpää, M. (2010) 'Natural organic matter removal by coagulation during drinking water treatment: A review', *Advances in Colloid and Interface Science*, 159(2), pp. 189–197.

Matsui, Y., Fukuda, Y., Inoue, T. and Matsushita, T. (2003) 'Effect of natural organic matter on powdered activated carbon adsorption of trace contaminants: Characteristics and mechanism of competitive adsorption', *Water Research*, 37(18), pp. 4413–4424.

Nabeerasool, M. A., Campen, A. K., Polya, D. A., Brown, N. W. and van Dongen, B. E. (2015) 'Removal of metaldehyde from water using a novel coupled adsorption and electrochemical destruction technique', *Water (Switzerland)*, 7(6), pp. 3057–3071.

Parsons, S. A. and Jefferson, B. (2006) *Potable Water Treatment Processes*. Oxford: Blackwell Publishing.

Ribeiro, P. and Daniel, L. A. (2016) 'Dissolved air flotation as a potential treatment process to remove Giardia cysts from anaerobically treated sewage', *Environmental Technology*. Taylor & Francis, 38:19(November), pp. 2392–2399.

Salvestrini, S., Vanore, P., Bogush, A., Mayadevi, S. and Campos, L. C. (2016) 'Sorption of metaldehyde using granular activated carbon', *Journal of Water Reuse and Desalination*, (1), p. jwr2016074.

Shutova, Y., Karna, B. L., Hambly, A. C., Lau, B., Henderson, R. K. and Le-

Clech, P. (2016) 'Enhancing organic matter removal in desalination pretreatment systems by application of dissolved air flotation', *Desalination*, 383, pp. 12–21.

Tang, L. L., DeNardo, M. A., Gayathri, C., Gil, R. R., Kanda, R. and Collins, T. J. (2016) 'TAML/H₂O₂ Oxidative Degradation of Metaldehyde: Pursuing Better Water Treatment for the Most Persistent Pollutants', *Environmental Science & Technology*, 50, p. acs.est.5b05518.

Tao, B. and Fletcher, A. (2016) 'Development of a novel dual-stage method for metaldehyde removal from water', *Chemical Engineering Journal*, 284, pp. 741–749.

Tomaszewska, M., Mozia, S. and Morawski, A. W. (2004) 'Removal of organic matter by coagulation enhanced with adsorption on PAC', *Desalination*, 161(1), pp. 79–87.

Uyak, V., Yavuz, S., Toroz, I., Ozaydin, S. and Genceli, E. A. (2007) 'Disinfection by-products precursors removal by enhanced coagulation and PAC adsorption', *Desalination*, 216(1–3), pp. 334–344.

Wang, Y.-J., Wu, C.-D., Duan, Y. and Zhang, Z.-L. (2016) 'Removal of pollutants by enhanced coagulation combined PAC with variable charge soils: flocs' properties and effect of pH', *Environmental Technology*, 3330(March), pp. 1–8.

Wilkinson, P. G. (2010) *Characterisation of the bacterial flora associated with the grey field slug Deroceras reticulatum and assessment of its suitability as a target for biological control*. Available at: <http://hdl.handle.net/1842/5276>.

Yu, W., Gregory, J. and Campos, L. C. (2011) 'Breakage and re-growth of flocs: Effect of additional doses of coagulant species', *Water Research*, 45(20), pp. 6718–6724.

Yukselen, M. A. and Gregory, J. (2004) 'The reversibility of floc breakage', *International Journal of Mineral Processing*, 73(2–4), pp. 251–259.

Zazouli, M. A., S., N., A.H, M., A.R., M., M., Y. and M., G. (2007) 'Determination of Hydrophobic and Hydrophilic Fractions of Natural Organic matter.pdf', *Journal of Applied Sciences*, 7(18), pp. 2651–2655. Available at: <http://www.sid.ir/FileServer/JE/1044620120103>.

Zhao, Y. X., Gao, B. Y., Shon, H. K., Cao, B. C. and Kim, J. H. (2011) 'Coagulation characteristics of titanium (Ti) salt coagulant compared with aluminum (Al) and iron (Fe) salts', *Journal of Hazardous Materials*, 185(2–3), pp. 1536–1542.

5 Overall Discussion

This work intended to answer some key questions to assess the treatability of metaldehyde by using PAC adsorption and DAF with respect to understanding the mechanisms that occurred during the process as well as to determine some operational aspects related to the PAC dosing addition and sequence. The following discussion answers these questions in turn (Figure 18).

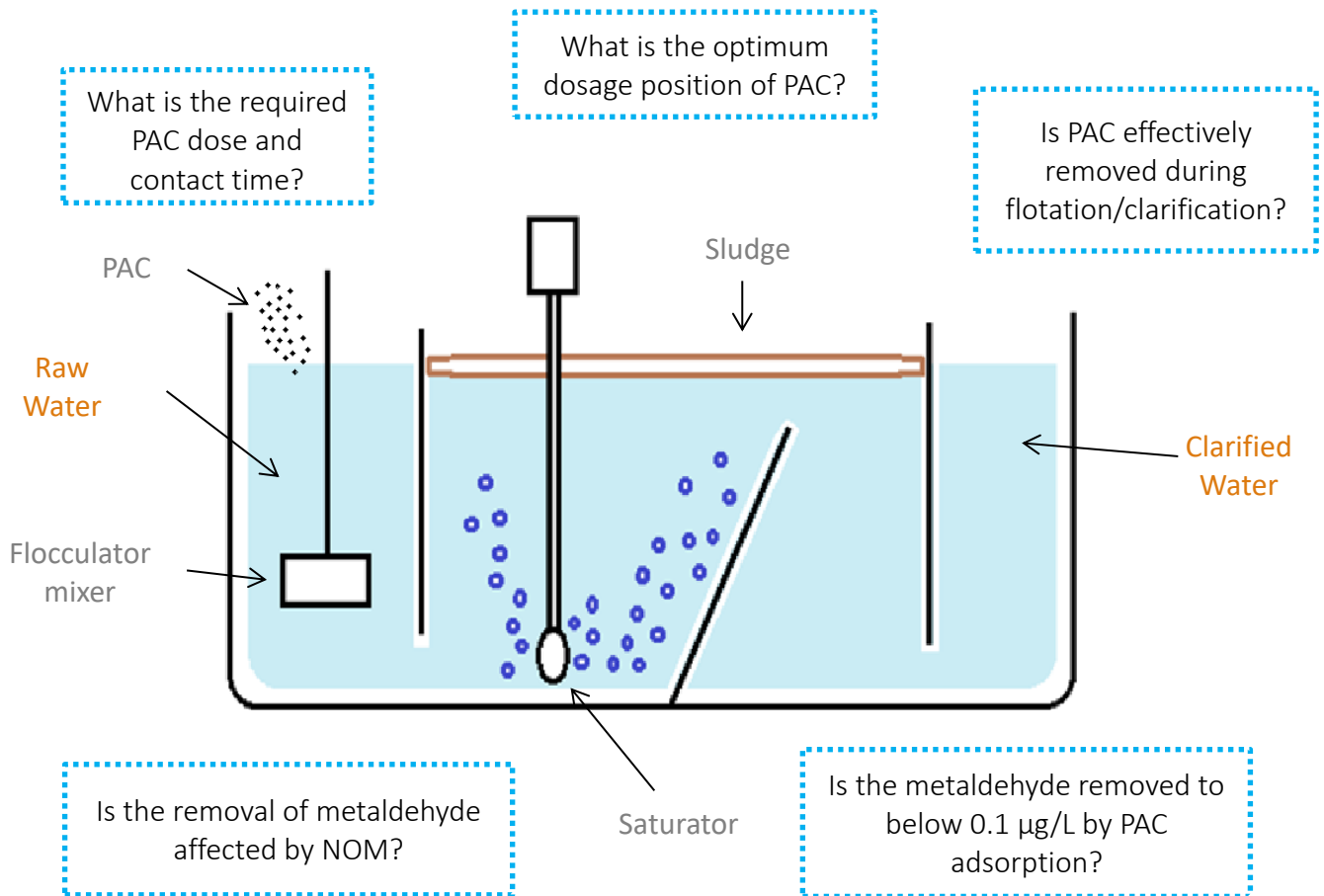


Figure 18 Schematic of the research questions answered by this research in the treatability of metaldehyde by the combination of PAC and DAF.

Is metaldehyde effectively removed by PAC adsorption to below the required concentrations?

The results showed that adsorption by PAC was able to remove metaldehyde to below 0.1 µg/L as required by the EU drinking water for pesticides. It should be noted that 2 µg/L of metaldehyde is a high concentration that is not usually found. In order to treat lower concentrations of metaldehyde, the required dose of PAC would not be as high.

What are the determined PAC dose and the contact time required to meet pesticide compliance concentrations for metaldehyde?

The required dose of PAC to reduce the metaldehyde concentration from 2 µg/L to below compliance levels in the four analysed waters was determined to be 100 mg/L for a contact time of 20 minutes.

This study tested PAC doses of 25-200 mg/L. A PAC dose of 50 mg/L was not enough to achieve the pesticide compliance concentrations for all the waters. The next PAC dose applied was 100 mg/L, which achieved the targeted metaldehyde concentrations and consequently was selected for further study. However, it would be advisable to test intermediate doses, as there might be a lower dose capable of removing metaldehyde to the desired concentrations.

A longer contact time could also be a way to achieve the targeted removal of metaldehyde at lower PAC doses. The dose of 100 mg/L was determined for a contact time of 20 minutes. However, the results show that after 60 minutes with a dose of 50 mg/L, the metaldehyde concentrations were below 0.1 µg/L for three out of four waters, and equal to 0.1 µg/L for the fourth water. This suggested that the metaldehyde removal might be achieved by a longer time and a lower PAC dose, or by a shorter contact time and a higher PAC dose. This provides the process with some flexibility to adapt to the needs of the treatment plant. However, such a strategy would require up-front adsorption contact tanks sufficient to provide long enough residence times.

Li *et al.* (2017) proposed a combination of adsorption and photolysis for the degradation of metaldehyde. They reported an improvement of 4% in the

removal of metaldehyde by PAC under UV-C light over PAC alone under dark conditions. Busquets *et al.* (2014) have shown positive results with mesoporous phenolic carbon with an adsorption capacity of 76 mg/g for a concentration of 64 mg/L metaldehyde. Both treatments could be an option to reduce the PAC doses and could be used in combination with DAF. Similarly a change in the type of carbon could be another way of improving metaldehyde removal, especially in a process where the kinetics were mainly controlled by the intra-particle diffusion. This was the case for the adsorption of metaldehyde by PAC according to the calculated Biot numbers. The kinetics of adsorption could be improved by selecting a carbon where the pore size distribution and the surface properties of the media promote more rapid rates of intra-particle diffusion.

In any case, the PAC dose should always be adjusted to each water to optimise the dosage and to prevent extra costs in terms of additional PAC or associated energy used during the clarification.

Is the removal of metaldehyde by PAC adsorption affected by NOM?

The PAC dose and the contact time required to achieve compliance levels of metaldehyde were different for each water. Furthermore, the results indicated that the K_{met} was lower at higher NPOC initial concentrations. Consequently, waters with higher NPOC contents will require longer contact times to achieve similar metaldehyde removal. Therefore, the efficiency of the removal of metaldehyde by PAC adsorption was affected by the water quality. Due to time constraints and sponsor requests, the organic matter was not fully characterised in this research and further conclusions could not be drawn without that data. Ideally, the organic matter would have been fractionated and characterised. Then, the type of NOM could have been compared to its effect on the overall adsorption to study possible relationships between NOM type and adsorption of metaldehyde efficiency. This could then be related to the water sources to suggest what sources would be more difficult to treat. Therefore, further research is required.

What is the optimum dosing position of PAC?

The factors that determined the optimum dosage position were the metaldehyde removal performance and the clarification efficiency. The first is mainly affected by the competition between metaldehyde and NOM, and the second by the impact that different dosing positions might have on the formation of flocs. Therefore, both are discussed below.

The results showed no significant difference in metaldehyde and NOM removal between dosing first PAC or the coagulant. It is possible that this was due to the PAC dose being high enough to adsorb metaldehyde and NOM. In this scenario the competition between NOM and metaldehyde would have had a limited impact on the metaldehyde removal. However, the results could be different with a lower PAC dose, since the available adsorption sites would be more limited. In such case, the competition could have a greater impact. Adding the coagulant first and allowing it to remove part of the NOM would reduce the competition of organics into PAC because part of the NOM will be removed potentially maximising the adsorption of metaldehyde into PAC. Therefore, further research is advised testing lower PAC doses.

The best metaldehyde removal was obtained when only PAC was dosed, which was also found to remove NOM. The metaldehyde adsorption achieved by simultaneous addition was lower than the other two dosing positions PAC-Coag and Coag-PAC. Tomaszewska et al. (2004) reported similar results from their study in the removal of phenol in which simultaneous addition resulted in lower phenol removals than when coagulant and PAC were dosed separately.

When the PAC was dosed after the coagulant, the PAC particles were immediately incorporated into the already formed flocs. According to the results the PAC was capable of adsorbing metaldehyde even though PAC was being incorporated into the floc. However, its adsorption capacity was reduced compared to the PAC dose alone. This could be explained by reduction in the PAC adsorption capacity through attachment of the PAC with the coagulant that forms the flocs.

Regarding the clarification, the PAC particles were poorly clarified when they were not incorporated or attached to a floc resulting in the highest turbidities and suspended solids (28.7 NTU and 55 mg/L).

When one minute of contact was applied, the simultaneous addition gave the lowest suspended solids. However, when 5 minutes of contact time were applied the suspended solids were more similar to the simultaneous addition. This suggests that the PAC was incorporated faster into the floc and thus clarified, when PAC was dosed before. However, if given the time, 5 minutes before applying the PAC, the Coag-PAC sequence could also achieve similar clarifications.

When the coagulant was dosed first, there was an increase in the particles with similar sizes to the PAC particles (27-98 μm). This was likely due to the PAC particles that were not successfully incorporated or attached to the flocs.

The following revised explanations are proposed to explain what occurs for the different dosing positions of PAC:

1. When dosing PAC first, there is more time to adsorb metaldehyde before being incorporated into the floc where its adsorption capacity is reduced. Once the coagulant is added to the sample, flocs grow quickly incorporating most of the PAC particles into the floc.
2. When the coagulant and PAC were dosed together, the floc is formed immediately, reducing its adsorption capacity which is lower than when dosed separately. PAC particles are incorporated into the floc and the clarification is efficient.
3. When dosing the coagulant first, the coagulant removes part of the NOM, reducing the competition for PAC which has then more available sites to adsorb metaldehyde. However, the addition of PAC after the flocs are formed resulted in an incomplete incorporation of the PAC into the floc and therefore, less efficient clarification.

Considering the advantages in terms of clarification and the small difference seen in metaldehyde removal between PAC/Coag and Coag/PAC. The

recommended sequence of dosing is PAC/Coag. However, further studies should be made to analyse if the impact of competition with NOM would be higher at lower PAC doses.

Due to the greater metaldehyde removal achieved by the PAC when dosed alone, this could be accounted for in future designs of treatment plants. The construction of a separate tank to allow the pre-treatment where only PAC and raw water are in contact could improve the efficiency of the metaldehyde removal. The coagulant would be added in the following tank where the flocs would then be formed incorporating the PAC that had already adsorbed the metaldehyde. Such a system would need to consider the availability of the space in the treatment plant as well as the cost of the tank construction in relation to the cost associated with the use of higher PAC doses or longer contact times.

Is the DAF able to cope with the PAC doses required to fulfil the regulations?

The clarified turbidity increased as the PAC doses increased. The required dose of 100 mg/L was found to produce higher turbidities than for systems with lower or no PAC dosing. In order to clarify such turbidity, different air-solid ratios were tested as well as different coagulant doses. The results showed no improvement on the clarification efficiency by increasing the air-solid ratio. In fact, higher rates of air-solid ratio showed a tendency to increase the turbidity, possibly due to the breakage of the flocs by the higher concentration of bubbles. In this regard, higher doses of PAC were more sensitive to this breakage leading to higher turbidities. Therefore, the DAF system showed some limitation to achieve a complete clarification when dealing with high doses of PAC.

Different approaches are possible to overcome this limitation. One possibility is to reduce the required PAC dose. As discussed before, this might be achieved by combinations with other treatments such as UV-C light; changing the carbon, or by the application of a longer adsorption contact time (Busquets *et al.*, 2014; Li *et al.*, 2017).

Improving the clarification efficiency is another option. The use of bubble modifiers such as surfactants and polymers as used in the PosiDAF process might be an option to improve the efficiency of the clarification. The addition of a chemical surfactant or polymer to the saturator could contribute to a better PAC attachment to the bubbles (Henderson et al., 2008; Henderson *et al.*, 2010). However, it would be necessary to ensure that no surfactant is present in the final drinking water and to consider the additional cost.

Alternatively, for a high doses with the studied clarification efficiency, it should be accounted that the downstream process will need to cope with a higher amount of particles when the treatment PAC-DAF is used with high PAC doses.

6 Conclusions

- The PAC dose required to remove the metaldehyde under 0.1 µg/L for the four water sources was 100 mg/L with a contact time of 20 minutes.
- The pseudo-second-order model provided the best fit for modelling the kinetics of metaldehyde adsorption by PAC.
- The water quality influenced the adsorption rate. Both the removal of metaldehyde and NOM were more efficient when there was less NOM present. PAC showed a better adsorption capacity for metaldehyde when NPOC was reduced. Conversely, $Q_{e,NOM}$, showed higher values at higher NPOC concentrations.
- The adsorption rate of metaldehyde was strongly dependent on intra-particle diffusion.
- The treatment should be adjusted to the particular conditions of each water to optimise the efficiency and avoid overdosing or longer contact time than needed.
- PAC can adsorb metaldehyde when it is incorporated into a floc, but its adsorption capacity is reduced compared to when in the absence of coagulant.
- Simultaneous addition of PAC and coagulant resulted in lower removal rates of metaldehyde compared to when they were dosed separately.
- Coagulant dosed before the PAC achieved better NOM removal compared to dosing PAC first or following simultaneous addition.
- After the application of the PAC dose of 100 mg/L required to remove metaldehyde, the results indicated that the DAF system was not able to effectively clarify the suspension as well as for a non-PAC dosed system. Therefore, the downstream process will need to cope with a higher amount of particles when a high PAC dose is prescribed.
- An increase in the air-solid ratio did not show any improvement in the clarification.
- Further research is required to investigate if the sequence of addition effect is the same at lower PAC doses, or if the coagulant removes NOM

before applying the PAC, reducing the competition and its effect on metaldehyde removal.

7 Future Research

For future research on this area there are some points that would be interesting to consider:

- Test different shear rates to study the effect on floc formation, adsorption, metaldehyde removal, and clarification. Ideally, optimise the shear rate prior to the experiments.
- Study different types of PAC with different surface area and pore diameter to assess the impact on metaldehyde removal.
- Test the effect of different coagulants on metaldehyde adsorption.
- Explore smaller PAC doses to better understand the impact of the dosing position of PAC on metaldehyde removal. Particularly the influence of bigger competition between NOM and metaldehyde adsorption.

REFERENCES

AHDB Potatoes (2014) *Appeal to adhere to metaldehyde stewardship*. Available at: <https://potatoes.ahdb.org.uk/news/appeal-adhere-metaldehyde-stewardship> (Accessed: 8 December 2017).

Amosa, M. K. (2016) 'Sorption of water alkalinity and hardness from high-strength wastewater on bifunctional activated carbon: process optimization, kinetics and equilibrium studies', *Environmental Technology*. Taylor & Francis, 37(16), pp. 2016–2039.

Autin, O., Hart, J., Jarvis, P., MacAdam, J., Parsons, S. A. and Jefferson, B. (2012) 'Comparison of UV/H₂O₂ and UV/TiO₂ for the degradation of metaldehyde: Kinetics and the impact of background organics', *Water Research*, 46(17), pp. 5655–5662.

Baup, S., Jaffre, C., Wolbert, D. and Laplanche, A. (2000) 'Adsorption of pesticides onto granular activated carbon: Determination of surface diffusivities using simple batch experiments', *Adsorption*, 6(3), pp. 219–228.

Bhatnagar, A. and Sillanpää, M. (2017) 'Removal of natural organic matter (NOM) and its constituents from water by adsorption – A review', *Chemosphere*, 166, pp. 497–510.

Busquets, R., Kozynchenko, O. P., Whitby, R. L. D., Tennison, S. R. and Cundy, A. B. (2014) 'Phenolic carbon tailored for the removal of polar organic contaminants from water: A solution to the metaldehyde problem?', *Water Research*, 61(0), pp. 46–56.

Castle, G. D., Mills, G. A., Gravell, A., Jones, L., Townsend, I., Cameron, D. G. and Fones, G. R. (2017) 'Review of the molluscicide metaldehyde in the environment', *Environ. Sci.: Water Res. Technol.*, 3(3), pp. 381–574.

Cook, D., Newcombe, G. and Sztajn bok, P. (2001) 'The application of powdered activated carbon for MIB and geosmin removal: Predicting PAC doses in four raw waters', *Water Research*, 35(5), pp. 1325–1333.

Crossley, I. A. and Valade, M. T. (2006) 'A review of the technological developments of dissolved air flotation', *Journal of Water Supply: Research and Technology—AQUA*, 55(7–8), pp. 479–491.

Díaz Delgado, C. (2003) *Agua potable para comunidades rurales, reuso y tratamientos avanzados de aguas residuales domésticas*, RIPDA-CYTED. Buenos Aires.

Duan, J., Wilson, F., Graham, N. and Tay, J. . (2001) 'Adsorption of humic acid by powdered activated carbon in saline water conditions', *Desalination*, 151, pp. 53–66.

Edzwald, J. K. (2010) 'Dissolved air flotation and me', *Water Research*, 44(7), pp. 2077–2106.

Edzwald, J. K., Walsh, J. P., Kaminski, G. S., Dunn, H. J., Journal, S., Water, A., Association, W., March, R. U., Edzwald, J. K., Walsh, J. P., Kaminski, G. S. and Dunn, H. J. (1992) 'Flocculation and Air requirements for dissolved air flotation', *American Water Works Association*, 84(3), pp. 92–100.

Etchepare, R., Oliveira, H., Azevedo, A. and Rubio, J. (2017) 'Separation of emulsified crude oil in saline water by dissolved air flotation with micro and nanobubbles', *Separation and Purification Technology*, 186, pp. 326–332.

Fabris, R., Chow, C. W. K., Drikas, M. and Eikebrokk, B. (2008) 'Comparison of NOM character in selected Australian and Norwegian drinking waters', *Water Research*, 42(15), pp. 4188–4196.

FERA (2016) *PUS Stats*. Available at: <https://secure.fera.defra.gov.uk/pusstats/> (Accessed: 10 September 2016).

Dissolved Air Flotation (DAF) (2018). *Dissolved Air Flotation*. Available at: www.edie.net/8385/products/Dissolved-Air-Flotation-DAF/7942 (Accessed: 26 March 2018)

Get Pelletwise! (2012) *Restriction period for metaldehyde begins*. Available at: http://www.getpelletwise.co.uk/news/restriction_period_for_metaldehyde_begin

s/ (Accessed: 11 August 2016).

Gheraout, D. (2014) 'The hydrophilic/hydrophobic ratio vs. dissolved organics removal by coagulation - A review', *Journal of King Saud University - Science*. King Saud University, 26(3), pp. 169–180.

Girish, C. R. and Murty, V. R. (2016) 'Mass Transfer Studies on Adsorption of Phenol from Wastewater Using Lantana camara, Forest Waste', *International Journal of Chemical Engineering*, 2016

Han, M. Y. (2002) 'Modeling of DAF: The effect of particle and bubble characteristics', *Journal of Water Supply: Research and Technology - AQUA*, 51(1), pp. 27–34.

Henderson, R. K., Parsons, S. A. and Jefferson, B. (2008) 'Surfactants as Bubble Surface Modifiers in the Flotation of Algae : Dissolved Air Flotation That Utilizes a Chemically Modified Bubble Surface', 42(13), pp. 4883–4888.

Henderson, R. K., Parsons, S. A., Jefferson, B., Henderson, R. K., Parsons, S. A. and Jefferson, B. (2010) 'Polymers as bubble surface modifiers in the flotation of algae', 31(January).

Ho, L. and Newcombe, G. (2005) 'Effect of NOM, turbidity and floc size on the PAC adsorption of MIB during alum coagulation', *Water Research*, 39(15), pp. 3668–3674.

Ho, Y. S. and McKay, G. (1999) 'Pseudo-second order model for sorption processes', *Process Biochemistry*, 34(5), pp. 451–465.

Jarvis, P., Jefferson, B., Gregory, J. and Parsons, S. A. (2005) 'A review of floc strength and breakage', *Water Research*, 39(14), pp. 3121–3137.

Jefferson, B., Jarvis, P., Bhagianathan, G. K., Smith, H., Autin, O., Goslan, E. H., MacAdam, J. and Carra, I. (2016) 'Effect of elevated UV dose and alkalinity on metaldehyde removal and THM formation with UV/TiO₂ and UV/H₂O₂', *Chemical Engineering Journal*, 288.

Kay, P. and Grayson, R. (2014) 'Using water industry data to assess the

metaldehyde pollution problem', *Water and Environment Journal*, 28(3), pp. 410–417.

Kegley, S.E., Hill, B.R., Orme S., Choi A.H. (2016) *Pesticides Database-Chemicals - Metaldehyde*, PAN - Pesticide Action Nertwork. Available at: http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC32878 (Accessed: 11 August 2016).

Kouras, A., Zouboulis, A., Samara, C. and Kouimtzis, T. (1995) 'Removal of pesticides from surface waters by combined physicochemical processes. Part I: Dodine', *Chemosphere*, 30(12), pp. 2307–2315.

Khraisheh MAM, Al-Degs YS, Allen SJ, and Ahmad M.N.. *Elucidation of controlling steps of reactive dye adsorption on activatedcarbon*. Ind Eng Chem Res. 2002;41:1651–1657.

Krishna Prasad, R. and Srivastava, S. N. (2009) 'Sorption of distillery spent wash onto fly ash: Kinetics and mass transfer studies', *Chemical Engineering Journal*, 146(1), pp. 90–97.

Li, Z., Kim, J. K., Chaudhari, V., Mayadevi, S. and Campos, L. C. (2017) 'Degradation of metaldehyde in water by nanoparticle catalysts and powdered activated carbon', *Environmental Science and Pollution Research*. Environmental Science and Pollution Research, 24(21), pp. 17861–17873.

Luo, T., Cui, J., Hu, S., Huang, Y. and Jing, C. (2010) 'Arsenic removal and recovery from copper smelting wastewater using TiO₂', *Environ Sci Technol*, 44(23), pp. 9094–9098.

Marshal, J. (2013) *Briefing paper on , Water UK*, Water UK. Available at: https://www.water.org.uk/sites/default/files/documents/Policy-Briefings/Water UK Policy briefing Metaldehyde 13 Aug 2013_0.pdf.

Martin, B. D., De Kock, L., Gallot, M., Guery, E., Stanowski, S., MacAdam, J., McAdam, E. J., Parsons, S. A. and Jefferson, B. (2017) 'Quantifying the performance of a hybrid anion exchanger/adsorbent for phosphorus removal using mass spectrometry coupled with batch kinetic trials', *Environmental*

Technology (United Kingdom). Taylor & Francis, 0(0), pp. 1–11.

Matilainen, A., Vepsäläinen, M. and Sillanpää, M. (2010) 'Natural organic matter removal by coagulation during drinking water treatment: A review', *Advances in Colloid and Interface Science*, 159(2), pp. 189–197.

Matsui, Y., Fukuda, Y., Inoue, T. and Matsushita, T. (2003) 'Effect of natural organic matter on powdered activated carbon adsorption of trace contaminants: Characteristics and mechanism of competitive adsorption', *Water Research*, 37(18), pp. 4413–4424.

Nabeerasool, M. A., Campen, A. K., Polya, D. A., Brown, N. W. and van Dongen, B. E. (2015) 'Removal of metaldehyde from water using a novel coupled adsorption and electrochemical destruction technique', *Water (Switzerland)*, 7(6), pp. 3057–3071.

Parsons, S. A. and Jefferson, B. (2006) *Potable Water Treatment Processes*. Oxford: Blackwell Publishing.

Ribeiro, P. and Daniel, L. A. (2016) 'Dissolved air flotation as a potential treatment process to remove Giardia cysts from anaerobically treated sewage', *Environmental Technology*. Taylor & Francis, 38:19(November), pp. 2392–2399.

Salvestrini, S., Vanore, P., Bogush, A., Mayadevi, S. and Campos, L. C. (2016) 'Sorption of metaldehyde using granular activated carbon', *Journal of Water Reuse and Desalination*, (1), p. jwrd2016074.

Shutova, Y., Karna, B. L., Hambly, A. C., Lau, B., Henderson, R. K. and Le-Clech, P. (2016) 'Enhancing organic matter removal in desalination pretreatment systems by application of dissolved air flotation', *Desalination*, 383, pp. 12–21.

Tang, L. L., DeNardo, M. A., Gayathri, C., Gil, R. R., Kanda, R. and Collins, T. J. (2016) 'TAML/H₂O₂ Oxidative Degradation of Metaldehyde: Pursuing Better Water Treatment for the Most Persistent Pollutants', *Environmental Science & Technology*, 50, p. acs.est.5b05518.

Tao, B. and Fletcher, A. (2016) 'Development of a novel dual-stage method for metaldehyde removal from water', *Chemical Engineering Journal*, 284, pp. 741–749.

Tomaszewska, M., Mozia, S. and Morawski, A. W. (2004) 'Removal of organic matter by coagulation enhanced with adsorption on PAC', *Desalination*, 161(1), pp. 79–87.

Uyak, V., Yavuz, S., Toroz, I., Ozaydin, S. and Genceli, E. A. (2007) 'Disinfection by-products precursors removal by enhanced coagulation and PAC adsorption', *Desalination*, 216(1–3), pp. 334–344.

Wang, Y.-J., Wu, C.-D., Duan, Y. and Zhang, Z.-L. (2016) 'Removal of pollutants by enhanced coagulation combined PAC with variable charge soils: flocs' properties and effect of pH', *Environmental Technology*, 3330(March), pp. 1–8.

Water UK (2013) Briefing paper on metaldehyde. Available at: <http://www.water.org.uk/publications/policy-briefings/metaldehyde> (Accessed 10 March 2018)

Wilkinson, P. G. (2010) *Characterisation of the bacterial flora associated with the grey field slug Deroceras reticulatum and assessment of its suitability as a target for biological control*. Available at: <http://hdl.handle.net/1842/5276>.

Yu, W., Gregory, J. and Campos, L. C. (2011) 'Breakage and re-growth of flocs: Effect of additional doses of coagulant species', *Water Research*, 45(20), pp. 6718–6724.

Yukselen, M. A. and Gregory, J. (2004) 'The reversibility of floc breakage', *International Journal of Mineral Processing*, 73(2–4), pp. 251–259.

Zazouli, M. A., S., N., A.H, M., A.R., M., M., Y. and M., G. (2007) 'Determination of Hydrophobic and Hydrophilic Fractions of Natural Organic matter.pdf', *Journal of Applied Sciences*, 7(18), pp. 2651–2655. Available at: <http://www.sid.ir/FileServer/JE/1044620120103>.

Zhao, Y. X., Gao, B. Y., Shon, H. K., Cao, B. C. and Kim, J. H. (2011) 'Coagulation characteristics of titanium (Ti) salt coagulant compared with aluminum (Al) and iron (Fe) salts', *Journal of Hazardous Materials*, 185(2–3), pp. 1536–1542.

APPENDICES

Appendix A

METHOD STATEMENT



Determinand:

Metaldehyde

Matrix:

Sample Type: Waters abstracted for potable supplies

Principle of Method:

250ml of sample is extracted onto a pre-rinsed Strata-X cartridge. The compound is eluted from the cartridge with an ethyl acetate/acetone mixture, followed by iso-octane and addition of working internal standard prior to analysis.

Metaldehyde is determined by capillary gas chromatograph with splitless injection, followed by mass spectrometric detection in selected ion mode (GCMS-SIM).

Interferences:

Any compound which passes through the extraction, and has similar gas chromatographic and mass spectrometric properties to the analyte.

Performance of Method:

Range of Application:

The operational range for metaldehyde is from the limit of detection, to 0.50 µg/l. Samples producing results above this range should be diluted to bring the sample response below that of the top standard. The PCV for this determinand is 0.1µg/l.

Limit of Detection and Recoveries of Compounds

GCMS01 Instrument

<u>Compound</u>	<u>St @ 0.100 µg/l</u>	<u>% Recovery in Medium hardness potable water</u>	<u>LOD/Reporting Limits µg/l</u>
Metaldehyde	0.0088	97.2	0.003

GCMS03 Instrument

<u>Compound</u>	<u>LOD/Reporting Limits µg/l</u>
Metaldehyde	0.005

Uncertainty of measurement

<u>Compound</u>	<u>Uncertainty % at 0.1µg/l</u>
Metaldehyde	20.3

References:

SCA Method 226b – "The determination of metaldehyde in waters using chromatography with mass spectrometric detection".

HP 5973MSD HP 6890 Series GC Quick reference guide Manual Part No. G1701-90033

GC Enviroquant Users Guide – Hewlett Packard. (G1032-90029)

Figure 19 Metaldehyde Analysis. Method Statement - ALS Environmental

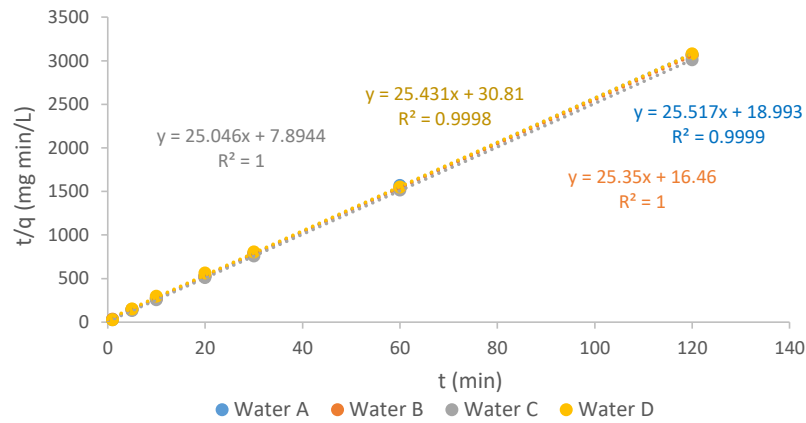
Appendix B

The first Linear Form is the most widely used, and it is the one that showed the best fit. However, in order to confirm the use of the best linear form, four different linear forms (Lima et al. 2015) of the pseudo-second-order were plotted.

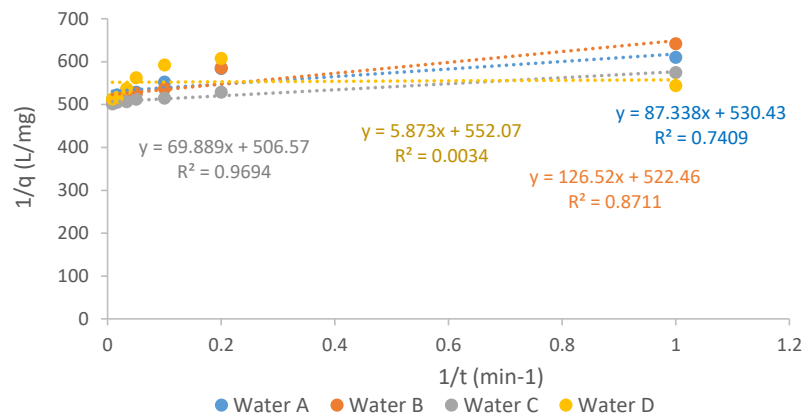
Tabla 1 Linear forms for the pseudo-second order (Lima E.C et al. 2015)

Linear form	Equation	Plot
Pseudo-second 1	$\frac{t}{q_t} = \frac{1}{kq_e^2} + \left(\frac{1}{q_e}\right)t$	$\frac{t}{q_t}$ versus t
Pseudo-second 2	$\frac{1}{q_t} = \left(\frac{1}{q_e}\right) + \frac{1}{kq_e^2} \frac{1}{t}$	$\frac{1}{q_t}$ versus $\frac{1}{t}$
Pseudo-second 3	$q_t = q_e - \left(\frac{1}{kq_e}\right) \frac{q_e}{t}$	q_t versus $\frac{q_t}{t}$
Pseudo-second 4	$\frac{q_t}{t} = k q_e^2 - k q_e q_t$	$\frac{q_t}{t}$ versus q_t

B.1 Metaldehyde adsorption fitted to pseudo-second order kinetic model

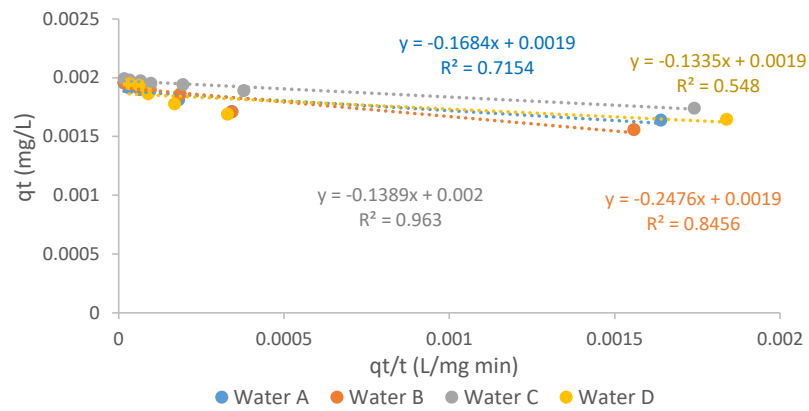


a Pseudo-second. Linear form 1

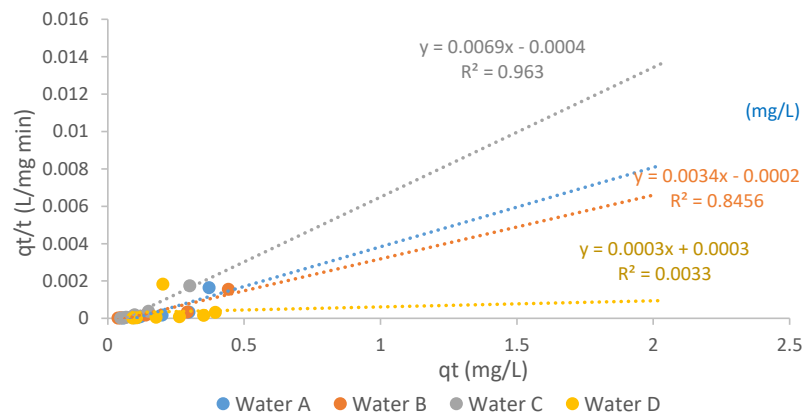


b Pseudo-second. Linear form 2

Figure 20 Data of metaldehyde adsorption fitted to pseudo-second order kinetic model. (a) linear form 1; (b) linear form 2.



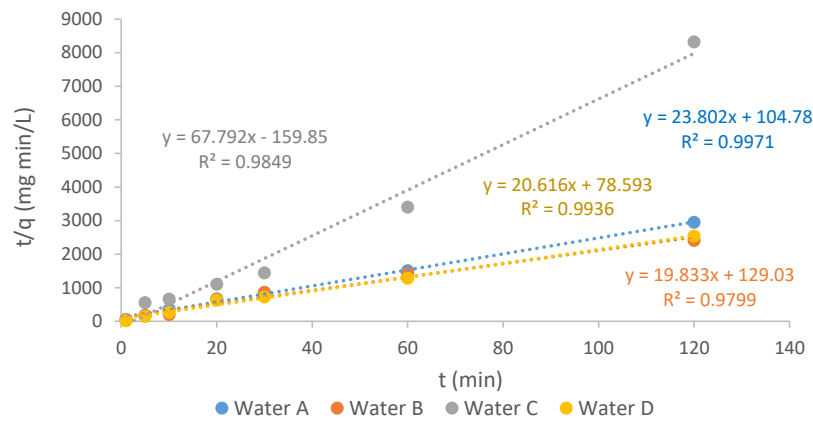
c Pseudo-second. Linear form 3



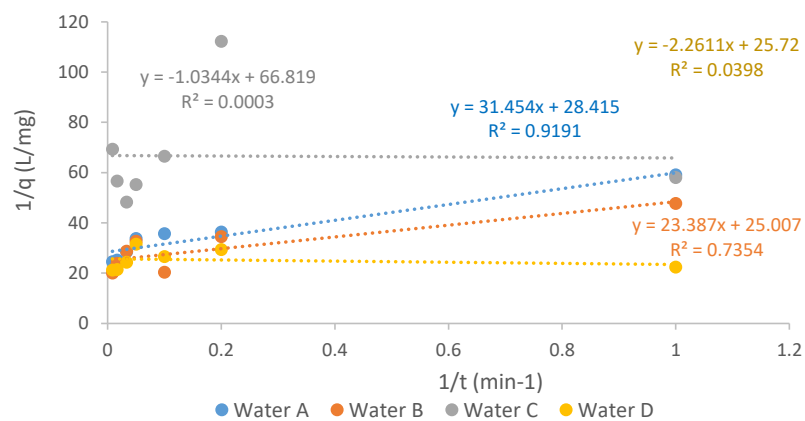
d Pseudo-second. Linear form 4

Figure 21 Data of metaldehyde adsorption fitted to pseudo-second order kinetic model. (c) linear form 3, and (d) linear form 4.

B.2 Data of NOM adsorption fitted to pseudo-second order kinetic model

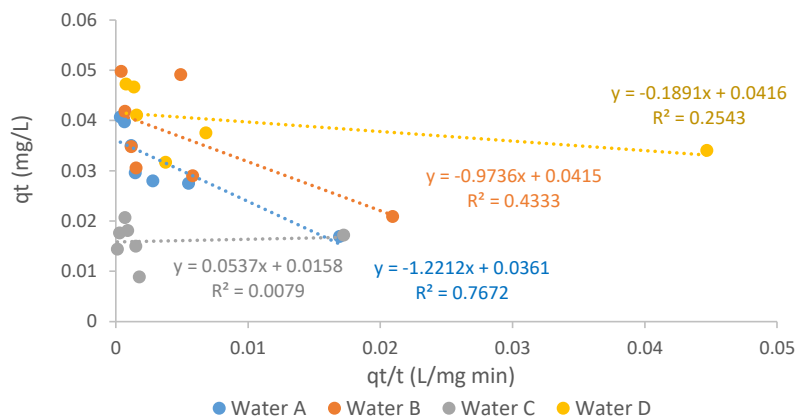


a Pseudo-second. Linear form 1

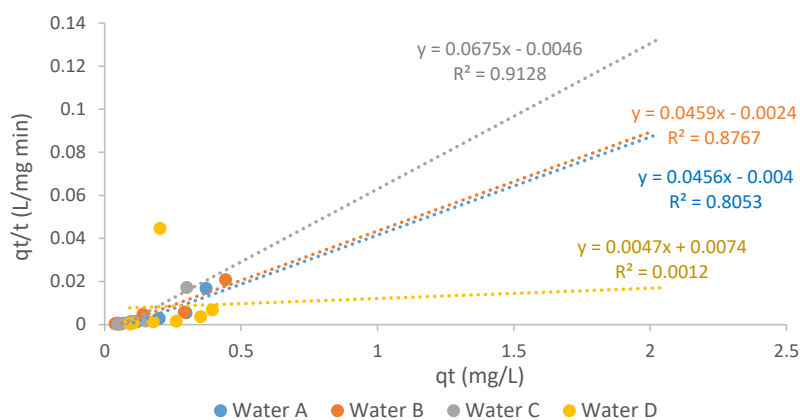


c Pseudo-second. Linear form 2

Figure 22 Data of NOM adsorption fitted to pseudo-second order kinetic model. (a) linear form 1; (b) linear form 2.



b Pseudo-second. Linear form 3



d Pseudo-second. Linear form 4

Figure 23 Data of NOM adsorption fitted to pseudo-second order kinetic model. (c) linear form 3, and (d) linear form 4.

Appendix C

Determination of the coagulant doses for Water D

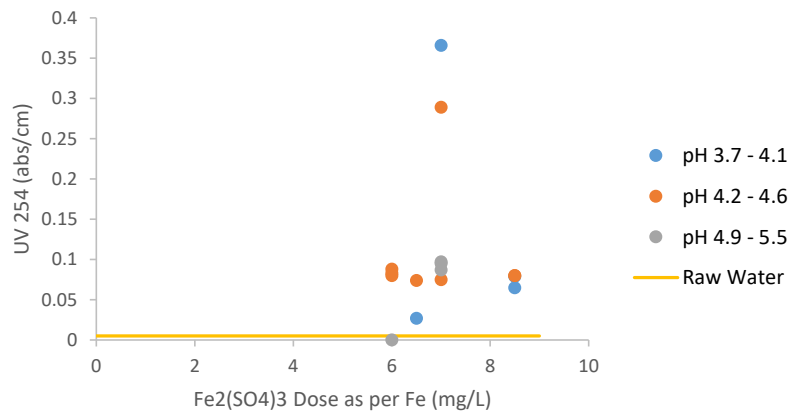


Figure 24 UV₂₅₄ against increasing doses of Fe₂(SO₄)₃ as per Fe in Water D.

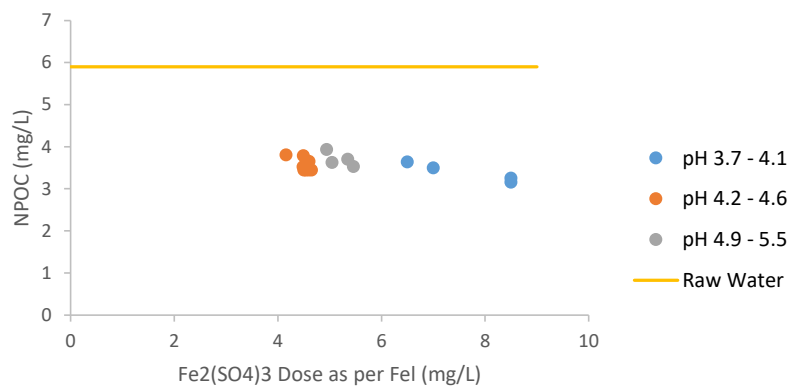


Figure 25 NPOC against increasing doses of Fe₂(SO₄)₃ as per Fe in Water D.

Appendix D

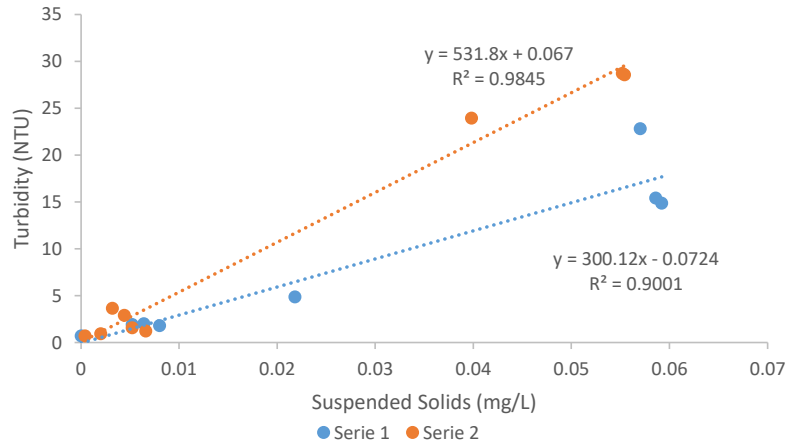


Figure 26. The relation between turbidity and suspended solids calculated from the data obtained during the experiments of the dosing position of PAC.

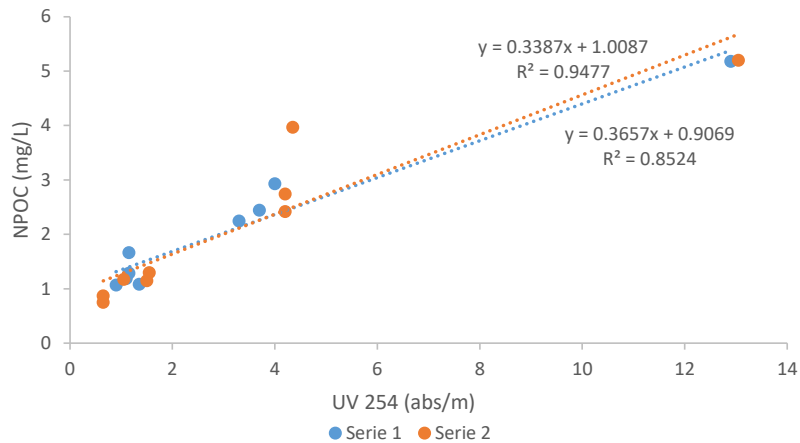


Figure 27 The relation between UV_{254} and NPOC calculated from the data obtained during the experiments of the dosing position of PAC.

The equation used to calculate the suspended solids is: $y = 531.8x + 0.067$ $R^2 = 0.9845$ and the equation used to calculate the NPOC is: $y = 0.3387x + 1.0087$ $R^2 = 0.9477$

Appendix E

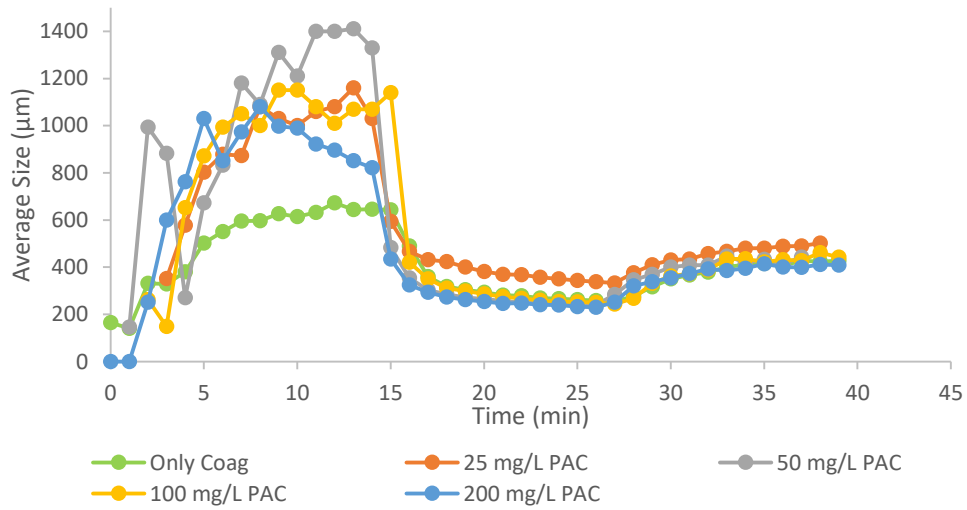
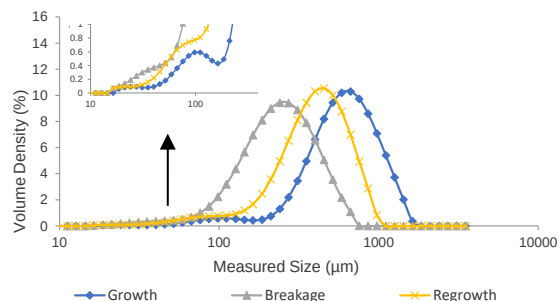
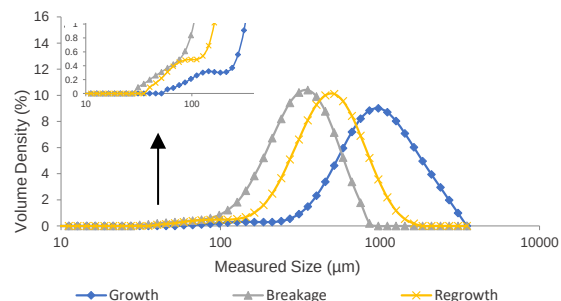


Figure 28 Results of floc's growth, breakage, and regrowth. Average size affected by different PAC doses. Replicate

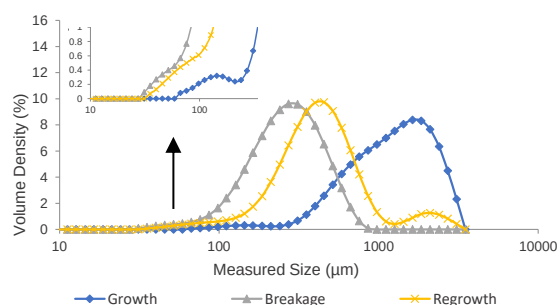
Appendix F



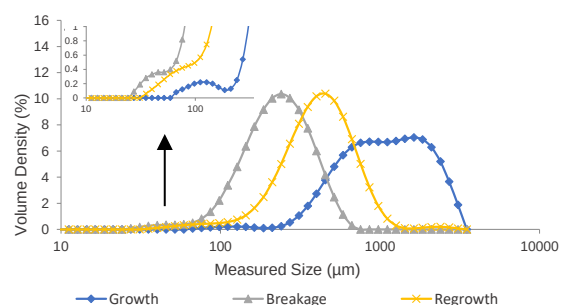
a. Only coagulant



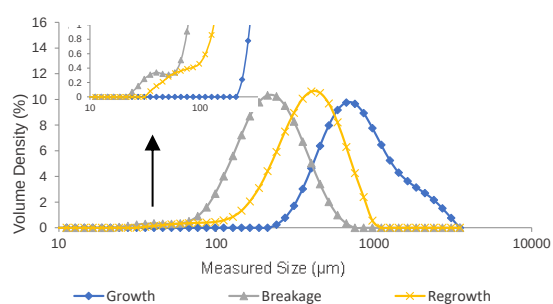
b. 25 mg/L PAC



c. 50 mg/L PAC



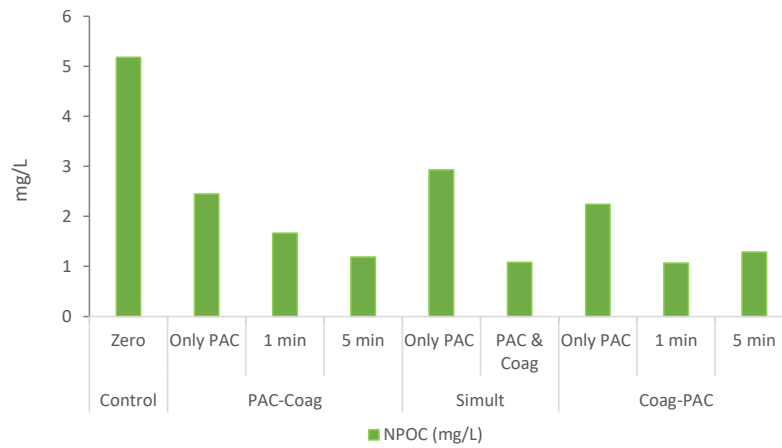
d. 100 mg/L PAC



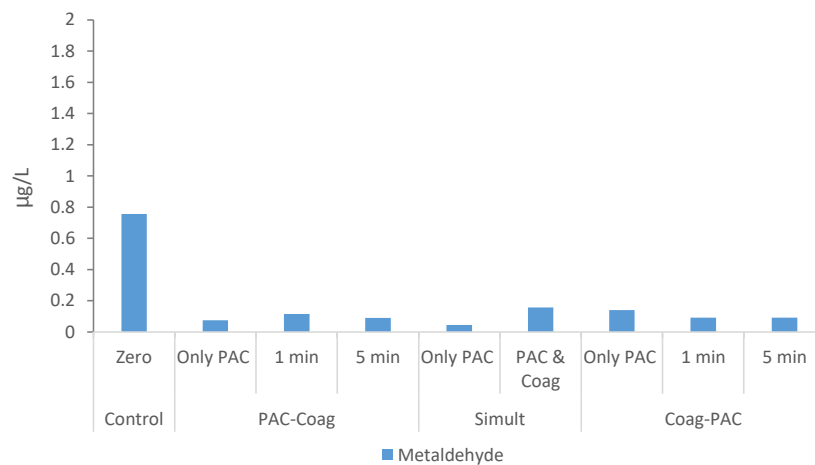
e. 200 mg/L PAC

Figure 29 Results of floc growth, breakage, and regrowth for systems with and without PAC. Volume density of flocs affected by different PAC doses. The inset figure shows a zoomed in graph of the small flocs present in the system. Replicate

Appendix G

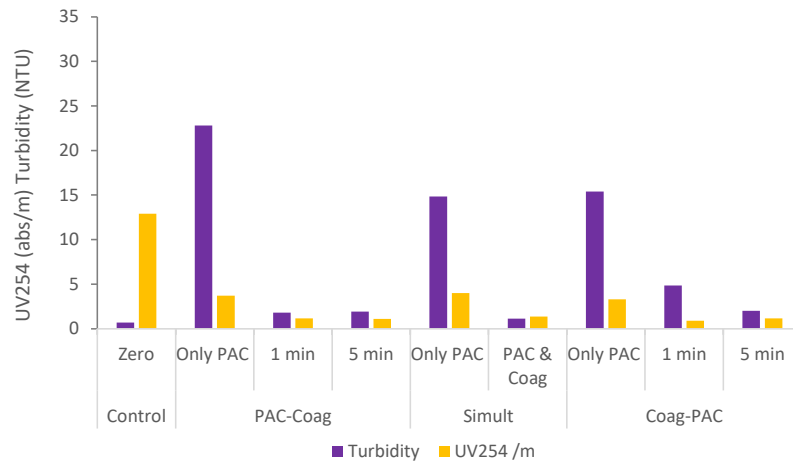


a. NPOC

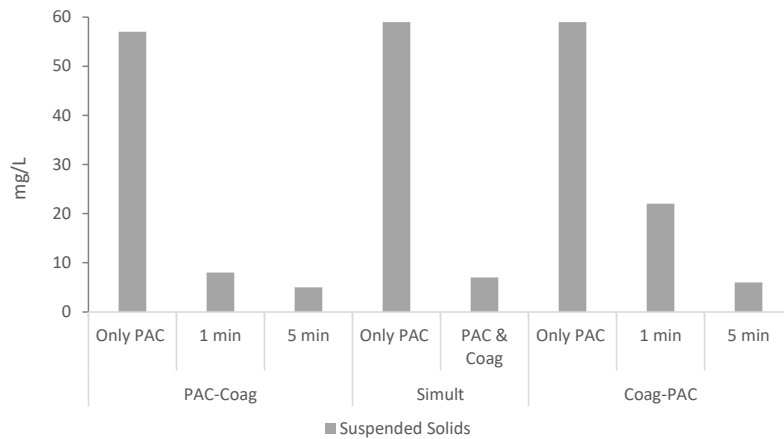


b. Metaldehyde

Figure 30 Results of (a) NPOC and (b) metaldehyde from the study of dosing position of PAC. 100 mg/L of PAC, 7 mg/L of coagulant, and 20 minutes of contact time after PAC and coagulant were dosed. Replicate



c. Turbidity / UV₂₅₄



d. Suspended Solids

Figure 31 Results of (a) turbidity and (b) suspended solids from the study of dosing position of PAC. 100 mg/L of PAC, 7 mg/L of coagulant, and 20 minutes of contact time after PAC and coagulant were dosed. Replicate.

Appendix H

Table 5 Raw data for the dosing position of PAC

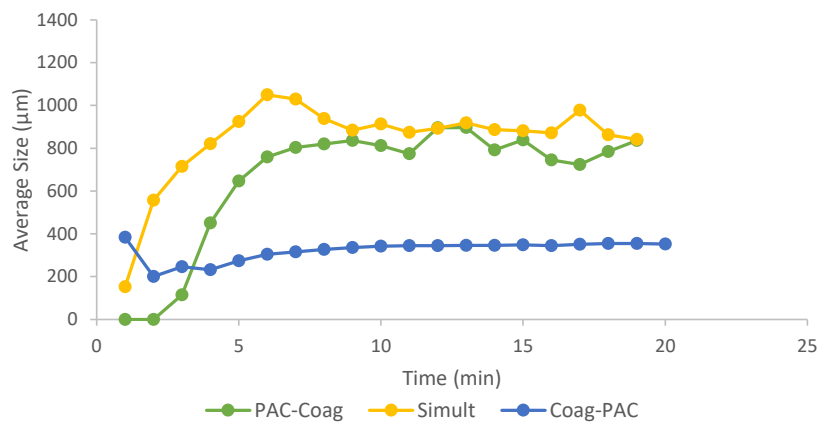
		pH	°C	UV254 (/m)	Turbidity (NTU)	Suspended Solids (mg/L)	Zeta Potential	NPOC (mg/L)	Metaldehyde (µg/L)	SUVA (L/mg cm)	Iron (µg/L)	Aluminium (µg/L)
	Control	-	21	12.9	0.7	0	-10.38	5.18	0.76	2.49	11.8	0.8
	Only PAC	-	21	3.7	22.8	57	-14.67	2.45	0.07	1.51	7.0	4.3
PAC-Coag	1 min	4.44	21	1.15	1.8	8	-13.17	1.66	0.11	0.69	151.0	78.7
	5 min	4.51	21	1.1	1.9	5	-13.60	1.19	0.09	0.93	44.8	37.9
	Only PAC	-	21	4	14.9	59	-12.20	2.93	0.05	1.36	8.3	4.3
Simult		4.54	21	1.35	1.1	-		1.08	0.16	1.25	188.0	93.6
	Only PAC	-	21	3.3	15.4	59	-10.04	2.24	0.14	1.47	7.4	4.2
Coag-PAC	1 min	4.56	21	0.9	4.9	22	-14.97	1.07	0.09	0.84	31.2	6.7
	5 min	4.54	21	1.15	2.0	6	-14.50	1.29	0.09	0.89	74.1	50.2

a.

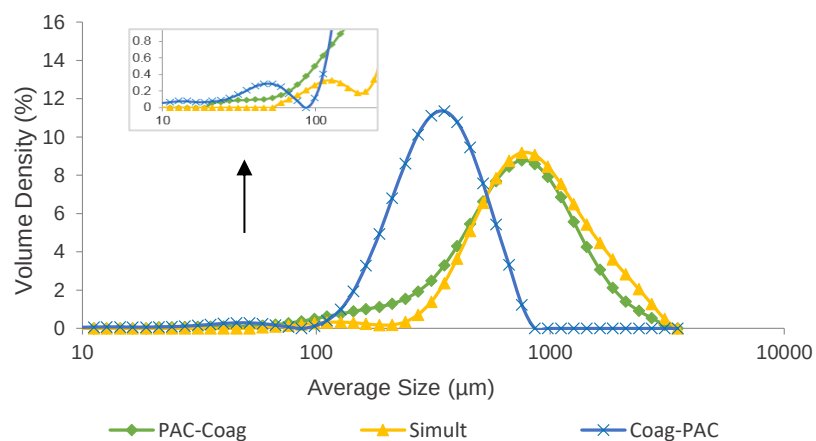
		pH	°C	UV254 (/m)	Turbidity (NTU)	Suspended Solids (mg/L)	Zeta Potential	NPOC (mg/L)	Metaldehyde (µg/L)	SUVA (L/mg cm)	Iron (µg/L)	Aluminium (µg/L)
	Control	8.31	20	13.05	0.7	0	-	5.20	1.96	2.51	15.3	5.0
	Only PAC	8.31	20	4.35	24.0	40	-	3.08	0.10	1.41	8.2	9.8
PAC-Coag	1 min	4.48	20	1.55	0.9	2	-	1.30	0.21	1.19	152.0	50.4
	5 min	4.52	20	1.05	1.6	5	-	1.17	0.18	0.89	113.0	33.1
	Only PAC	8.29	20	4.2	28.7	55	-	2.42	0.10	1.74	7.9	8.6
Simult		4.46	20	1.5	3.7	3	-	1.15	0.30	1.31	190.0	53.0
	Only PAC	8.31	20	4.2	28.6	55	-	2.74	0.08	1.53	10.8	9.7
Coag-PAC	1 min	4.48	20	0.65	1.2	7	-	0.87	0.18	0.75	85.8	51.4
	5 min	4.42	20	0.65	2.9	4	-	0.75	0.16	0.86	116.0	57.4

b.

Appendix I



a.



b.

Figure 32 Results of the monitoring of flocs for the study of PAC dosing position.
a. Average size of flocs for different sequences of addition. b. Particle size distribution for flocs after 15 minutes of flocculating. Replicate.