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IMPACT OF MIEX® PRE-TREATMENT ON FLOC STRENGTH AND STRUCTURE

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ABSTRACT

In drinking water treatment regulation standards for natural organic matter (NOM) are tightening owing the fact that NOM leads to formation of carcinogenic disinfection by-products which can be harmful for human health. To further remove NOM from water, advanced NOM removal processes are developed such as the magnetic ion exchange (MIEX) resin process. MIEX followed by coagulation has been shown to improve the dissolved organic carbon removal in comparison with coagulation alone. However knowledge is lacking about how the magnetic resin influences the floc structure which is of major importance for the efficiency of the downstream processes. The present thesis aimed to evaluate and understand the impacts of MIEX pre-treatment on floc properties. To meet these aims, a literature review was carried out in order to provide sufficient background on floc size, floc strength, re-growth potential and fractal dimension concepts. It showed that almost all of factors influencing these properties act on the floc structural properties via a modification of either the nature of the primary particles, or the conditions of coagulation process, or the hydrodynamic conditions of the surrounding water. De facto, these pre-cited properties are all linked together. It is especially recommended to interpret with care the floc strength concept.

The pre-defined objective was to compare properties of flocs generated by coagulation alone and combined treatment (MIEX pre-treatment followed by coagulation). Coagulation steps were operated with three different coagulants - $FeCl_3$, $AlCl_3$, PACl - at optimum pH and dose conditions on jar test bench. A light scattering instrument measured floc size and fractal dimension during growth, breakage and re-growth periods. Additional fractal dimension measurements for ferric flocs were gathered by image analysis using a microscope. MIEX pre-treated flocs were larger but withstood less well increases in shear rate than conventional flocs. This reduced robustness to increases in shear rate was thought to be due to the initial larger size of the pre-treated flocs. Light scattering and image analysis gave different fractal dimension values for the same floc system. It is probably because they are applicable for different size ranges: light scattering for the small primary particles and image analysis for the overall flocs. Of more operational interest, image analysis results showed that MIEX pre-treated flocs were more compact. Combined treatment gave an overall improvement in floc structure quality, producing flocs with better filterability and settleability.

EXECUTIVE SUMMARY

The presence of natural organic matter (NOM) in raw water used by the water treatment works (WTW) to produce drinking water can be a major problem. Indeed, since they have been proven to generate harmful and carcinogenic substances during the final disinfection step in the WTW, regulation standards have been tightened. In some cases, this leads to the need of advanced NOM removal processes. The magnetic ion exchange (MIEX) resin has been developed by Orica Watercare specifically for NOM removal.

Indeed, MIEX pre-treatment followed by coagulation has been seen to be more efficient than conventional coagulation in removing NOM and to require lower coagulant doses for NOM laden water. It has also been proven that MIEX pre-treatment influences floc properties and therefore the efficiency of downstream processes.

The economical benefit assessment of installing a new MIEX pre-treatment in a WTW has to consider the benefits coming from the reduction of the coagulant dose, the reduction of sludge volume (but new waste brine), the reduction in chlorine for disinfection and the impacts on downstream processes.

The aim of this thesis was to assess the reduction of coagulant demand and the potential impacts on downstream processes using the raw water from Kluizen WTW (VMW, Belgium). Consequently, the objectives of this bench-scale research project were to:

- compare the NOM removal for raw and MIEX pre-treated water after coagulation using three different coagulants (Aluminium chloride – $AlCl_3$, polyaluminium chloride – PACl and ferric chloride – $FeCl_3$).
- evaluate, compare and understand the impacts of MIEX pre-treatment on the physical properties of flocs, i.e. floc size, floc strength, floc potential regrowth and fractal dimension, using three different coagulants.
- assess based on the floc properties the advantages and disadvantages of a MIEX pre-treatment stage before coagulation on downstream processes such as filtration, sedimentation and flotation.

- investigate in parallel to the previous goals a potential relationship between floc fractal dimension and other floc properties.

To meet these objectives, six treatment options were studied. The six treatments were the combinations of raw water or MIEX pre-treated water and three different coagulants (Aluminium chloride – $AlCl_3$, polyaluminium chloride – PACl and ferric chloride – $FeCl_3$). Coagulation-flocculation experiments were carried out using a jar test apparatus. After investigation of the optimum pH and coagulant dose, floc size for each system was monitored with a Malvern Mastersizer 2000 during a sequence allowing rapid mixing for 2.5 min, floc growth for 15 min, breakage at different shear rates for 20 min and re-growth for 15 min (re-growth only for some experiments). Floc size data enabled the floc strength to be determined using the size value in itself and other parameters such as the floc strength constant. Fractal dimension of the flocs was worked out by two different methods: small angle laser light scattering technique and by image analysis using a light microscope coupled with an image analysis (IA) software. However, the latter technique was applicable only to ferric flocs since aluminium flocs were too transparent to mark the floc boundaries using the software.

Results of the bench-scale experiments lead to draw the following conclusions:

- Given the removal of dissolved organic carbon (DOC) material due to the MIEX pre-treatment, optimum coagulant doses were reduced and overall DOC removals for combined treatment were higher than for conventional coagulation, reducing the potential for formation of DBP during chlorination.
- According to the floc properties, the beneficial effects of MIEX pre-treatment were dependent on the coagulant choice. After MIEX pre-treatment ferric flocs were 2.5 times larger compared to conventional ferric flocs. Ferric chloride was seen to give a better regrowth potential to the flocs. The strongest flocs considering the γ values were generated from the raw water with PACl.
- The explanation for the improved floc properties after MIEX pre-treatment was thought to be as a result of improved removal of lower molecular weight substances, leaving behind polymeric like molecules in the water which when coagulated increased the floc size and compactness (according to the fractal dimension worked out by image analysis with ferric flocs). The effect on floc

size was especially observed for the ferric coagulant owing to its high selectivity for polyhydroxyaromatic compounds.

- MIEX pre-treated flocs could be considered stronger. Although they were more affected by the increased shear rates because of their larger size, they were still larger than conventional flocs (exception was for PACl of which MIEX treated floc size converged to a similar if not smaller floc size than conventional flocs).
- Fractal dimension values supported the hypothesis that SALLS and IA methods do not apply to the same length scales. SALLS applied to particles smaller than 2.5 µm and IA method to the whole floc making the latter method of more operational interest.

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NOMENCLATURE

A	Area	(µm^2)
$AlCl_3$	Aluminium chloride	
d	Floc diameter	(µm)
D	Fractal dimension	
d_1	Median steady-state floc diameter at the end of growth phase	(µm)
D_1	Fractal dimension in one-dimensional working space	
d_{10}	10th percentile floc size	(µm)
d_2	Median steady-state floc diameter at the end of breakage phase	(µm)
D_2	Fractal dimension in two-dimensional working space	
D_{2P}	Perimeter-based fractal dimension	
d_3	Median steady-state floc diameter at the end of regrowth phase	(µm)
D_3	Fractal dimension in three-dimensional working space	
d_{50}	Median floc size	(µm)
d_{90}	90th percentile floc size	(µm)
DAF	Dissolved air flotation	
DBP	Disinfection by-products	
DLA	Diffusion limited aggregation	
DOC	Dissolved organic carbon	(mg C L^{-1})
ERD	Effective resin dose	(mL L^{-1})
$FeCl_3$	Ferric chloride	
G	Velocity gradient	(s^{-1})
g	Gravity acceleration	(m s^{-2})
HA	Humic acid	
I	Intensity of the scattered light beam	
IA	Image analysis	
L	Characteristic length	(µm)
log(C)	Floc strength co-efficient	
MIEX	Magnetic ion exchange	

MW	Molecular weight	(Da)
n	Refractive index of the medium	
NOM	Natural organic matter	
NTU	Nephelometric turbidity unit	
P	Perimeter	(µm)
PACl	Polyaluminium chloride	
PHA	Polyhydroxyaromatic	
Q	Scattering vector	(nm^{-1})
$R_{aggregate}$	Aggregate size	(µm)
R_{br}	Rate of floc breakage	(s^{-1})
R_{col}	Rate of collision between particles	(s^{-1})
R_{floc}	Floc growth rate	(s^{-1})
RGD	Rayleigh-Gans-Debye	
RLA	Reaction limited aggregation	
$R_{particle}$	Primary particle size	(µm)
SALLS	Small angle laser light scattering	
SUVA	Specific ultra-violet absorbance	(L m^{-1} mg^{-1})
THM	Trihalomethane	
UV_{254}	Ultra-violent absorbance at 254 nm	(m^{-1})
V	Volume	(µm^{3})
VMW	Vlaamse maatschappij voor watervoorziening (Flemish water supply company)	
v_s	Terminal settling velocity	(µm s^{-1})
WTW	Water treatment works	
α	collision efficiency	
γ	Floc strength constant	
ζ	Zeta potential	(mV)
λ	Wavelength of the light in vacuum	(nm)
μ	Viscosity	
θ	Incident-scattered light beam angle	(rad)

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Last but not least, I thank my family for supporting me during my studies. Fortunately for me but for them too, it is done!

"On the cosmic scale, liquid water is rarer than gold.

For life, it is infinitely more valuable. "

Hubert REEVES
(13/07/1932)
BSc MSc PhD

French-Canadian
Astrophysicist and writer

CHAPTER 1 - INTRODUCTION

1. Background

Natural organic matter (NOM) derives from the biodegradation of plant and animal material and is found in natural water. NOM is a vaguely defined assortment of organic molecules with spatially and temporally changing properties (Vilgé-Ritter et al., 1999; Sharp et al., 2006). Organic compounds in drinking water are not themselves particularly harmful. However, they increase the coagulant demand, they affect the biostability of the water leading to bacterial regrowth and taste and odour issues (Parsons and Jefferson, 2006; Mergen, 2008), and finally they are precursors of carcinogenic and regulated disinfection by-products (DBP) such as trihalomethanes (THM) when disinfected (Crittenden and Montgomery Watson Harza, 2005).

Orica Watercare has designed a magnetic ion exchange (MIEX) resin (strong base anionic exchange) for NOM removal. Application of MIEX as a substitute to coagulation or as a pre-treatment before the coagulation stage in water treatment works (WTW) has already shown its ability in removing dissolved organic carbon (DOC) and reducing the coagulant demand (Singer and Bilyk, 2002; Jarvis et al., 2008). However, few studies reported the impacts of MIEX pre-treatment on downstream processes. This can be achieved by characterising the flocs generated by the subsequent coagulation flocculation processes as suggested by Jarvis et al. (2008a).

2. Approach

This research project has been commissioned by the Vlaamse Maatschappij voor Watervoorziening (VMW, Belgium), a Flemish water supply company. The objective of this work was to evaluate the positive and negative impacts of MIEX pre-treatment followed by coagulation on downstream processes and the impact of the coagulant choice on the performance of the combined processes. This was carried out by studying the physical properties of flocs formed by coagulation of the NOM laden water from Kluizen WTW using three different chemicals at bench-scale experiments.

In parallel, fractal dimensions of the flocs generated by the various combinations of treatments were worked out by two different methods and compared in order to assess the operational use of the fractal dimensions.

3. Report layout

This thesis report consists of four chapters including the introduction which sets the scene for the rationale behind this work. The second chapter is a literature review that describes the physical floc properties and discusses the factors affecting these properties. Chapter 3 defines the objectives of the project. The report of the experiments is presented in Chapter 4 in the form of a paper for publication in Water Research, including the usual sections: abstract, introduction, materials and methods, results, discussion and conclusions. The instructions for authors for Water Research are given in the appendices as well as reports of raw used data.

CHAPTER 2 - LITERATURE REVIEW: IMPACT ON FLOC STRUCTURE

1. Introduction

Regulations such as the European Directive (Council Directive 98/83/EC) define standards for the quality of drinking water in order to provide clean and safe water to people. Obviously all water sources (groundwater, surface water and seawater) need treatment to comply with these regulations. The role of the water treatment works (WTW) is to provide the required treatment necessary to meet these regulations.

To meet the water quality standards WTW remove dissolved and suspended components from the raw water and disinfect it in a final stage. To achieve this, the majority of WTW use coagulation and flocculation to provide bulk removal of dissolved and solid material. Coagulation destabilises fine particles and colloids after the addition of chemical coagulants leading to the formation of small aggregates. The following step of flocculation helps these particles and small aggregates to meet and collide with each other through gentle stirring leading to larger aggregates which are called flocs. WTW use the coagulation-flocculation sequence to generate flocs that are easier than fines and colloids to remove from water using one, or a combination, of settlement, filtration, adsorption or flotation.

Flocs therefore have then a critical importance in solid-liquid separation (Parsons and Jefferson, 2006; Bache and Gregory, 2007). It is therefore relevant to study their characteristics and also the parameters that influence floc properties in order to select and optimise the most appropriate separation processes.

The aim of this literature survey is: (1) to describe the main properties of flocs and (2) to explain the mechanisms that influence them, particularly for natural organic matter (NOM) flocs.

2. Floc properties

2.1. Number frequency distribution

Coagulation and flocculation increases the size and reduces the number of particles in water in order to increase the efficiency of downstream processes such as dissolved air flotation (DAF) and filtration. These processes can have operational problems in meeting their removal objectives when incoming water contains too many particles, especially when the particles are smaller than 50 µm (Mergen, 2008). Indeed these small and numerous particles can cause the early breakthrough of particles from filters or can be difficult to be floated because they do not collide and attach with enough bubbles.

The number of particles in water is also an indicator of the flocculation performance because of its influence on the floc growth rate (R_{floc}) which is a balance between floc formation and breakage as indicated in Eq.(1) (Jarvis et al., 2005):

$$R_{floc} = \alpha \cdot R_{col} - R_{br} \tag{1}$$

where α is the collision efficiency, R_{col} is the rate of collision between particles and/or aggregates which depends on particle size, mixing conditions and importantly the number of particles (concentration) (Yukselen and Gregory, 2004; Parsons and Jefferson, 2006). R_{br} is the rate of floc breakage. Consequently, for the same mixing conditions, an abnormally higher concentration of particles indicates a problem in the flocculation process (lower α value or higher R_{br}). Indeed given the same starting number of primary particles, if the final number of aggregates is higher than usual it means that the formed flocs are small and therefore will be more difficult to remove from water by solid-liquid separation techniques.

2.2. Size

The steady-state floc size distribution is a dynamic balance between formation and breakage (Eq.(1)). Growth beyond this steady-state floc size distribution is controlled by the applied shear rate (Bouyer et al., 2001). Floc size is strongly linked to floc strength. Table 2.1 provides information on how floc size is influenced by different factors such as the nature of the majority of the impurities, the addition of polymers, and the mixing conditions. Some general trends can be observed. Floc size depends on the nature of their primary particles. Magnetic ion exchange (MIEX) resin pre-treatment removes some of the impurities upstream the coagulation step. Addition of polymer changes the nature of these primary particles. Since organic and inorganic molecules have different properties, e.g. lengths and binding sites, the pre-cited treatments have an influence on the number and strength of bonds, and therefore on the aggregate size. Flocs are allowed to grow larger in low shear rate conditions since less destructive forces from tensile and shear stresses are applied on the floc. More details on the mechanisms of the different impacts are given in the second part of this literature review.

Table 2. 1: Size impact of different factors.
Symbols +/- mean that floc size tends to increase (+) or decrease (-) due to the factor.

Factors	Impact on floc size	Comment	Section
Nature of primary particles	+/-	Depends on intrinsic properties of primary particles: Algae flocs > kaolin flocs > NOM flocs	3.1
MIEX pre-treatment	+	MIEX removes small molecular weight (MW) NOM, dissolved organic carbon (DOC) to coagulant ratio decreases. These factors increase floc size in subsequent coagulation stage.	3.1.3
Polymer addition	?/+	When used as flocculant aid, floc bridging generally increases floc size. When used as primary coagulant polymer can increase number of bonds in floc	3.2.2
Increased temperature	+	Smaller floc size formed at lower temperatures	3.2.5
Increased shear rate	+	Floc size inversely related to the velocity gradient	3.2.7

2.3. Strength

The concept of floc strength refers to the number and intensity of the bonds amongst the components of the floc (Bache and Gregory, 2007). The nature of these bonds is variable: steric interactions (influenced by the conformation of molecules), van der Waals forces (very weak and instantaneous electrostatic forces arising from dipoles) and electrostatic attractions and polymer bridging (Mosley et al., 2003; Sharp et al., 2006). Floc strength is therefore very complex to characterize and measure. Nevertheless it can be assessed by parameters such as floc size, resistance to increasing shear rate and the degree of floc compaction.

Indeed, for the same given conditions, a larger floc is considered stronger as it can better withstand breakage factors (Jarvis et al., 2004; Yukselen and Gregory, 2004). Greater floc compaction is considered to increase floc strength because of the formation of more bonding interactions within the aggregate (Gregory, 1997).

Several quantitative factors have been proposed to characterise floc strength. These are described in more detail below.

2.3.1. Strength factor

Based on the fact that a stronger floc will be less affected by an increase of shear rate, the strength factor (Eq. (2)) for a given shear rate condition measures the relative decrease in size due to breakage (Francois, 1987).

$$\text{Strength factor} = \frac{d_2}{d_1} \times 100 \tag{2}$$

where d_1 is the average steady-state floc size before breakage and d_2 the size after breakage. Comparison of strength factors is possible only if the same breakage conditions are applied.

From the strength factor point of view, the largest flocs cannot be considered as always the strongest. Indeed small flocs are often less affected by breakage forces. These breakage forces often result from eddies. Eddies are swirls of water that are generated by a fluid flowing past an obstacle such as an impeller or a weir. Breakage eddies can entrain small flocs rather than break them (Parker et al., 1972). Under high shear rate conditions large flocs can break at their weakest points that generates smaller and more compact flocs with the strongest connections. In this way, small flocs resulting from the breakage of large flocs are usually stronger than the previous flocs (Spicer et al., 1998; Jarvis et al., 2005).

A theory about the energy dissipation of turbulent flow explains the different impacts that eddies have on flocs according to their sizes (Bache and Rasool, 2001; Jarvis et al., 2005a). In comparison with the Kolmogoroff's microscale of turbulence which indicates the length scale of the energy-dissipating eddies, bigger and smaller eddies dissipate their energy respectively in inertial convection (mixing of the system) and viscous energy (major energy dissipation). These two energy dissipation modes have impact on flocs according to the size of the flocs. Flocs smaller than the Kolmogoroff's microscale are thought to be eroded by eddies while bigger flocs are thought to be broken by large-scale fragmentation.

2.3.2. Floc strength co-efficient and constant

The empirical equation (Eq. (3)) relates the stable floc diameter to the applied shear rate:

$$\log(\mathrm{d}) = \log(\mathrm{C}) - \gamma \cdot \log(\mathrm{G}) \tag{3}$$

where d is the stable diameter, log (C) is the floc strength co-efficient, γ is the floc strength constant and G is the average velocity gradient (Bache and Rasool, 2001; Jarvis et al., 2005). On a plot of log (d) against log (G), log (C) is the y-axis intercept and γ is the slope of the line. The value of log (C) varies according to the value of d used, usually the d_{10}, d_{50} or d_{90}. Therefore to compare log (C) values these experimental parameters have to be the same. The value of γ can be used to compare results of different experiments whichever d value is used (if the same units are used for d and G respectively). The lower γ, the less withstanding the flocs are to increased shear rate.

Many authors suggest that γ value also indicates the main mode of floc breakage; surface erosion when $\gamma = 1$ or fragmentation when $\gamma = 0.5$ (Parker et al., 1972). But application of this theory is still subject to debate (Jarvis et al., 2005; Henderson et al., 2006).

Several parameters have been shown to impact on the floc strength (Table 2.2). The two major factors are the time and intensity of breakage conditions and the nature of the bonds holding the particles of the aggregate together. The nature of the bonds depends on the composition of the aggregate, the kind of coagulation mechanism used to generate the floc. Internal repulsive forces can appear when primary particles are of same sign of charge. In consequent, it is important to have an overall charge close to zero. The floc strength constant γ has to be interpreted carefully. Indeed, because larger flocs (considered then stronger) are more affected by an increased shear rate (higher γ) they withstand less well to breakage conditions and then can be considered weaker. However, initially larger flocs can sometimes remain larger after breakage than initially smaller flocs but more resistant.

Table 2. 2: Strength trends and impacts of different parameters.

Symbols +/- mean that floc strength parameter tends to increase (+) or decrease (-) due to the factor.

Factors	Floc strength in general	Comment	Section
Increased concentration of DOC content in floc	-	Steric effect of organic molecules impacts on floc bonding.	3.1.1
MIEX pre-treatment	+	Removes small MW NOM, DOC:coagulant ratio decreases.	3.1.3
Coagulant type	+/-	Different impacts thought to be due to optimum pH.	3.2.1 & 3.2.3
Increased pH	-	Deprotonation of phenolic groups creating internal repulsive forces.	3.2.3
	Strength factor under similar breakage conditions		
Increased temperature	-	Floc strength increases with decreasing water temperature	3.2.5
Breakage shear rate and time	-	Decrease in floc strength for longer and higher breakage shear rate.	3.2.7
	Floc strength constant, γ		
Increased floc size	-	Better resistance to breakage for small flocs due to fewer impacts from breakage eddies.	2.3.1
Nature of primary particles	+/-	NOM < kaolin < algae (NOM withstands better increases in shear rates).	3.1
Increased alkalinity	-	Low alkalinity flocs better withstand increases in shear rates.	3.1.2
Polymer addition	+	More bonds formed from addition of polymer.	3.2.2
Zeta potential	+/-	More or less repulsive forces within the floc.	3.2.4
Flocculation mode	+/-	Charge neutralization > sweep flocculation > bridging	3.2.6

2.4. Re-growth potential

After breakage, the residual flocs have the relative ability to re-aggregate into larger flocs (Yukselen and Gregory, 2004). This is an important property of the flocs. Indeed flocs can encounter high shear zones in WTW (e.g. up to 7600 s^{-1} in the contact zone of a DAF unit (Jarvis et al., 2008), or zones close to flocculator impellers (McCurdy et al., 2004) that can break flocs. If the broken flocs have the ability to re-grow when returned to lower shear rates, the efficiencies of the downstream processes will be less affected by the breakage (such as sedimentation and filtration). However, complete re-growth to the initial size is seldom observed. The recovery factor (Eq.(4)) quantifies the relative floc re-growth after breakage(Francois, 1987).

$$\text{Recovery factor} = \frac{d_3\text{-}d_2}{d_1\text{-}d_2} \times 100 \tag{4}$$

where d_1, d_2 and d_3 are respectively the average steady-state floc sizes before breakage, after breakage and after re-growth.

Table 2.3 provides information on how recoverability is influenced by different factors. The critical factor is the nature of the internal bonds between the macromolecules in the floc. Physical bonds such as van der Waals forces are able to reform after breakage whereas chemical bonds remain broken during regrowth phase (Yukselen and Gregory, 2004; Jarvis et al., 2005a). Time and intensity of the breakage phase also are important when considering regrowth. Long and intense shear periods break more bonds and allow the macromolecules to find another conformation within the floc.

Table 2. 3: Recoverability impact of different parameters.

Symbols +/- mean that degree of reversibility tends to increase (+) or decrease (-) due to the factor.

Factors	Reversibility impact	Comment	Section
Type of bonds within the floc	+/-	Ability of bond reformation after breakage for physical bonds.	This section
Polymer addition	+	Numerous physical bonds.	3.2.2
Floc formation mechanism	+/-	Depends on the nature of the bonds. Reformation of chemical bonds is not possible following breakage	3.2.7
Increased exposure to high shear rate	-	Bonds are broken and internal restructuring takes place which prevents re-growth.	3.2.7

2.5. Fractal dimension

2.5.1. Background

Floc density, porosity, settling velocity, permeability (Waite et al., 2001) and strength are physical parameters that strongly depend on floc structure. Fractal geometry developed by Mandelbrot offers the possibility to describe these structures. A fractal object presents a self-similar structure whichever the degree of magnification and shows a power law relationship between two of its geometrical parameters (Eqs. (5), (6) and (7) below). An example of a fractal object is given in Figure 2.1 showing the feature of self-similarity.

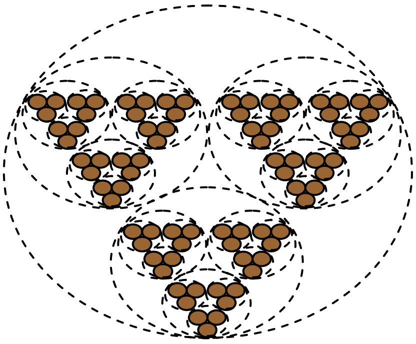

Figure 2. 1: Self-similarity character and porosity of a fractal object (adapted from Gregory, 1997).

Several studies have shown that flocs generated in WTW can be considered as fractal objects (Huang, 1994; Waite et al., 2001). Aggregation of primary particles and clusters generates the porous fractal-like structure that is the floc. This explains the decreasing density with increasing size observed for flocs (Gregory, 1997; Tang et al., 2002).

The fractal dimension of a fractal object gives an indication about how it occupies space. For instance, the three-dimensional fractal dimension of an aggregate indicates how well packed are the particles forming the aggregate. Its value varies between 1 and 3. A fractal value around 1 corresponds to a highly porous and branched aggregate whilst a value approaching 3 indicates a solid filled object.

Different fractal dimensions (D_1, D_2 and D_3) result according to the power-law relationships used (Kim et al., 2001). These power-laws (Eqs.(5) to (7)) relate the characteristic length of the object (L) to its perimeter (P), area (A) and volume (V), respectively in one-, two- and three-dimensional working space.

$$P \propto L^{D_1} \tag{5}$$

$$A \propto L^{D_2} \tag{6}$$

$$V \propto L^{D_3} \tag{7}$$

Spicer and Pratsinis (1996) used a perimeter-based fractal dimension (D_{2P}) to relate perimeter to area (Eq.(8)).

$$A \propto P^{\frac{2}{D_{2P}}} \tag{8}$$

By plotting these relationships on a log-log scale these different fractal dimensions can be calculated from the slope of the line generated.

D_1, D_2, D_{2P} and D_3 do not have the same meanings and are generated in different ways. Therefore they cannot be compared each other.

2.5.2. Fractal dimension measurement techniques

2.5.2.1. Sedimentation

One feature of fractal objects such as three dimensional flocs is that they have a high degree of porosity (Gregory, 1997); this porosity increases as the flocs get larger (Figure 2.1). The porosity can enable flow to pass through a floc aggregate when it settles which can modify its settling behaviour. Therefore the settling rate is not properly described by the traditional Stokes law which is applicable for spherical objects (Gorczyca and Ganczarczyk, 1999; Atkinson et al., 2005; Liss et al., 2005). An expression for the settling rate therefore has to take into consideration this porosity. This can be done by including the fractal dimension. Floc fractal dimension can therefore be calculated by measuring floc settling rate.

Floc settlement can be measured using image analysis to allow direct recording of individual floc sizes (d) and terminal sedimentation rates (v_s). It is demonstrated that these two variables are related to the fractal dimension (D_3) by Eq.(9) (Jarvis et al., 2005b):

$$v_s = \frac{4\,C}{3\,A(\beta)} \frac{g}{\mu} d^{D_3 - 1} \tag{9}$$

where C is the proportionality constant, g is the gravity acceleration, A(β) is a correction factor accounting for advection through the floc pores (constant for floc sedimentation) and μ is the viscosity of the medium (usually water in most cases involving floc).

By plotting v_s against d on a log-log scale, the average D_3 of the flocs in the system can be worked out from the slope of the line which is D_3-1.

2.5.2.2. Light scattering methods

Light scattering methods such as photon correlation spectroscopy, turbidity fluctuation method and small angle laser light scattering (SALLS) are able to determine the fractal dimension of aggregates (Gregory, 1997). Because SALLS is more commonly used, this fractal measurement is described in the next paragraphs.

The principle of the SALLS technique is the following: a particle of the fractal aggregate sample scatters the incident light beam. The intensity and the scattering angle are recorded by a series of photo-sensitive detectors. The magnitude of this angle is inversely related to the size of the particle scattering (Jarvis et al., 2005a). According to the scattering theory, under the Rayleigh-Gans-Debye (RGD) regime the intensity (I) of the scattered light beam is related to the scattering momentum (Q), also called the scattering vector (Eq.(10)) (Tang et al., 2002; Jarvis et al., 2005a; Li et al., 2006).

$$\mathrm{I} \propto \mathrm{Q}^{-\mathrm{D}_3} \tag{10}$$

where D_3 is the average fractal dimension of the sample aggregates and Q is the scattering momentum which depends on the incident-scattered light beam angle (θ), the refractive index of the medium (n) (usually water) and the wavelength of the light in vacuum (λ) (Eq.(11)).

$$Q = \frac{4\pi\mathrm{n}}{\lambda}\sin\left(\frac{\theta}{2}\right) \tag{11}$$

The photo-sensitive detectors measure the light intensities at known angles. Consequently Eq.(10) can be drawn on a log-log plot where the magnitude of the slope of the linear part of the curve (corresponding to the RGD regime) is the average fractal dimension of the aggregates of the system (Figure 2.2).

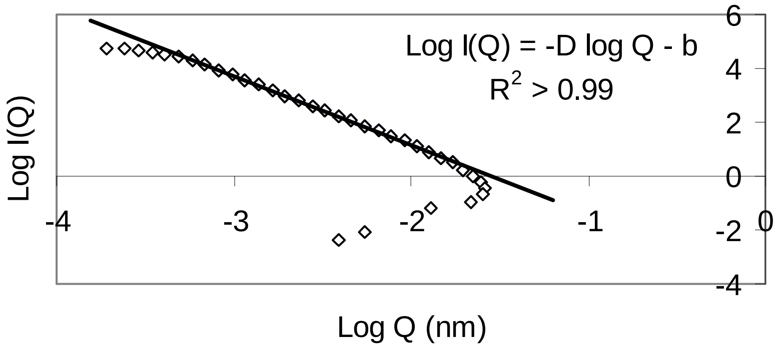

Figure 2. 2: Scattering plot to work out the fractal dimension of the system.

However use of the SALLS method is subject to some debate. Indeed, to apply the RGD law (Eq.(10)) some assumptions are made that are not all in accordance with the reality. Assumptions are that light beams are scattered only once by individual particles (for high concentrations of particles, multiple scattering can occur) and that the refractive index of the scattering particle is low (as this avoids shortening of the incident light) (Waite et al., 2001; Tang et al., 2002). Another condition to apply for Eq.(10) is that the length scale of investigation (corresponding to Q^{-1}) has to be much larger than the primary particle size ($R_{particule}$) and much smaller than the size of the aggregates ($R_{aggregate}$) (Eq.(12)). When the aggregate size is too close to the length scale the I-Q-D relationship (Eq.(10)) is modified because it is influenced by the edge of the cluster. In the case of an aggregate size larger than the length scale, the measured intensity does not depend on the aggregate structure anymore (Waite et al., 2001; Jarvis et al., 2005a).

$$\begin{aligned} & R^{-1}_{\text{aggregate}} << Q << R^{-1}_{\text{particle}} \\ \Leftrightarrow\ & R_{\text{aggregate}} >> Q^{-1} >> R_{\text{particle}} \end{aligned} \tag{12}$$

Nevertheless the SALLS method is generally regarded as being a reliable technique to work out the fractal dimension of aggregates in water and wastewater treatment (Bushell and Amal, 2000; Waite et al., 2001).

2.5.2.3. Image analysis

Image analysis (IA) is a useful tool to derive fractal dimension from pictures. However, the fractal dimensions that can be obtained are not the mass fractal dimension (D_3) but either the D_1 or D_2 or D_{2P}. This is because pictures represent only the aggregate projected area and information about the third-dimension is lost (Gregory, 1997). However an ellipse approximation of the two-dimensional object provides a three-dimensional object by rotation about one axis. From this newly generated volume, D_3 can be worked out (Atkinson et al., 2005). This method is not commonly used. This might be because it assigns a third dimension length to the object under investigation without knowing its actual three-dimensional shape.

The Richardson "hand and dividers" method is used to calculate the boundary fractal dimension of an object (Podsiadlo and Stachowiak, 1998). This method calculates D_1 from Eq.(5) where the perimeter is related to the characteristic length by the fractal dimension. The characteristic length corresponds in this case to a yardstick that is used to measure the perimeter (Soille and Rivest, 1996). For short yardsticks the measured perimeters are longer than with long yardsticks. This is because short yardsticks measure more accurately the actual perimeter (Figure 3.3). If perimeters and corresponding yardstick lengths are plotted on a log-log plot, D_1 is the slope of the relationship. The more irregular the boundary of the object under investigation is, the higher D_1 value is obtained.

This fractal dimension D_1 is measured for each individual object.

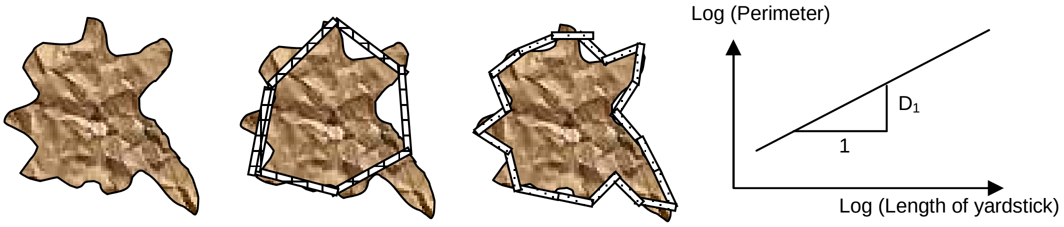

Figure 2. 3: The Richardson "hand and dividers" method to calculate the boundary fractal dimension.

When perimeters or areas of objects in a system are known, D_2 can be derived from these parameters (Eqs.(6) and (8)). In this case, the characteristic length corresponds usually to the largest length or the major axis of the best ellipse approximation of the object (Kim et al., 2001; McCurdy et al., 2004; Atkinson et al., 2005). In contrast to the D_1 value, the resulting D_2 is an average fractal dimension of the aggregates of the system under investigation rather than individual flocs. IA software exists that can be used to measure the required parameters more quickly

2.5.3. Trends

In order to evaluate the influences of different parameters on the strength and fractal dimension of an aggregate, data from the literature have been compiled inTable 2.4. Characteristics of aggregates are described and fractal dimension(s) and floc strength constant (γ), when available, are provided. The first criterion for classification is the method used for the fractal dimension measurement.

Table 2. 4: Collection of fractal dimension values from various sources in the literature.

Aggregate type	Method used	D_3 (unless specified)	γ	Reference
NOM + Fe	Settling	1.97	0.47	(Jarvis et al., 2008)
NOM + Fe + MIEX	Settling	1.76	0.54	
NOM + polymer	Settling	1.99	0.74	
NOM + Fe + polymer	Settling	1.86	0.32	
Fe precipitate	Settling	2.14	1.17	(Jarvis et al., 2006)
NOM + Fe	Settling	2.01	0.44	
NOM + Fe+ polymer	Settling	1.86	0.32	
NOM + Fe	Settling	2.10	0.52	(Sharp et al., 2006)
└> HAF + Fe	Settling	1.78	0.75	
└> FAF + Fe	Settling	2.24	0.64	
└> HPIA +Fe	Settling	1.90	0.74	
└> HPINA + Fe	Settling	1.88	0.82	
NOM-spring + Fe	Settling	2.00	0.34	(Jarvis et al., 2004)
NOM-summer + Fe	Settling	2.01	0.47	
NOM-autumn + Fe	Settling	1.81	0.49	
NOM-winter + Fe	Settling	1.97	0.31	
DOC:Fe ratio = 0	settling	2.20	1.17	(Jarvis et al., 2005b)
DOC:Fe ratio = 0.33	settling	2.04	0.9	
DOC:Fe ratio = 0.75	settling	2.01	0.65	
DOC:Fe ratio = 1	settling	1.88	0.65	
DOC:Fe ratio = 1.75	settling	1.91	0.60	
DOC:Fe ratio = 3.8	settling	1.78	0.53	
activated sludge flocs	settling	1.45-2.0		(Li and Ganczarczyk, 1989)
activated sludge flocs	settling	1.44-1.49		(Magara et al., 1976)
activated sludge flocs	settling	1.4		(Tambo and Watanabe, 1979)
clay + Fe	settling	1.92		
clay + Mg	settling	1.91		
kaolin + Fe	settling	2.06	0.77	(Jarvis et al., 2008)
alum aggregates	settling	1.59-1.97		{{36 Tambo,N. 1979}}
colloidal nickel hydroxycarbonate at high concentration	SALLS	1.7-1.8		(Hoekstra et al., 1992)
colloidal nickel hydroxycarbonate at low concentration	SALLS	2.0-2.1		
lowland water flocculated by sweep flocculation	SALLS	2.20		(Kim et al., 2001)
lowland water flocculated by charge neutralisation	SALLS	1.84		
iron hydroxide from $FeCl_3$ hydrolysis	SALLS	2.25→2.52		(Jung et al., 1996)
kaolin + alum flocculated by sweep flocculation	SALLS	2.58-2.91	0.56	(Li et al., 2006)
kaolin + alum flocculated by charge neutralisation	SALLS	2.55-2.76	0.61	

kaolin + alum flocculated by charge neutralisation + polymer	SALLS	2.40-2.63	0.37	(Li and Ganczarczyk, 1989)
NOM + alum	SALLS	2.43		(Jarvis et al., 2005a)
NOM + Fe	SALLS	2.21		
NOM + polymer	SALLS	2.56		
Fe precipitate	SALLS	2.17		
latex particles in presence of NaCl	SALLS	1.66		
polystyrene particles + alum	SALLS	2.3		(Spicer et al., 1998)
river @ pH 5.5 + $FeCl_3$	SALLS	2.42		(Vilgé-Ritter et al., 1999)
river @ pH 7.5 + $FeCl_3$	SALLS	2.28		
lake @ pH 5.5 + $FeCl_3$	SALLS	2.93		
lake @ pH 7.5 + $FeCl_3$	SALLS	2.11		
aluminium oxide from $AlCl_3$ hydrolysis in 0.2M $CaCl_2$ solution	SALLS	2.11		(Waite et al., 2001)
aluminium oxide from $AlCl_3$ hydrolysis in 0.6M $CaCl_2$ solution	SALLS	2.23		
aluminium oxide from $AlCl_3$ hydrolysis in 0.6M NaCl solution	SALLS	2.09		
aluminium oxide from $AlCl_3$ hydrolysis in 0.21mM Na_2SO_4 solution	SALLS	1.85		
aluminium oxide from $AlCl_3$ hydrolysis in 0.31mM Na_2SO_4 solution	SALLS	1.91		
humic acid + $AlCl_3$ (Al_{mono}) after 8min breakage	SALLS	2.27		(Wang et al., 2009)
humic acid + PACl (32%Al_{13}) after 8min breakage	SALLS	2.17		
humic acid + PACl (97%Al_{13}) after 8min breakage	SALLS	1.91		
lowland water flocculated by sweep flocculation	IA	D_1=1.31 D_2=1.48		(Kim et al., 2001)
lowland water flocculated by charge neutralisation	IA	D_1=1.08 D_2=1.53		
river water + alum settleable	IA	D_2=1.86		(McCurdy et al., 2004)
river water + PACl settleable	IA	D_2=1.61		
river water + PACl + alum settleable	IA	D_2=1.58		
river water + alum non-settleable	IA	D_2=1.63		
river water + PACl non-settleable	IA	D_2=1.69		
river water + PACl + alum non-settleable	IA	D_2=1.61		
river water + polymer @ $10s^{-1}$	IA	D_2=1.55		(Atkinson et al., 2005)
river water + polymer @ $40s^{-1}$	IA	D_2=1.70		
river water + polymer @ $100s^{-1}$	IA	D_2=1.75		
latex particles + polymer @ $10s^{-1}$	IA	D_2=1.65		
latex particles + polymer @ $40s^{-1}$	IA	D_2=1.70		
latex particles + polymer @ $100s^{-1}$	IA	D_2=1.85		
latex particles + alum @ $20s^{-1}$	IA	D_2=1.62		
latex particles + alum @ $80s^{-1}$	IA	D_2=1.75		
latex particles + alum @ $20s^{-1}$ after 10min	IA	D_2=1.65 D_3=2.47		

From Table 2.4, several conclusions can be drawn based on these fractal dimension and strength values, provided the assumption that these results from different studies are comparable each other in respect with their dimension working space (D_1, D_2 or D_3) as explained previously. Indeed some trends amongst the different aggregate studies are observed and are common to the three techniques used to calculate the fractal dimension (Settling, SALLS and IA) and to all the dimensional working spaces (D_1, D_2, D_3).

There is not a direct relationship between fractal dimension and floc strength factor as expected. Indeed, the floc strength factor does not depend only on the compactness of the floc but also a lot of other parameters such as the nature of the primary particles, presence of polymer and pH.

Table 2.4 shows that D_3 fractal dimensions are similar for NOM and inorganic aggregates. However, biological flocs have lower D_3 values because of the living nature of their components that produce substances such as extracellular organic matters. These substances are polymeric type molecules and lead to form more branched aggregates.

A statistically significant difference between D_3 values obtained from the settling method and the SALLS method (Table 2.5) is observed (Kruskall-Wallis test, $P < 0.001$). This difference has already been observed in other studies (Jarvis et al., 2008b). Higher SALLS values refer to the structure of small aggregates within the overall floc structure due to the limitations of the scale of investigation using this method (Eq.(12)). The D_3 value obtained from settling refers to the structure of the overall floc structure.

Table 2. 5: Averages and standard deviations of the fractal dimensions D_3 for different natures of aggregate and methods.

Methods	**Organic flocs**	**Inorganic flocs**	**Biological flocs**
Settling	1.94 ± 0.12	1.97 ± 0.20	1.56 ± 0.25
SALLS	2.28 ± 0.29	2.23 ± 0.35	No data

Atkinson et al. (2005) found that floc fractal dimension increases and floc size decreases as the velocity gradient used for floc growth increases (cf. Hydrodynamics and breakage, section 3.2.7).

Sweep flocculated flocs have higher fractal dimension than charge neutralization flocs (Kim et al., 2001; Li et al., 2006). This trend is observed for both organic and inorganic aggregates (cf. Floc formation mechanisms, section 3.2.6).

About the coagulation-flocculation process of humic acid (HA) with aluminium salts, Wang et al. (2009) showed that a coagulant with a higher Al_{13}-concentration such as polyaluminium chloride generates more branched flocs because of the unstable HA-Al_{13} complexes formed. Coagulants with higher Al_{mono}-concentration such as aluminium chloride produce more compact flocs due to formation of HA-Al_{mono} octahedral coordinated complexes (cf. Coagulant type and dose, section 3.2.1).

Vilgé-Ritter et al. (1999) noticed that fractal dimensions of organic flocs decreased as the coagulation pH increase due to the deprotonation of phenolic OH groups (cf. Coagulation pH, section 3.2.3).

Another conclusion drawn from the above table is that aggregates composed of many different types of primary particles are stronger (smaller γ values). As explain previously, this γ parameter has to be interpreted carefully. Indeed, in most of the cases, flocs which were initially larger were still larger (hence stronger) than the initially smaller flocs, or had a similar floc size after breakage.

Table 2.6 presents a summary of these conclusions and the impact of others factors not developed above. More details on the mechanisms of the different impacts are given in the second part of this literature review.

Table 2. 6: Fractal dimension trends and impacts of different parameters.
Symbols +/- mean that fractal dimension tends to increase (+) or decrease (-) due to the factor.

Factors	Fractal dimension impact	Comment	Section
Non-isometric particles (e.g. fibres, mica)	-	Poor packing.	-
MIEX pre-treatment	+	Removes small MW NOM, DOC:coagulant ratio decreases.	3.1.3
Increasing coagulation pH	-	Higher pH generates repulsive forces from deprotonation of organic molecules	3.2.3
Flocculation mode	+/-	Sweep flocculation > charge neutralization > bridging	3.2.6
Aggregation mechanism	+/-	Reaction limited aggregation (RLA) > diffusion limited aggregation (DLA)	3.2.6
Shear rate during floc formation	+	More restructuring at high shear rate increases floc compaction.	3.2.7

3. Factors influencing floc properties

All the floc properties described in the first part of this literature review vary with numerous factors. A number of these factors are inherent to the nature of the raw water, such as the chemical composition, hydrophobicity and alkalinity. Other factors are a result of the conditions in which the coagulation-flocculation processes are operated, such as the coagulation pH, coagulant type and dose, formation and the breakage hydrodynamics.

The following section gives an overview of the factors influencing floc properties and their mechanisms with a particular focus on NOM flocs.

3.1. Raw water characteristics

The first and most important parameter that influences floc properties is the nature of the primary particles. It is well-known and easy to understand that flocs from algae, NOM or clay laden waters have very different characteristics (Henderson et al., 2006). For instance, Henderson et al. (2006) showed that the rank for median floc size was algae > kaolin > NOM and the rank for the floc strength constant (γ) was NOM < kaolin < algae. In other words, the smaller NOM flocs were able to better withstand the increased shear rate than the other floc systems.

3.1.1. Natural organic matter and hydrophobicity

NOM is a vaguely defined assortment of organic molecules. NOM properties such as acidity, molecular weight, molecular structure and charge density often vary spatially and temporally. NOM derives from the biodegradation of plant and animal material (Vilgé-Ritter et al., 1999; Sharp et al., 2006). Organic compounds in drinking water are not themselves particularly harmful but they are precursors of carcinogenic disinfection by-products (DBP) such as trihalomethanes (THM) when chlorinated (Crittenden and Montgomery Watson Harza, 2005).

NOM is composed of hydrophilic and hydrophobic materials (Jarvis et al., 2008a). A good indicator of the degree of hydrophobicity is the specific ultra-violet absorbance (SUVA) which is the ratio of UV absorbance at 254 nm (m^{-1}) to DOC concentration (mg L^{-1}) (Edzwald, 1993). Waters with a SUVA value above 4 $Lm^{-1}mg^{-1}$ are considered hydrophobic and greater than 50 % DOC removal is easily achievable with coagulation-flocculation process. Water with a SUVA under a value of 2.5 Lm^{-}

^{1}mg^{-1} waters are considered hydrophilic and lower DOC removal is achieved (Parsons and Jefferson, 2006). Although hydrophobicity does not have any proven direct impact on floc strength, it influences some processes such as the MIEX pre-treatment described below in section 3.1.3.

It is generally accepted that NOM flocs are weaker and have a lower density than inorganic flocs (Bache et al., 1999). This observation can be explained by the steric repulsion effect. Indeed NOM molecules with high MW are generally polymeric type molecules. The tails and loops formed by these molecules keep the primary particles separated, reducing the intensity of the bonds which means that the flocs are weaker (Sharp et al., 2006).

3.1.2. Alkalinity

The total alkalinity of water is the concentration of alkaline salts (bicarbonate, carbonate and hydroxide ions) which react with acids. It gives the water a buffering capacity which is important for maintaining optimum pH conditions when coagulant is added (Gregory and Dupont, 2001). Moreover unstable particles such as clay can be destabilized in the presence of high calcium content (Ca^{2+}) leading to slow coagulation (Gregory and Dupont, 2001).

Bache and Rasool (2001) observed in their study that flocs formed in high alkalinity water were more affected by increased shear rate in term of size than low alkalinity flocs (high alkalinity flocs have a higher γ value).

3.1.3. MIEX pre-treatment

Orica Watercare of Victoria (Australia) has developed the magnetic ion exchange (MIEX) resin in order to treat water with high DOC content which has a high coagulant demand and DBP formation potential. The MIEX resin combines traditional strong base anion exchange properties (hydrophobic and hydrophilic acid removal) with magnetic components (iron oxide) integrated into the resin beads. The MIEX process is illustrated in Figure 2.4. The resin is added to the raw water in slurry form, mixed and then settled in a clarifier very quickly because of its magnetic property that leads the beads to agglomerate rapidly. A recycle loop is operated with a generation step. The fact that the beads settle very quickly allows the use of smaller beads than traditional resin (180 µm mean diameter), increasing their specific surface area available for ion exchange (Singer and Bilyk, 2002; Boyer and Singer, 2005; Singer et al., 2009).

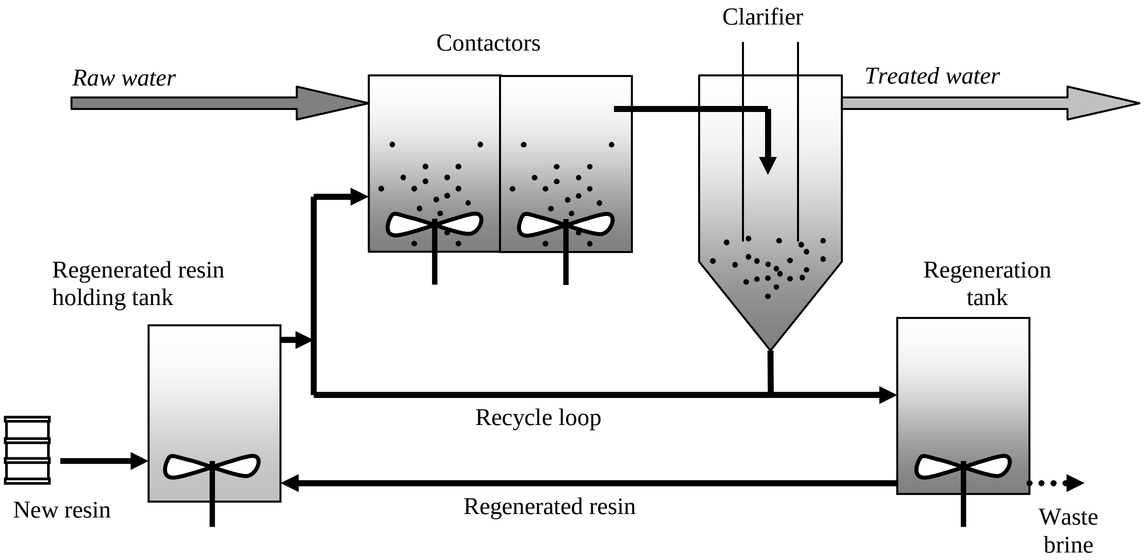

Figure 2. 4: Schematic of the MIEX process (adapted from Singer et al., 2009).

Whilst conventional coagulation removes only hydrophobic NOM (high MW and charged organic compounds with high SUVA) (Jarvis et al., 2008a), the MIEXprocess removes both hydrophobic and hydrophilic acids (low MW NOM) (Singer and Bilyk, 2002; Jarvis et al., 2008a). However, MIEX does not remove organic compounds with high MW (>5000 Da) or small neutral organics (Mergen et al., 2008).

Some studies have shown that the effectiveness of the MIEX process is water specific (Morran et al., 2004; Mergen et al., 2008) although Singer and Bilyk (2002) have shown that it was efficient when applied on nine NOM laden waters with different characteristics. MIEX resin showed to be more effective when applied on waters with SUVA above 3 $Lmg^{-1}m^{-1}$ (Johnson and Singer, 2004; Boyer and Singer, 2005).

When used as a pre-treatment before coagulation, MIEX improves the DOC removal and lowers the coagulant demand (Singer and Bilyk, 2002; Morran et al., 2004; Jarvis et al., 2008a). It also influences floc properties (Mergen, 2008). Indeed, the DOC to metal coagulant ratio decreases and the combined treatment leads to higher floc structural quality (larger size, higher fractal dimension) (Jarvis et al., 2005b). Furthermore, because MIEX leaves in the water residual NOM molecules that are polymer-like in nature, more effective binding NOM is incorporated into the floc. Bridging bonds and electrostatic patching are therefore possible between components in the floc. This could explain why flocs generated after MIEX pre-treatment have larger size and generally higher fractal dimensions which was shown in Mergen (2008). 3 out of 4 waters which produced flocs with higher fractal dimensions when compared with conventional coagulation

Concerning the possible impact of alkalinity on the MIEX process, Mergen et al. (2008) noticed no change in DOC removal for high or low alkalinity water. However, on long term use and at pilot scale, precipitation of calcium bicarbonate can occur on the surface of the resin beads, limiting the surface exchange and hence the efficiency of the process (Cromphout et al., 2008).

3.2. Coagulation flocculation processes

To remove colloids and DOC from the water WTW commonly use aluminium or iron salts for the coagulation process. The two main mechanisms of coagulation are charge neutralization (decrease of the repulsive forces in order to agglomerate particles) and sweep flocculation (inclusion of NOM in growing precipitates). Their relative importance depends on factors such as pH, dose and temperature (Vilgé-Ritter et al., 1999; Duan and Gregory, 2003). According to the dominant coagulation mode, floc properties change (cf. Section 3.2.6)

3.2.1. Coagulant type and dose

From the hydrolysing metal salts, the most widely used in water treatment practice are aluminium and iron salts. Their coagulation mechanisms are similar: the positively charged products of the metal hydrolysis destabilises the negative particles of the water and precipitate into insoluble hydroxides or metal-NOM complexes on which NOM is adsorbed (Vilgé-Ritter et al., 1999). However, the optimum pH for aluminium coagulation with aluminium is higher than for coagulation with iron. Therefore, aluminium coagulant generates weaker flocs because internal repulsive forces due to deprotonation of phenolic groups at higher pH (cf. section 3.2.3) (Uyak and Toroz, 2005; Jarvis et al., 2008).

Pre-hydrolysed coagulants give better removals than conventional coagulants at low temperature and are less sensitive to pH since they are already hydrolysed for most types of water (Bache and Gregory, 2007). However for NOM laden waters and at optimum pH and doses, pre-hydrolysed coagulants do not significantly improve DOC removal over traditional metal coagulants (Duan and Gregory, 2003). The mechanism of coagulation of pre-hydrolysed coagulants is still not clear. As Al_{13} (contained in aluminium-based pre-hydrolysed coagulants such as polyaluminium chloride) is very stable, occurrence of hydroxide precipitation is questionable. However, on balance it appears that precipitation does occur as it has been shown that sweep flocculation takes part in the removal process using these coagulants (Duan and Gregory, 2003). Also, reactions of Al_{13} and humic acid (HA) form unstable HA-Al_{13} complexes. Al_{mono} (found at higher concentration in simple aluminium salts than in polyaluminium salts) forms octohedrally co-ordinated complexes, leading to form stronger and more compact flocs (Wang et al., 2009).

Coagulant dose is important in order to perform efficient coagulation. To operate in the sweep flocculation mode, a large amount of coagulant has to be dosed (Duan and Gregory, 2003). When the DOC:coagulant ratio is high, more coagulant is available and hence, flocs grow faster (Jarvis et al., 2004; Sharp et al., 2006). Jarvis et al. (2005) found that floc quality decreases with increasing DOC:coagulant ratio. With higher DOC content included in the flocs, flocs were smaller, their fractal dimension decreased and the floc strength constant decreased. This better ability to withstand increases in shear rates was explained by the fact that they were smaller (cf. section 2.3.1).

3.2.2. Polymer addition

In WTW polymers can be added into water as flocculant aids after coagulant addition (bridging destabilized particles) or as primary coagulants (charge neutralization mechanism) (Jarvis et al., 2008).

When used as coagulant aids, polymers improve resistance of flocs to increases in shear rate (Jarvis et al., 2006; Jarvis et al., 2008b). Concerning the floc size, studies have given contradictory results. For one (Jarvis et al., 2006) polymer decreased floc size, for another polymer increased floc size (Jarvis et al., 2008b) although the same combination of coagulant and polymer was used for both studies (Ferripol XL supplied by Huntsman Tioxide Europe Ltd. and polyDADMAC with a charge density of 100% supplied by SNF UK Ltd.).

When used as primary coagulants, polymers form larger floc than with traditional coagulants (Jarvis et al., 2008a) but much longer time is needed to reach the steady-state floc size due to the slow adsorption of the polymer on the suspended particles. Very good reversibility is observed thanks to the reversibility of the physical bonds that form (Yukselen and Gregory, 2004).

3.2.3. Coagulation pH

Coagulation pH determines the relative importance of the two coagulation modes. Hydrolysis of metal salts produces different chemical species according to the pH. Most of these species are cationic under the pH conditions of most water treatment (anionic products generally form at high pH). It is close to neutral pH that aluminium and iron have their lowest solubility. Then, it is the most favourable pH for sweep flocculation (significant hydroxide precipitation) (Johnson and Amirtharajah, 1983; Duan and Gregory, 2003).

Vilgé-Ritter et al. (1999) studied the impact of an increase in pH on organic matter. As a solution becomes more basic, organic molecules and particularly phenolic OH groups are more subject to deprotonation. This generates repulsive forces within the macromolecules. Structures are then less strongly connected and also less dense at high pH.

3.2.4. Zeta potential

The zeta potential (ζ) is the measurement of the effective electrostatic charge on the surface of particles (Gregory and Carlson, 2003; Parsons and Jefferson, 2006). Knowing that charge neutralization dominates the flocculation of NOM, ζ is a good indicator of coagulation performance (Gregory and Carlson, 2003; Henderson et al., 2006). For instance, if too high dose of coagulant has been added into the water, the ζ measurement will be positive indicating that particles repel each other and have re-stabilized (Duan and Gregory, 2003).

Sharp et al. (2006b) has observed that when flocs form, the closer to zero the zeta potential is during coagulation the more resistant to increases in shear rate the flocs are (lower γ value). The reason for this being that there are less electrostatic repulsive force amongst particles in the floc aggregate,

3.2.5. Temperature

Duan and Gregory (2003) reported that hydrolysing metal coagulants have lower efficiencies with decreasing temperature. Indeed, temperature can affect coagulation both physically and chemically. The viscosity of water increases with decreasing temperature therefore the transport of particles and collision rates are slower. Also, the Kolmogoroff's microscale of turbulence changes as it is related to the viscosity (Jarvis et al., 2005).

Chemically, temperature affects the rates of hydrolysis reactions of the metal salts. Decreasing water temperature lowers the minimum solubility of the metal hydroxide and slightly shifts it to more alkaline conditions (Duan and Gregory, 2003; Bratby, 2006).

In colder water, floc formation rates are slower and the flocs generated are smaller and weaker (Duan and Gregory, 2003). Floc strength factors increase with decreasing water temperature (Jarvis et al., 2005).

3.2.6. Floc formation mechanisms

Charge neutralization, sweep flocculation and bridging mechanisms generate flocs which present different characteristics.

Flocs formed by charge neutralisation have slower formation rates and their size is smaller than those formed by sweep flocculation (Kim et al., 2001; Duan and Gregory, 2003; Jarvis et al., 2006).

An interesting study (Li et al., 2006) measured floc fractal dimensions and strength constants for the three different floc formation mechanisms. Due to the intrinsic nature of each flocculation mode, the rank for the higher fractal dimension was sweep flocculation > charge neutralization > bridging. The rank for the higher floc strength constant was charge neutralization > sweep flocculation > bridging. The number and length of internal bonds explain this last rank, polymer bridging generating the more resistant flocs to increase in shear rate. The flocs that were most susceptible to high shear rate were the charge neutralisation flocs. This is because these flocs are bonded together by weak forces such as van der Waals bonds.

Models have been developed to explain the aggregation mechanisms (Gregory, 1997; Waite et al., 2001). Cluster-cluster aggregation is the more realistic case to model the flocculation process. Two types of cluster-cluster models exist: the diffusion limited aggregation (DLA) model and the reaction limited aggregation (RLA) model. In DLA there is no repulsion amongst particles and each collision results in attachment. In RLA there are repulsive forces between particles which contribute to decreased collision efficiency. According to these models, flocs generated in RLA regime are more compact because clusters can move and inter-penetrate each other before becoming attached.

Waite et al. (2001) associated rapid aggregation rate to the DLA regime and slow aggregation rate to RLA regime. They controlled the aggregation rates by adding indifferent ions in the water and measured the fractal dimension of the flocs by SALLS. Fractal dimensions were slightly higher for faster aggregation rate systems (DLA regime). This observation contradicts the predictions of the DLA and RLA aggregation models but no clear reason was provided. More work to understand this unexpected behaviour should be done.

3.2.7. Hydrodynamics and breakage

Hydrodynamics have a very high impact on floc properties. To form flocs, rapid mixing is required to disperse the coagulant into the water in order to destabilize the primary particles to allow them to collide with each other (Bache and Gregory, 2007). Mixing has to be maintained after destabilization to promote orthokinetic collisions leading to larger aggregates. As explained in section 2.3, floc size is determined by the combination of the breakage conditions due to the hydrodynamics and the strength of the internal bonds within the floc.

Several studies agree on the fact that flocs can be subject to internal restructuring due to higher shear rates leading to more compact flocs (Huang, 1994; Gregory, 1997; Spicer et al., 1998; McCurdy et al., 2004; Jarvis et al., 2006). In water treatment practice, flocs go through high and low shear rate zones and are squashed and stretched allowing some degree of restructuration.

Under breakage conditions floc bonds are partially destroyed by the mixing energy (cf. section 2.3.1). The time of exposure to breakage forces influences the floc strength factor and the recovery factor. These three parameters have been seen to decrease with longer breakage periods (Duan and Gregory, 2003; Yukselen and Gregory, 2004). The degree of reversibility depends also on the floc formation mode. Reformation after breakage is possible for flocs generated by charge neutralization effects but impossible for flocs generated by sweep flocculation since their chemical bonds are unable to re-form after breakage. Full reversibility of floc growth is almost never observed for flocs formed by charge neutralisation or electrostatic patch. A good reason is that during breakage, restructuring takes place producing smaller flocs which thus cannot reach their initial size after re-growth.

4. Conclusion

Floc properties have been defined with a specific focus on the floc fractal dimension. It has been seen that all properties are linked together. Indeed, factors such as the nature of the primary particles, the conditions of coagulation and the hydrodynamic conditions have a major influence on size, re-growth potential, strength and fractal dimension of flocs.

One objective of this literature review was to highlight the difficult interpretation of the floc strength concept. Indeed, a low floc strength constant (γ) indicating that the flocs withstand less well increased shear rates does not always implicate that the floc is weaker. On the contrary, very often, larger flocs remain larger than small flocs after breakage in spite of their higher floc strength constant, indicating that there are still stronger. In consequence, floc size should be considered as the main criteria for floc strength and the floc strength constant as an additional information on the floc breakage behaviour.

Concerning the methods used to work out fractal dimension, it is thought that SALLS and settling methods measure fractal dimension at different scales. SALLS gives D_3 values for small particles within its application range while settling method gives D_3 values for the overall aggregates that are of more operational use.

Different factors which influence the floc properties and their mechanisms have been described. Almost all of them act on the floc structural properties via a modification of either the nature of the primary particles, or the conditions of coagulation process, or the hydrodynamic conditions of the surrounding water. This literature review showed the complexity of the parameters which determine the floc structure.

CHAPTER 3 – OBJECTIVES

MIEX pre-treatment followed by coagulation has been seen to be more efficient than conventional coagulation in removing DOC matter and to require lower coagulant doses for NOM laden water. It has also been proven that MIEX pre-treatment influences floc properties and therefore the efficiency of downstream processes.

The aim of this thesis was to assess these benefits using the raw water from Kluizen WTW (VMW, Belgium). Consequently, this bench-scale research project had for objectives to:

- compare the NOM removal for raw and MIEX pre-treated water after coagulation using three different coagulants ($AlCl_3$, PACl and $FeCl_3$).
- evaluate, compare and understand the impacts of MIEX pre-treatment on the physical properties of flocs, i.e. floc size, floc strength, floc potential regrowth and fractal dimension, using three different coagulants.
- assess based on the floc properties the advantages and disadvantages of a MIEX pre-treatment stage before coagulation on downstream processes such as filtration, sedimentation and flotation.
- investigate a potential relationship between floc fractal dimension and other floc properties.

CHAPTER 4 – PAPER FOR PUBLICATION: WATER RESEARCH

Impact of MIEX pre-treatment on floc strength and structure

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Abstract

In drinking water treatment magnetic ion exchange (MIEX) resin treatment followed by coagulation has been shown to significantly improve dissolved organic carbon removal and reduce disinfection by-product formation in comparison with coagulation alone. However, knowledge is lacking about how the magnetic resin influences the floc structure which is of major importance for the efficiency of the downstream processes. The present study compares properties of flocs generated by coagulation alone and combined treatment (MIEX pre-treatment followed by coagulation) of a raw water characterised by a high natural organic matter content and high alkalinity (Kluizen water treatment works, VMW, Belgium). Coagulation was achieved using three different coagulants – ferric chloride ($FeCl_3$), aluminium chloride ($AlCl_3$), and polyaluminium chloride (PACl) - at optimum pH and dose conditions. Experiments were performed using jar test apparatus. A light scattering instrument (Malvern Mastersizer) measured floc size and fractal dimension during growth, breakage and re-growth periods. Additional fractal dimension measurements for ferric flocs were obtained from images from a light microscope using image analysis software. MIEX pre-treated flocs were larger for all the coagulants tested but were more affected by increased shear rate than conventional flocs. This was thought to be due to the larger initial size of the MIEX pre-treated flocs being more impacted by breakage eddies. Light scattering and image analysis gave different fractal dimension values for the same floc system. This was because they are applicable to different length scales: light scattering for the small primary particles and image analysis for the overall flocs. Of more operational interest, image analysis results showed that MIEX pre-treated flocs were more compact. Combined treatment using MIEX and coagulation gave an overall improvement in floc structure quality. The implications for water treatment practice being that MIEX pre-treated flocs will be easier to clarify and remove by filtration processes.

Keywords:
Floc, MIEX pre-treatment, floc strength, fractal dimension, image analysis, natural organic matter.

Abbreviations

$AlCl_3$	Aluminium chloride
DBP	Disinfection by-products
DOC	Dissolved organic carbon
ERD	Effective resin dose
$FeCl_3$	Ferric chloride
IA	Image analysis
MIEX	Magnetic ion exchange
NOM	Natural organic matter
PACl	Polyaluminium chloride
PHA	Polyhydroxyaromatic compounds
RGD	Rayleigh-Gans-Debye
SALLS	Small angle laser light scattering
SUVA	Specific UV_{254} absorbance
UV_{254}	Ultraviolet absorbance at 254 nm
VMW	Vlaamse maatschappij voor watervoorziening (Flemish water supply company)
WTW	Water treatment works

1. Introduction

Water treatment works (WTW) have to comply with regulations such as those laid out in the European Drinking Water Directive (Council Directive 98/83/EC) which defines standards for the quality of drinking water. There is no current drinking water quality standard for natural organic matter (NOM) in this legislation because in itself it is not generally harmful when consumed. However, residual NOM leads to the formation of carcinogenic disinfection by-products (DBP) such as trihalomethanes (THM) which are regulated when water is chlorinated and has a negative effect on the biostability of the water (Parsons and Jefferson, 2006). To remove NOM many WTW use the coagulation-flocculation processes with metal salt coagulant. In the coagulation stage, the coagulant is added into the water and form positive hydrolysis products that destabilise impurities of the water owing the fact that most of them are negatively charged (Duan and Gregory, 2003). Flocculation stage provides a slow stir mixing allowing destabilised particles to collide and aggregate, forming flocs. These flocs are removed from water by a solid-liquid separation process. However, in some case this succession of processes does not provide enough NOM removal in order to stay in compliance with the THM standards. One solution to cope with this NOM problem is use of the magnetic ion exchange (MIEX) resin developed by Orica Watercare specifically for NOM removal. This strong base anionic exchange resin has been shown to be very effective in removing NOM and reducing the subsequent coagulant dose when MIEX is used as a pre-treatment of the coagulation stage (Singer et al., 2009).

It is interesting to investigate the properties of the flocs since the efficiency of solid-liquid separation processes such as filtration, sedimentation and flotation depends on the characteristics of the impurities to be removed. There has been limited work showing how MIEX pre-treatment impacts on the downstream floc properties formed using ferric sulphate coagulant (Jarvis et al., 2008a; Mergen, 2008).

Flocs can be characterised by their size, their response to increased shear rates, their regrowth potential and their fractal dimension. Indeed, flocs generated in WTW can be considered as fractal objects since aggregation of primary particles and clusters gives rise to a porous self-similar structure (Huang, 1994; Waite et al., 2001). The fractal dimension of an object gives an indication about how it occupies space. Its value varies between 1 and 3. A fractal value around 1 corresponds to a highly porous and branched aggregate whilst a value approaching 3 indicates a solid filled object. Like every fractal object flocs show power law relationships between two of their geometrical parameters such as:

$$P \propto L^{D_1} \quad (1)$$

$$A \propto L^{D_2} \quad (2)$$

$$V \propto L^{D_3} \quad (3)$$

where P is the perimeter, A is the area, V is the volume, L is the characteristic length (usually the largest length of the object) and D_1, D_2 and D_3 are the fractal dimensions respectively in one-, two- and three-dimensional space.

Some recent research has shown that MIEX pre-treatment upstream of coagulation can have a positive effect on flocs properties but these studies have not studied the possible interaction between the MIEX pre-treatment and the choice of the coagulant. The main objective of this study was to provide a comparison between the combinations of either conventional coagulation or MIEX pre-treatment followed by coagulation. Three different metal salt coagulants have been tested (aluminium chloride, polyaluminium chloride and ferric chloride) to determine if there were any differences in the properties of the flocs with and without MIEX treatment.

2. Materials and methods

All experiments were carried out at laboratory regulated temperature (20 ± 2°C).

2.1. Raw water and MIEX pre-treatment

The studied raw water was a lowland water from a reservoir at Kluizen WTW (VMW, Belgium). The MIEX pre-treated water was from the same source but treated using an upflow fluidised bed reactor (2 m height, 0.1 m diameter with c. 0.3 m resin height (c. 150 mL L^{-1}). No recycling of resin was operated during treatment. After resin regeneration in situ, 1000 bed volumes of raw water were treated, collected and mixed. This corresponds to an effective resin dose (ERD) of 1 mL L^{-1} (Cromphout, 2009). The two waters were stored in a refrigerated room at 4°C until use. Measurements of the pH, DOC (actually, measurement of the non-purgeable organic carbon (NPOC)), UV_{254}, zeta potential, turbidity and alkalinity were carried out on both types of water.

2.2. Treatment options

Raw water and MIEX pre-treated water were both coagulated with three chemicals: aluminium chloride ($AlCl_3$, 6% w as Al), polyaluminium chloride (PACl Aqualenc F1, 9.6% w Al_2O_3) and ferric chloride ($FeCl_3$, 9.6% w as Fe).

Preliminary coagulation tests were carried out with raw water to determine the optimum pH for coagulation since the optimum pH was found to be the same for coagulation of MIEX pre-treated water (Jarvis et al., 2008) (pH between 3 to 7.5 were investigated). 1 L square jars were filled with 0.5 L sample of water and placed on a PB-900 variable speed jar tester (Phibbs and Bird, Virginia, USA) (flat paddle impeller dimensions: 76 x 25 mm). A rapid mixing of 2.5 minutes was operated at 200 rpm (536 s^{-1}) during which coagulant was added (1 minute after the start) followed by the addition within 30 seconds of the coagulant of either sulphuric acid (1 M) or sodium hydroxide (1 M) (both chemicals from Fisher Scientific UK, Loughborough) to adjust the pH to the desired value. A slow stir stage followed at 30 rpm (31 s^{-1}) from 15 minutes which allowed the flocs to grow. Samples for analysis were taken after a settling period of 10 minutes.

Using the optimum pH and the same procedure additional jar tests were carried out to determine the best coagulant dose for each of the six treatment options (doses between 2 and 20 mg L^{-1} as metal were investigated). Optimum pH and dose conditions were selected according to the more effective combination of DOC removal, UV_{254} removal, turbidity removal and zeta potential.

DOC (NPOC) was measured using a TOC-$V_{CPH/CPN}$ analyser (Shimadzu, Kyoto, Japan), UV_{254} using a 6505 UV-Vis spectrophotometer (Jenway, Dunmow, UK), turbidity using a 2100N turbidimeter (Hach Lange, Manchester, UK), and zeta potential using a Zetasizer (Malvern Instruments, UK).

2.3. Floc size

Jar tester and laser diffraction instrument (Malvern Mastersizer 2000, Malvern Instruments, UK) were coupled to monitor the floc size using a method as described in Jarvis et al. (2005b). From the jar (1 cm above paddle) water was drawn by a peristaltic pump at 1.5 Lhr^{-1} through the measurement cell. The tubing used had a 5 mm internal diameter. The pump was placed downstream of the measurement cell to avoid any floc damage into the measurement system.

The floc size jar test sequence proceeded as previously noted using a 1 L sample filled square jar. But after the slow stir phase at 15 minutes at 30 rpm, a breakage phase of 20 minutes was operated at 30, 40, 50, 75, 100, 150 and 200 rpm (31, 47, 66, 122, 188, 347 and 536 s^{-1} respectively). After the breakage phase of 30, 75 and 200 rpm flocs were allowed to re-grow for 15 minutes at 30 rpm. Floc size measurement was taken every minute. Each experiment was conducted in triplicate.

2.4. Floc strength and recovery

The following strength factors and relationships were established for all of the floc conditions tested. Floc size is an indicator of floc strength considering that for the same given conditions a larger floc is stronger as it withstands better breakage factors (Yukselen and Gregory, 2004; Jarvis et al., 2005). Additional parameters derived from the floc size data have been proposed by Francois (1987) to characterise floc strength and regrowth potential.

The strength factor indicates how big the floc is after breakage (d_2) compared to its initial growth floc size (d_1):

$$\text{Strength factor} = \frac{d_2}{d_1} \times 100 \tag{4}$$

Recovery factor indicates in which proportion the floc recovered its initial size after regrowth (d_3):

$$\text{Recovery factor} = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \tag{5}$$

Another way to characterise floc strength is to use the following empirical relationship:

$$\log(d_2) = \log(C) - \gamma \cdot \log(\text{rpm}) \tag{6}$$

where log (C) is the floc strength co-efficient and γ the floc strength constant. A lower γ value in magnitude means that flocs are less affected by an increased shear rate.

2.5. Floc fractal dimension

Floc fractal dimensions were calculated by the small angle laser light scattering technique (SALLS) and by image analysis (IA). The SALLS method has previously been used and explained in other studies (Kim et al., 2001; Jarvis et al., 2005a; Li et al., 2006). The principle is to work out the fractal dimension of the system (D_3) from the relationship between the intensities of the scattered light (I) measured by the photosensitive detectors of the laser diffraction instrument and the scattering vector (Q):

$$I \propto Q^{-D_3} \tag{7}$$

This linear relationship (on a log-log plot) applies only for independently scattered light and under the Rayleigh-Gans-Debye (RGD) regime. In other words, the length scale of investigation (corresponding to Q^{-1}) has to be much larger than the primary particle size ($R_{particule}$) and much smaller than the size of the aggregates ($R_{aggregate}$):

$$R_{aggregate} >> Q^{-1} >> R_{particle} \tag{8}$$

To work out the fractal dimension by IA, flocs were sampled with an adapted pipette to avoid any floc damage after growth, breakage and regrowth and placed on a microscope slide bordered with 2 mm high rubber rim. Another microscope slide enclosed the suspension containing whole flocs. Flocs were observed using a light BHB microscope (Olympus European, Hamburg, Germany). A CCD QICAM 12 bit Mono Fast 1394 camera (Q-imaging, Surrey, Canada) coupled with the Image Pro Plus software (Media Cybernetics, Bethesda, USA) allowed images to be acquired on a computer. Pixels representing the floc were selected by manual threshold selection. Floc projected areas and maximum Feret diameters were measured after calibration using a microscope graticule. In order to be representative databases a minimum of 100 flocs were measured for each stage of the jar test sequence for 30, 75 and 200 rpm. Values of the projected areas and the maximum Feret diameters allowed the D_2 fractal value to be calculated from the previously cited power law relationship (Eq.2).

2.6. Statistical analysis

Standard deviation and standard error calculations were carried out using the Analysis ToolPak of Microsoft Excel™. Other statistical analyses were carried out using the software Minitab 14™.

3. Results

3.1. Water quality parameters

The measured water quality parameters (Table 4.1) showed that the raw water had a high DOC concentration (10.2 mg C L^{-1}) and a high alkalinity (266 mg L^{-1} as $CaCO_3$). The specific UV_{254} absorbance (SUVA value of 2.7 L $mg^{-}1$ m^{-1} indicated that the water was predominantly hydrophilic in nature given that the guideline value for a hydrophilic water is generally considered for SUVA values < 2.5 L mg^{-1} m^{-1} (Parsons and Jefferson, 2006).

Following treatment by MIEX 57% of the DOC and 74% of the UV_{254} was removed from the water. This DOC removal agrees with the DOC removal of around 55% found by Singer et al. (2009) for a raw water with a SUVA of 2.7 L mg^{-1} m^{-1} and an ERD of 1 mL L^{-1}.

3.2. Treatment options

The first series of jar tests was carried out to find the best conditions to coagulate the water. For all the coagulants and both the raw and MIEX treated water, pH 5 was selected as the pH that gave the most effective combination of UV_{254} and DOC removals and the conditions where the zeta potential in the coagulated water was within the optimum window (see experiment data report in Appendix B.1.). This pH value of 5 is in compliance with the recommended pH to coagulate NOM (between pH 5 and 6) (Henderson et al., 2006). Under this pH range, the dominant coagulation mechanism is charge neutralisation. PACl was the only coagulant that was able to give similar removals over a wide range of pH (from pH 5 to 7.5). This was expected as a result of its pre-hydrolysed character which gives to PACl a lower dependence on the process conditions such as pH and temperature that rule the hydrolysis reactions (Bratby, 2006).

The second set of jar tests was made at pH 5 to find the best coagulant doses. Doses were selected based on the most effective combination of UV_{254}, DOC, turbidity removals (Table 4.1) (see experiment data report in Appendix B.2.). The zeta potential was also checked to ensure that it was in the correct zone. For the raw water, higher ferric coagulant dose (18 mg L^{-1} as Fe) was required than the aluminium based coagulants (12 mg L^{-1} as Al). These doses are quite high compared with other doses used for NOM removal for source waters with a similar DOC content (8 mg L^{-1} as Fe and 10 mg L^{-1} as Al in Jarvis et al. (2006) and Jarvis et al. (2008) respectively). For MIEX pre-treated water, coagulant doses were reduced to 6 mg L^{-1} as metal for all coagulants. This was expected as result of the reduced DOC content of this water and evidence from previous trials of this type (Singer et al., 2009). In percentage terms, the reductions in coagulant doses were 50% for aluminium based coagulants and 66% for iron based coagulant.

For both types of water, $FeCl_3$ gave the best DOC removal. This agrees with other studies that found iron based coagulants more efficient in DOC removal than aluminium based coagulants (Uyak and Toroz, 2005; Jarvis et al., 2008). The reduction in the SUVA value by 41% after MIEX treatment revealed that MIEX resin removed a higher proportion of hydrophobic material than hydrophilic matter. This SUVA reduction has already been observed by Boyer and Singer (2005) (from a study of 4 waters, between 10 and 44% SUVA reductions were observed) and by Cromphout et al. (2008) where 38% SUVA reductions were observed. However, for other waters no significant SUVA reductions have been seen (Johnson and Singer, 2004; Jarvis et al., 2008a), indicating that both hydrophilic and hydrophobic materials were removed by MIEX in the same proportion.

3.3. Floc size and strength

Monitoring the d_{50} floc size during growth, breakage and regrowth phases showed that the MIEX pre-treatment and the choice of coagulant greatly impacted on the floc size (Figure 4.1) (see experiment data report in Appendix C). Floc size was improved following coagulation after MIEX pre-treatment to 153%, 132% and 247% of the raw water floc size for $AlCl_3$, PACl and $FeCl_3$ respectively. This improvement in floc size due to MIEX pre-treatment has already been reported by Jarvis et al. (2008) where a floc increase of 39% after MIEX pre-treatment using ferric sulphate as a coagulant was observed. For flocs generated from raw water, the size decreased according to the following coagulant ranking: PACl (306 ± 13 µm), $FeCl_3$ (208 ± 8 µm) and $AlCl_3$ (169 ± 6 µm). For flocs generated from MIEX pre-treated water, the size decreased according to the following coagulant ranking: $FeCl_3$ (513 ± 34 µm), PACl (403 ± 29 µm) and $AlCl_3$ (260 ± 12 µm). Statistical analysis showed that all these steady-state d_{50} floc sizes were significantly different from each other (Kruskall-Wallis tests, all $P < 0.001$). A 2-way ANOVA (assumption of equal variances) demonstrated that the MIEX pre-treatment factor and the coagulant factor do not impact independently on the floc size. In other words the different floc sizes resulted from a combined effect of the choice of coagulant and MIEX pre-treatment (Balanced ANOVA, $P < 0.001$ for hypothesis of no interaction between the two factors). This was illustrated by the greater increase in size seen for ferric flocs after MIEX pre-treatment compared to the other coagulants.

When analysing the evolution of floc size during breakage, two types of floc breakage were observed; the first stage being a large-scale decrease in size and the second a gradual decrease. However, for shear rates of 30 (no breakage), 40 and 50 rpm, the first large-scale decrease was not observed. Gaps between 50 and 75 rpm curves are observed for $AlCl_3$ and $FeCl_3$. The absence of this gap for PACl was probably due to its polymer type molecules that provide an "elastic" resistance to increased shear rates. With PACl it was also observed that the onset of flocculation was faster because PACl is pre-hydrolyzed allowing it to destabilise the particles earlier than the other coagulants.

Calculated strength factors (see raw data in Appendix D) for each breakage shear rate revealed no significant difference between raw flocs and MIEX pre-treated flocs (Kruskal-Wallis test, $P = 0.190$). Only floc strength factors for 75 and 200 rpm are shown in Table 4.2 to simplify presentation. Recovery factors calculated for floc regrowth at 75 and 200 rpm revealed no significant difference between raw flocs and MIEX pre-treated flocs (Kruskal-Wallis test, $P = 0.631$) (see raw data in Appendix D). However, small but significant differences (Kruskal-Wallis tests, all $P = 0.021 < 0.05$) were seen between each coagulant in term of recovery factors. $FeCl_3$ gave the best regrowth, followed by $AlCl_3$ and then PACl for both types of water.

All the systems investigated followed the expected relationship between floc size and the applied shear rate (Figure 4.2). On a log-log scale, R^2 correlation coefficients for each of the regression lines were between 0.949 and 0.996. According to the value of the slope (the floc strength constant (γ)), systems withstand better increase in shear rate in the following order: Raw+PACl (0.50), Raw+$FeCl_3$ (0.59), Raw+$AlCl_3$ (0.65), MIEX+PACl (0.72), MIEX+$FeCl_3$ (0.73), and MIEX+$AlCl_3$ (0.74). From these values, it is obvious that flocs generated with MIEX pre-treated water were less able to withstand increased shear rates. This trend has already been observed by Jarvis et al.

(2008) who found γ values of 0.47 and 0.54 respectively for NOM flocs without and with MIEX pre-treatment. Slight differences in floc strength constant suggest that PACl provided more resistant flocs than the other coagulants. The γ values can be used to give an indication of the floc degradation mode (Francois, 1987). According to the calculated γ values, breakage mode of raw water flocs was dominated by large-scale fragmentation mechanisms and MIEX pre-treated flocs were broken by both fragmentation and erosion mechanisms.

Even if the initial larger flocs generated after MIEX pre-treatment broke more easily, they still kept a larger size than conventional flocs and should therefore be considered stronger (except for PACl flocs that gave similar floc sizes at high rpm regime due to the low increase in size due to MIEX pre-treatment (32%)). This indicated that the floc strength concept has to be interpreted carefully and with a critical mind.

3.4. Fractal dimensions

(For fractal dimension raw data, see Appendix E)

The SALLS method was used to work out D_3 fractal dimensions for all floc systems at the end of the floc growth phase, the breakage phase at 75 rpm and the regrowth phase. Using the IA method it was only possible to measure the fractal dimension (D_2) of the ferric flocs. This was because the aluminium flocs were too transparent to differentiate them from the background.

Analysis of the D_3 values of the flocs generated by the different treatment options (Figure 4.3 a) did not reveal an obvious difference between raw water flocs and MIEX pre-treated flocs. The D_3 averages (for both raw and MIEX pre-treated waters) were 2.44 ± 0.05, 2.70 ± 0.12 and 2.61 ± 0.06, respectively for after growth, breakage and regrowth flocs. $AlCl_3$ generated aggregates which seem to be a little more compact than the two other coagulants. The D_3 increased for flocs after breakage and then slightly decreased after regrowth. For example for PACl coagulant on raw water the initial fractal value was 2.36, this increased to 2.73 after breakage and then decreased to 2.57 following re-growth. The reverse trend (lower D_3 after breakage) was seen by Jarvis et al. (2008b) when flocs were broken at 200 rpm in circular jars (G value estimated to 128 s^{-1} (Sharp et al., 2006) which is similar to 75 rpm in square jars where G is 122 s^{-1}).

Comparison of the D_2 values for ferric flocs (Figure 4.3 b) highlighted three major differences. Firstly, D_2 values were smaller than D_3 values. This was expected because the difference of dimension between the working spaces (2-dimensional for D_2 and 3-dimensional for D_3). Secondly, D_2 revealed an increase of 8.7% in fractal dimension for MIEX pre-treated flocs. Finally, the trend seen for the D_3 was not observed from the D_2 fractal dimension where the D_2 for raw water and MIEX pre-treated water decreased by 8.4% in average after breakage and then slightly increased by 2.2% after regrowth.

5. Discussion

The results from this work have shown that the presence of a MIEX resin pre-treatment had beneficial impacts on both DOC removal and floc structure and, in combination with the selection of the coagulant, give rise to different floc properties (Table 4.3).

MIEX pre-treatment followed by coagulation reduced the amount of coagulant required. The main reason for this was the reduction in the DOC of the water after MIEX treatment. The DOC removal obtained in this study by the combined MIEX and coagulation processes was better when compared to enhanced coagulation alone which is in agreement with other studies (Singer and Bilyk, 2002; Fearing et al., 2004; Jarvis et al., 2008a; Mergen, 2008).The MIEX process has been seen to remove both hydrophilic and hydrophobic molecules which have a low molecular weight (MW) (<1500 Da) (Singer and Bilyk, 2002; Jarvis et al., 2008a). Following DOC removal, the SUVA composition of the water upstream of the coagulation stage was reduced from 2.7 to 1.6 L mg^{-1} m^{-1} indicating that MIEX preferentially removed hydrophobic NOM. This means that the treated water became more hydrophilic which explains the lower DOC removal seen for the subsequent coagulation because coagulation preferentially removes high MW and hydrophobic molecules (Jarvis et al., 2008a) (between 16% and 30% compared with removals between 45% and 64% coagulation-flocculation process on raw water). But still coagulation after MIEX treatment removes compounds that are very hard to eliminate from water and not removed by conventional coagulation.

The modified DOC composition impacted on the floc properties. Indeed, MIEX pre-treatment generated larger flocs which can be explained by two reasons. Firstly, compared to conventional coagulation, the DOC to coagulant ratio decreased following MIEX treatment (Table 4.1) (except for $FeCl_3$). Smaller DOC to coagulant ratios have been proven to generate flocs with higher structural quality (floc size, strength and fractal dimension) (Jarvis et al., 2005b). Secondly, because MIEX removes low MW molecules (except small and neutral compounds), a higher proportion of high MW polymer-like molecules are left in the water, improving the binding within the flocs (bridging bonds and electrostatic patching) leading to larger floc size (Mergen, 2008). These two reasons could also explain the increased D_2 for MIEX flocs (Figure 4.3 b). Mergen (2008) has observed this trend for fractal dimensions for 3 out of 4 studied waters.

The significantly larger flocs observed after MIEX pre-treatment seen for ferric flocs (254% of the conventionally coagulated floc size) was not explained by changes in the DOC to coagulant ratio because this was observed to increase. Further evidence for the hypothesis that improved binding occurs in the flocs by polymer like NOM molecules is given by other research (Henderson et al., 2006). Ferric chloride coagulant has been demonstrated to preferentially aggregate with polyhydroxyaromatic compounds (PHA). This selectivity for PHA is thought to be more important for iron coagulants than for aluminium based coagulants (Vilgé-Ritter et al., 1999). This selectivity could explain why ferric flocs were larger after MIEX pre-treatment and why their recovery factor is higher than the two other coagulants. Low MW PHA and other organic compounds were thought to be removed by the MIEX process. Consequently, a higher proportion of polymeric-like PHA molecules are included in the ferric flocs after MIEX pre-treatment when compared with the proportion of the same compounds in the flocs generated from raw water. This higher proportion of large polymeric-like PHA molecules leads to the formation of the larger flocs after MIEX treatment for ferric chloride.

From the floc size point of view, larger MIEX pre-treated flocs may be considered stronger than conventional flocs since they reach a larger size under the same mixing conditions (Yukselen and Gregory, 2004). However, MIEX pre-treated flocs were less resistant to increases in shear rate (higher γ values) than conventional flocs. This is because larger initial flocs are more exposed to breakage from turbulence eddies. Smaller flocs are more likely to be entrained by these swirling turbulences rather than broken by them (Parker et al., 1972).

This study supports the fact that the light scattering method to work out the fractal dimension of aggregate has a limited applicability to NOM flocs (Jarvis et al., 2005a). Indeed, the linear relationship ($I \propto Q^{D3}$) on the log-log graph of I against Q was always seen between log Q = -3.4 and -1.7 nm^{-1}. This means that RGD regime and its laws are not applicable to aggregates larger than 2.5 µm. In the current study median floc sizes were larger than 160 µm. Thus, it is considered that SALLS measures only the fractal dimension of the microflocs located on the surface of the floc. Because D_3 data were not significantly different from each other it can be concluded that microflocs have the same structure regardless of the presence or absence of MIEX pre-treatment. The tendency of D_3 to increase under breakage shear rate could be explained by an internal re-organisation of the bonds within the microflocs, making them more compact (Huang, 1994; McCurdy et al., 2004; Jarvis et al., 2006).

The IA method gave D_2 fractal dimensions which revealed a reverse trend after breakage: the D_2 decreased because of the higher shear rate. As already described, larger aggregates were more affected by eddies than small aggregates such as microflocs (Francois, 1987). Consequently, eddies damage the overall floc, making it more branched, more loosely connected and therefore less compact. Another observation was the increase in D_2 values seen for MIEX flocs. This was thought to be explained by the low MW DOC molecules removed by the MIEX pre-treatment that left a higher proportion of polymer-like molecules in the water. These polymeric-like molecules increased median floc size and made them more compact by binding primary particles closer together to one another. This is in agreement with previous research that has shown that higher polymer doses increases floc fractal dimension (Jarvis et al., 2008b). In the current work the fractal dimension worked out by IA (D_2) were considered as more representative and operational data than the SALLS D_3 since the D_2 is related to the bulk of the flocs.

It has been seen in this study that by removing specific DOC from the water, the MIEX process reduced the coagulant requirement, lowered the final DOC and improved floc characteristics. The practical implication of this work is that the modified floc characteristics after MIEX treatment may impact on downstream processes such as filtration, settling or flotation. The larger floc size should improve removal by solid-liquid separation processes including sedimentation, flotation and filtration. Because they are more compact (higher D_2) and larger, flocs generated after MIEX should settle faster. This improved settleability has already been observed by Mergen (2008). Concerning a potential change in flotability, assessment is less clear. Jarvis et al.(2008a) have seen better final turbidity removal after dissolved air flotation with MIEX pre-treated water on their pilot scale facilities. As the flocs are larger they should rise to the surface entrained by more air bubbles. However, the larger MIEX flocs showed a lower resistance to increased shear rate. Their advantage for flotation may be reduced at higher shear rates such that those experienced in the contact zone of a dissolved air flotation unit which have been estimated between 1000 and 7600 s^{-1} (Fukushi et al., 1995). Nevertheless, this needs to be balanced by the fact that the flocs still remain larger after breakage for MIEX treated flocs compared to conventional flocs. Only PACl flocs after MIEX pre-treatment have been seen to show similar floc sizes, if not smaller, at high breakage shear rates compared to conventional flocs. Consequently, the removal improvement of flotation process due to MIEX pre-treatment should be greater for $AlCl_3$ or $FeCl_3$ than for PACl coagulation. Finally, given the increased DOC removal due to MIEX pre-treatment, combined treatment should reduced the production of DPB during the chlorine disinfection process.

6. Conclusions

The present research investigated the impacts of MIEX pre-treatment on coagulation and flocculation of a NOM laden water with a particular focus on the resulting floc characteristics. Results of the bench-scale experiments lead to draw the following conclusions:

- Given the removal of DOC material due to the MIEX pre-treatment, optimum coagulant doses were reduced and overall DOC removals for combined treatment were higher than for conventional coagulation, reducing the potential for formation of DBP during chlorination.
- According to the floc properties, the beneficial effects of MIEX pre-treatment were dependent on the coagulant choice. After MIEX pre-treatment ferric flocs were 2.5 times larger compared to conventional ferric flocs. Ferric chloride was seen to give a better regrowth potential to the flocs. The strongest flocs considering the γ values were generated from the raw water with PACl.
- The explanation for the improved floc properties after MIEX pre-treatment was thought to be as a result of improved removal of lower MW substances, leaving behind polymeric like molecules in the water which when coagulated increased the floc size and compactness. The effect on floc size was especially observed for the ferric coagulant owing to its high selectivity for PHA.

- MIEX pre-treated flocs could be considered stronger. Although they were more affected by the increased shear rates because of their larger size, they were still larger than conventional flocs (exception was for PACl).
- Fractal dimension values supported the hypothesis that SALLS and IA methods do not apply to the same length scales. SALLS applied to particles smaller than 2.5 µm and IA method to the whole floc making the latter method of more operational interest.

Further work on interactions between MIEX pre-treatment and coagulant choice could validate the hypothesis that some chemicals are more prone to produce higher quality flocs after MIEX treatment. The explanation that better floc structure characteristics are observed after MIEX pre-treatment owing to the consecutive higher proportion of polymer like substances should be further investigated using synthetic model organic compounds.

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9. Tables

Table 4. 1: Quality parameters for the raw water and the final waters.

Parameters	Site water quality		Treated water					
			$AlCl_3$		PACl		$FeCl_3$	
	Raw	MIEX	Raw	MIEX	Raw	MIEX	Raw	MIEX
pH	8.15	8.05	5	5	5	5	5	5
Coagulant dose (mg L^{-1} as metal)	N/A	N/A	12	6	12	6	18	6
DOC (mg C L^{-1})	10.2	4.4	5.6	3.5	4.9	3.7	3.7	3.1
UV_{254} (m^{-1})	27.8	7.1	8.9	5.5	9.4	6.2	7.0	5.3
Zeta potential (mV)	-5.6 ± 1.1	-2.3 ± 1.0	3.0 ± 0.1	4.6 ± 0.1	2.2 ± 0.9	3.6 ± 0.2	-7.7 ± 1.0	-3.1 ± 2.0
Turbidity (NTU)	0.6	0.4	5.1	1.4	1.4	1.0	2.2	0.4
Alkalinity (mg L^{-1} as $CaCO_3$)	266 ± 2	223 ± 3	-	-	-	-	-	-
DOC to coagulant ratio	N/A	N/A	0.85	0.73	0.85	0.73	0.57	0.73
Final SUVA (L mg^{-1} m^{-1})	2.7	1.6	1.6	1.6	1.9	1.7	1.9	1.7

Table 4. 2: Strength factors and recovery factors for the different combinations of treatments.

	Breakage shear rate	Strength factor (%)			Recovery factor (%)		
		$AlCl_3$	PACl	$FeCl_3$	$AlCl_3$	PACl	$FeCl_3$
Raw	75	55	47	56	21	8	52
	200	28	25	26	27	13	38
MIEX	75	57	55	66	22	10	55
	200	27	33	35	29	14	44

Table 4. 3: Treatment option rank according to NOM floc properties

Parameter	Highest	→				Lowest
DOC removal	MX+Fe	MX+Al	MX+PACl	≈Raw+Fe	Raw+PACl	Raw+Al
Size, d_1	MX+Fe	MX+PACl	MX+Al	Raw+PACl	Raw+Fe	Raw+Al
Regrowth potential	MX+Fe	≈Raw+Fe	MX+Al	≈Raw+Al	MX+PACl	≈Raw+PACl
Resistance to high shear rate, $-\gamma$	Raw+PACl	Raw+Fe	Raw+Al	MX+PACl	MX+Fe	MX+Al
Compactness after regrowth, D_3	Raw+Al	MX+Al	≈MX+PACl	≈Raw+PACl	≈MX+Fe	≈Raw+Fe
Compactness after regrowth, D_2	MX+Fe	Raw+Fe	(Not applied to the other treatment options)			

(MX = MIEX pre-treated, Al = $AlCl_3$, Fe = $FeCl_3$, and ≈ = similar to the previous value).

10. Figures

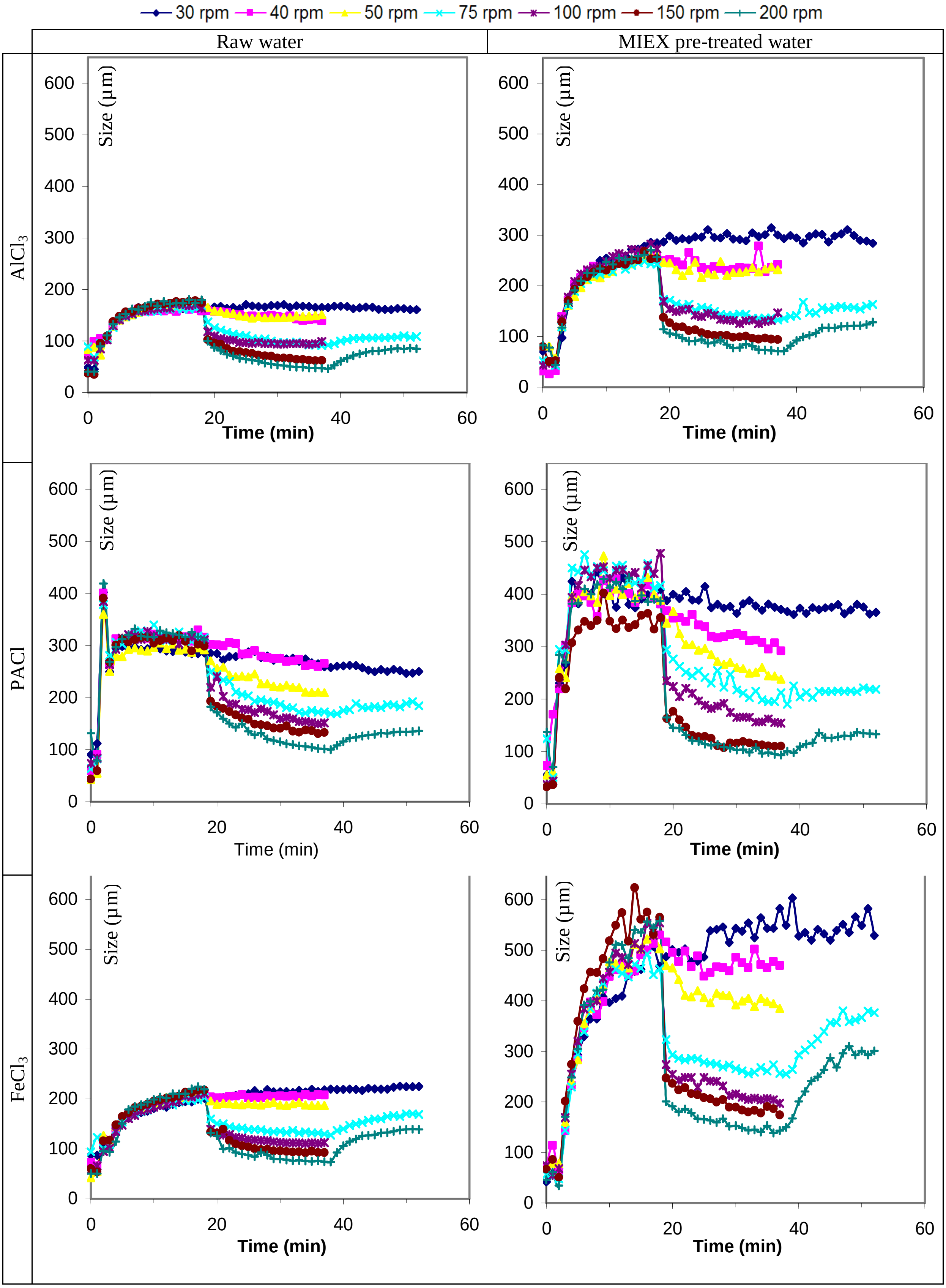

Figure 4. 1: Evolution of floc size (d_{50}) for the different combinations of water types and coagulants. The mean standard deviation for each rpm curve was around 10% of the size value.

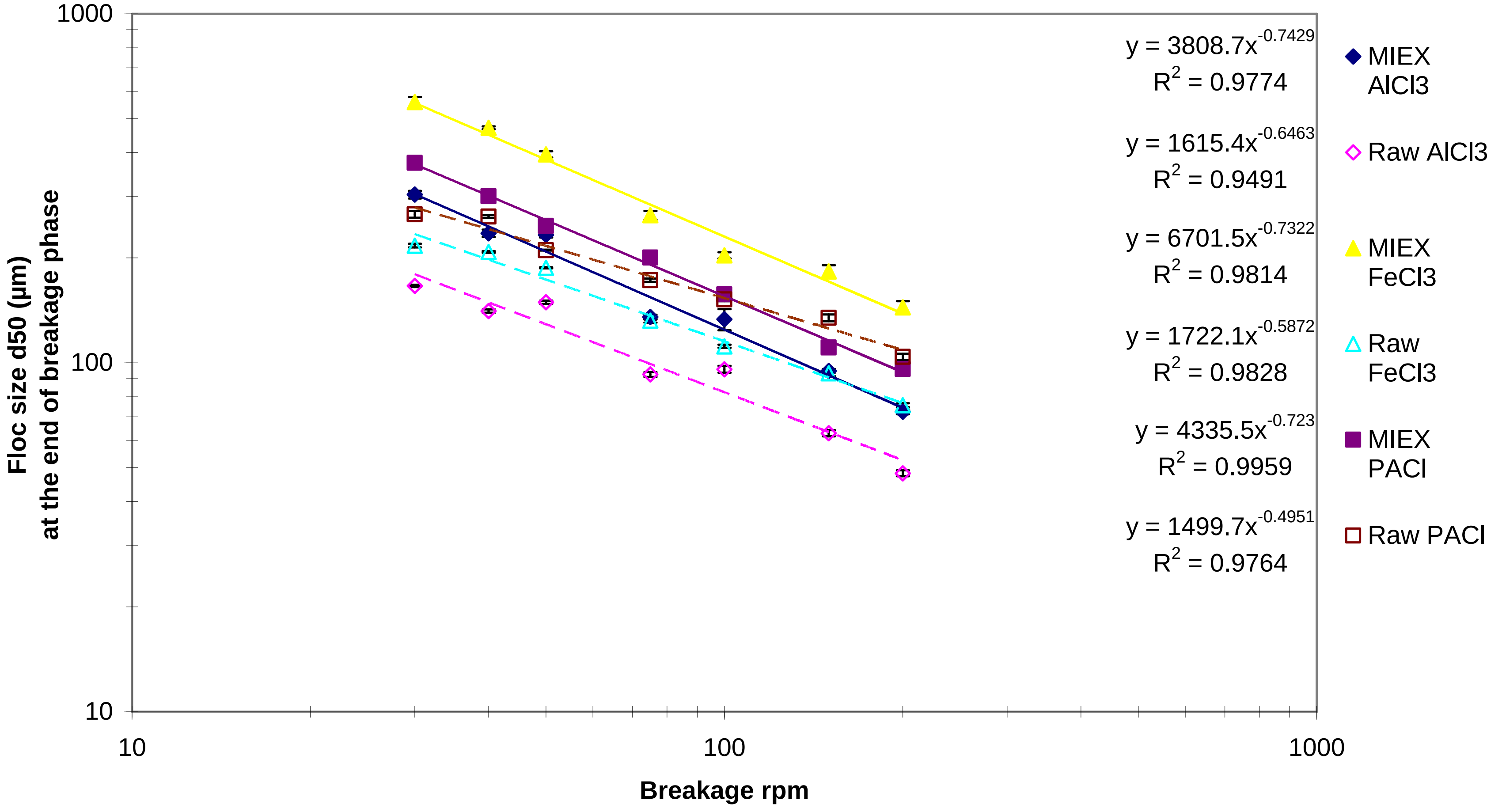

Figure 4. 2: Floc strength profiles for the different combinations of treatments.

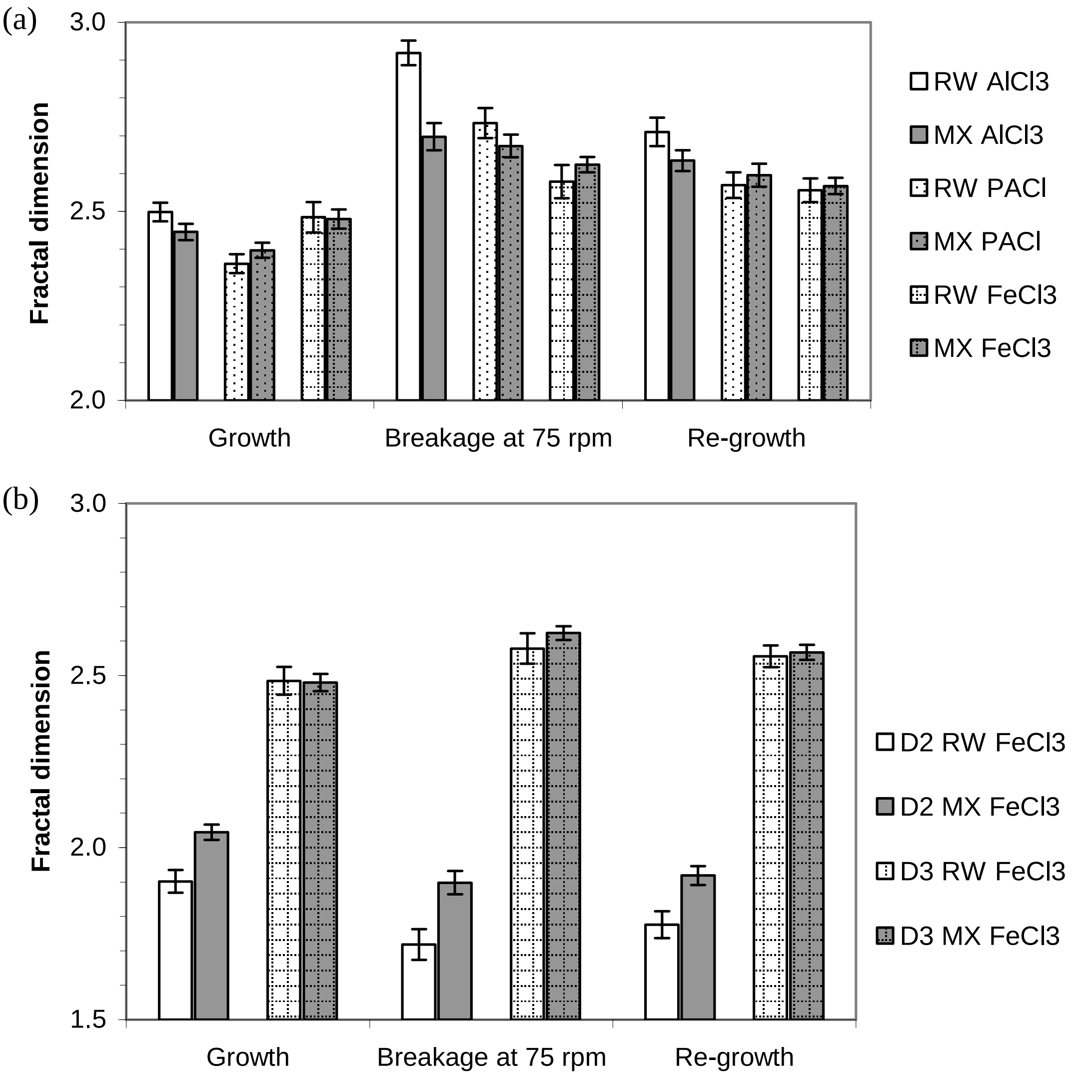

Figure 4. 3: Fractal dimensions of flocs: (a) comparison of D_3 for three different coagulants and (b) comparison of D_2 and D_3 for ferric flocs.

Error bars show the 95% condidence interval of the regression line (calculated by the standard error of characteristic length for D_2 or log Q for D_3).

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APPENDICES

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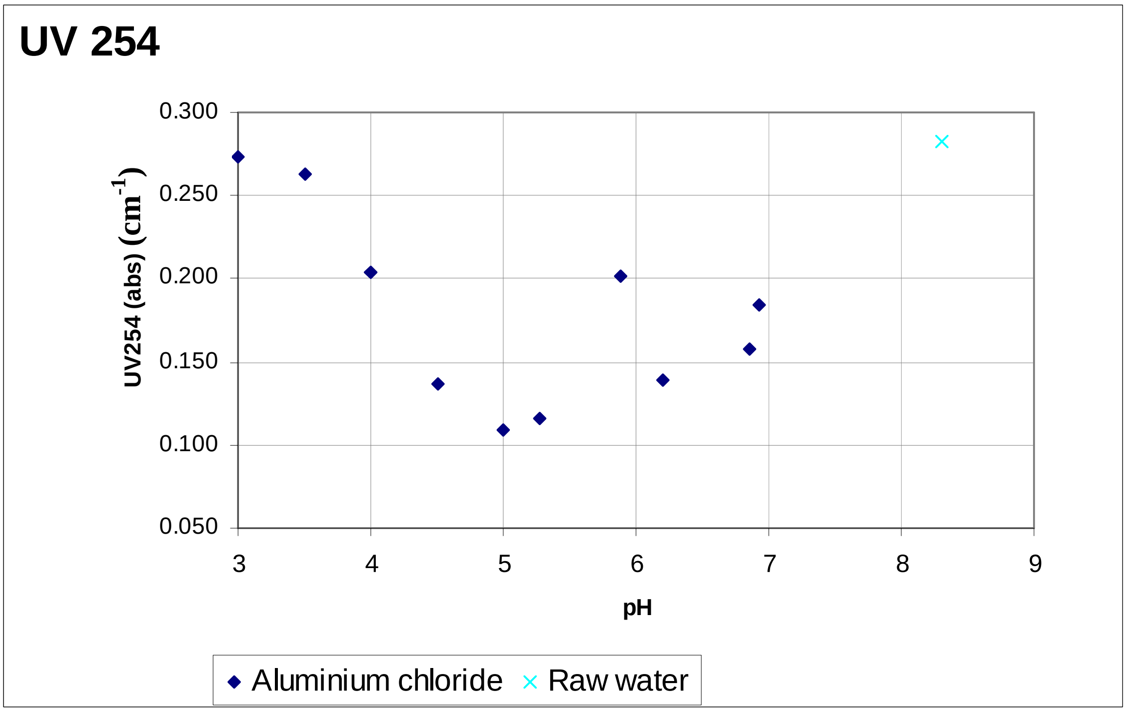
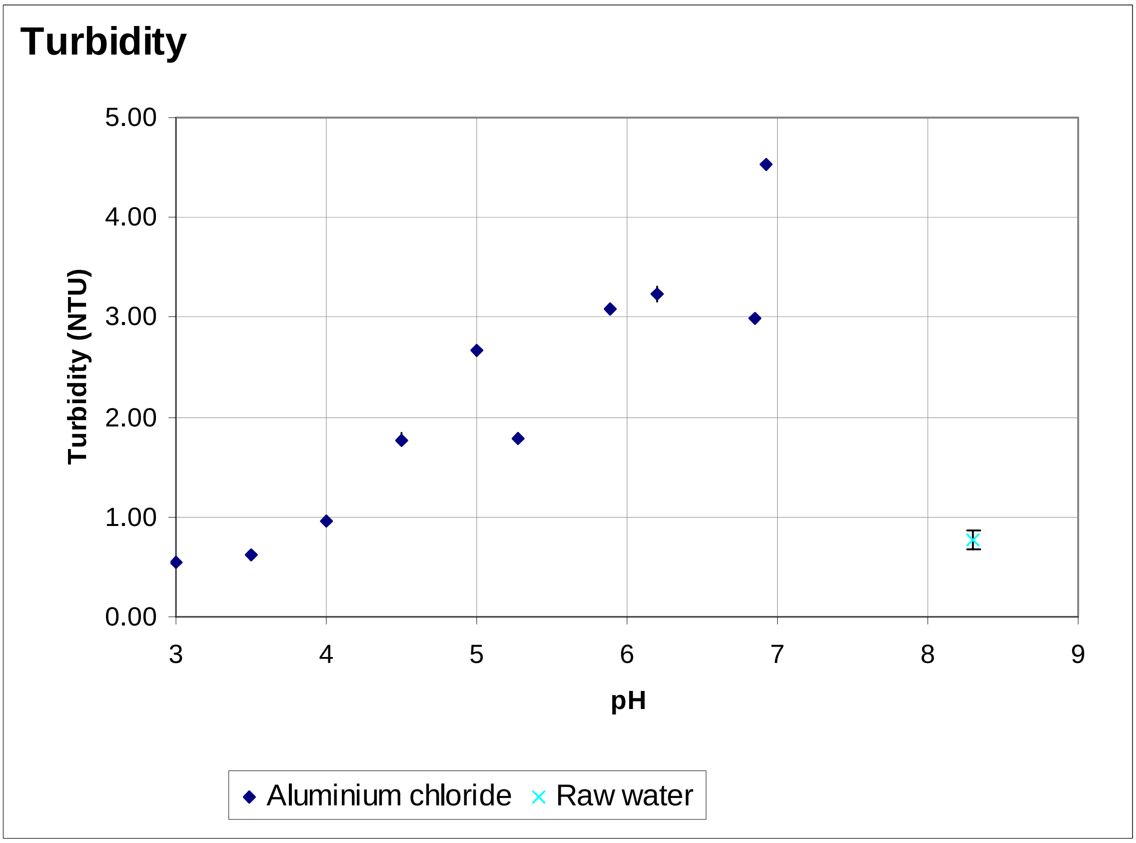
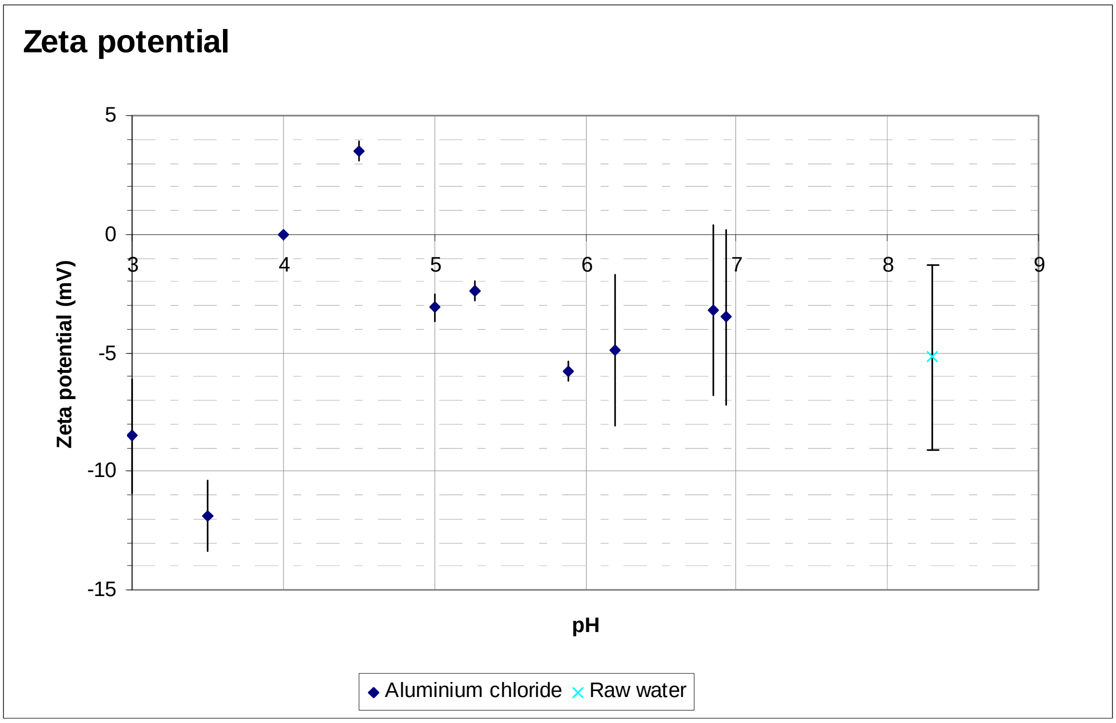
Appendix B: Coagulation optimisation

B.1. pH optimisation

Aluminium chloride






Zeta potential
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Zeta potential (mV)
pH
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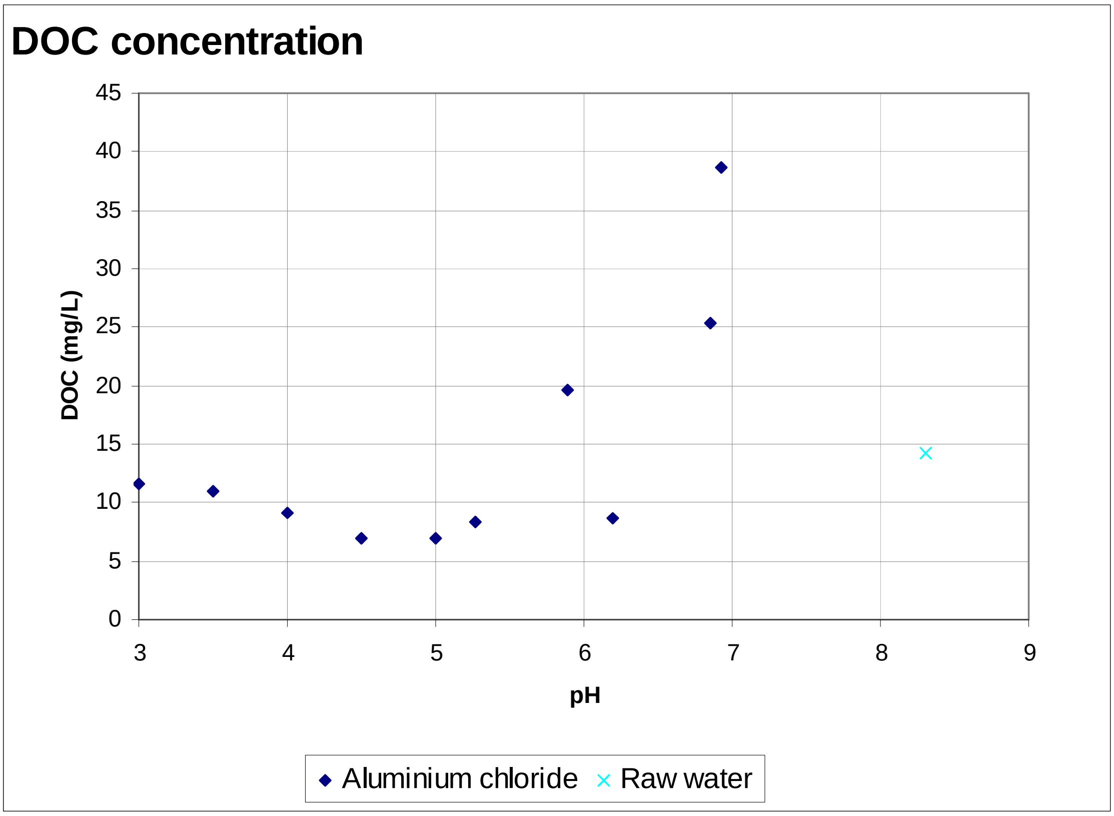
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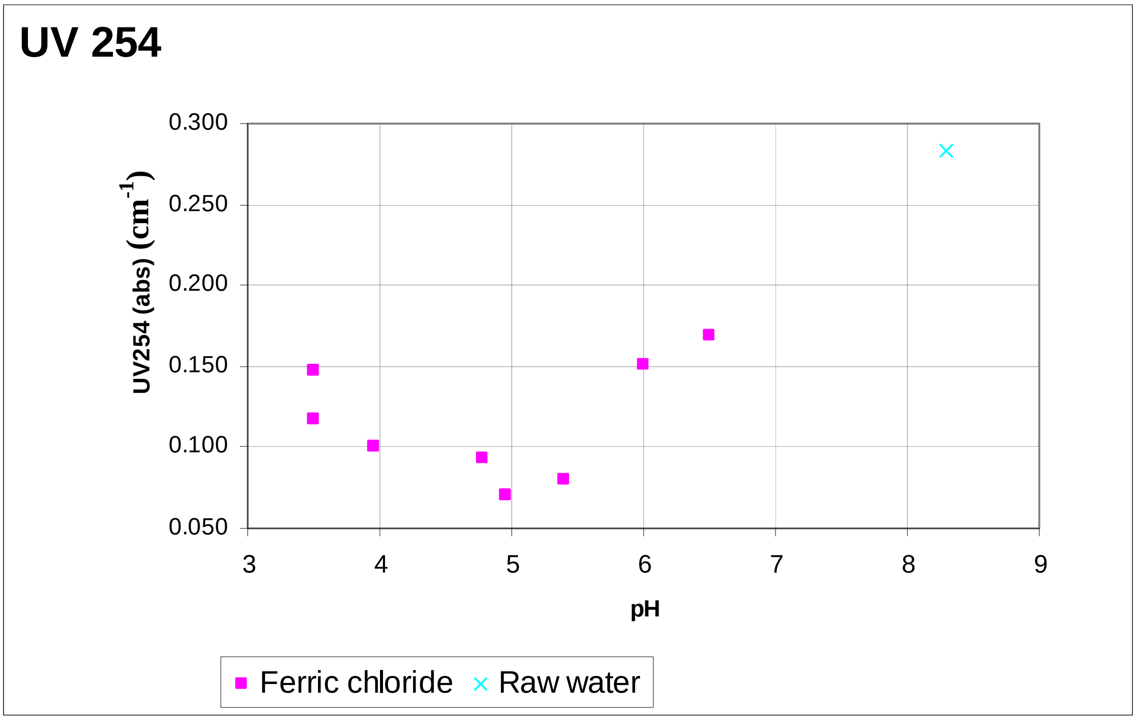
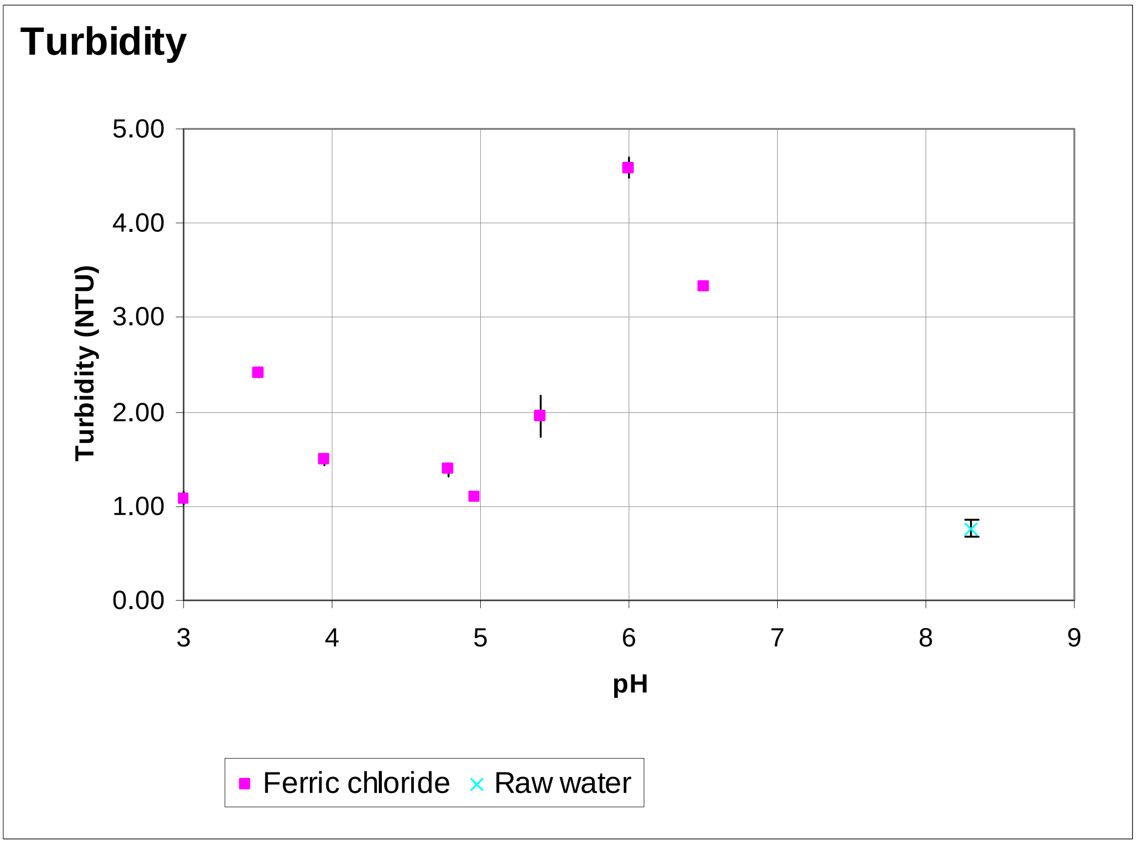
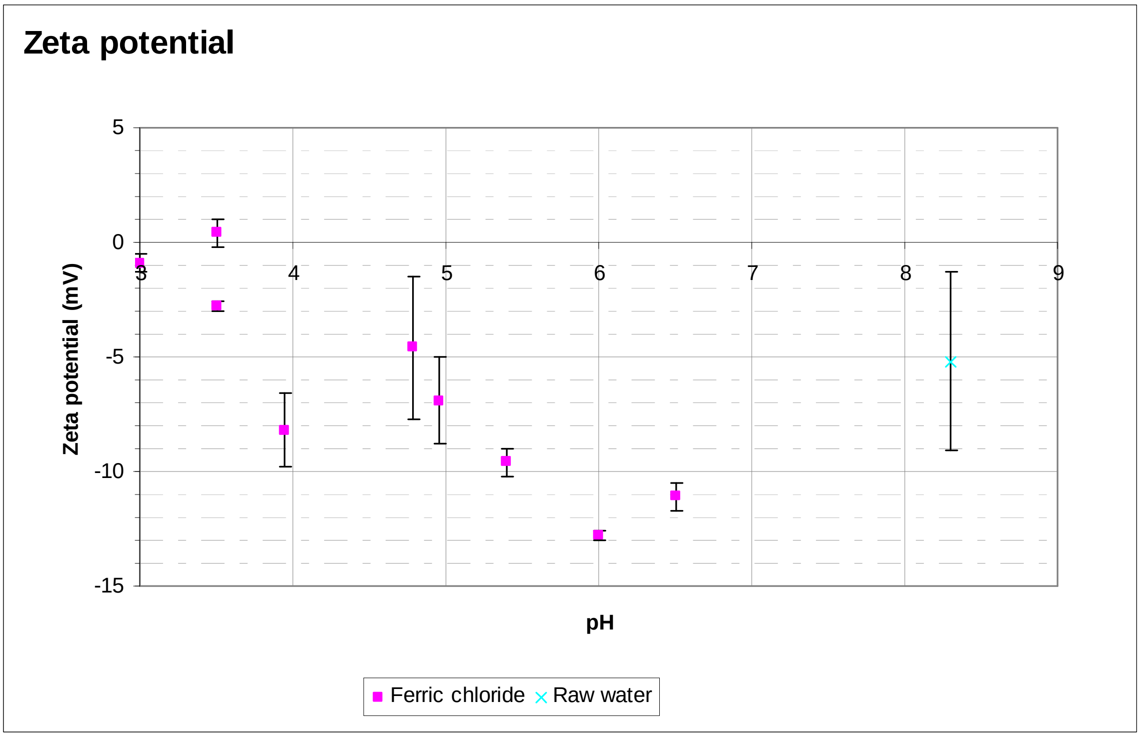
DOC (mg/L)
pH
◆ Aluminium chloride × Raw water

Ferric chloride






Zeta potential
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Zeta potential (mV)
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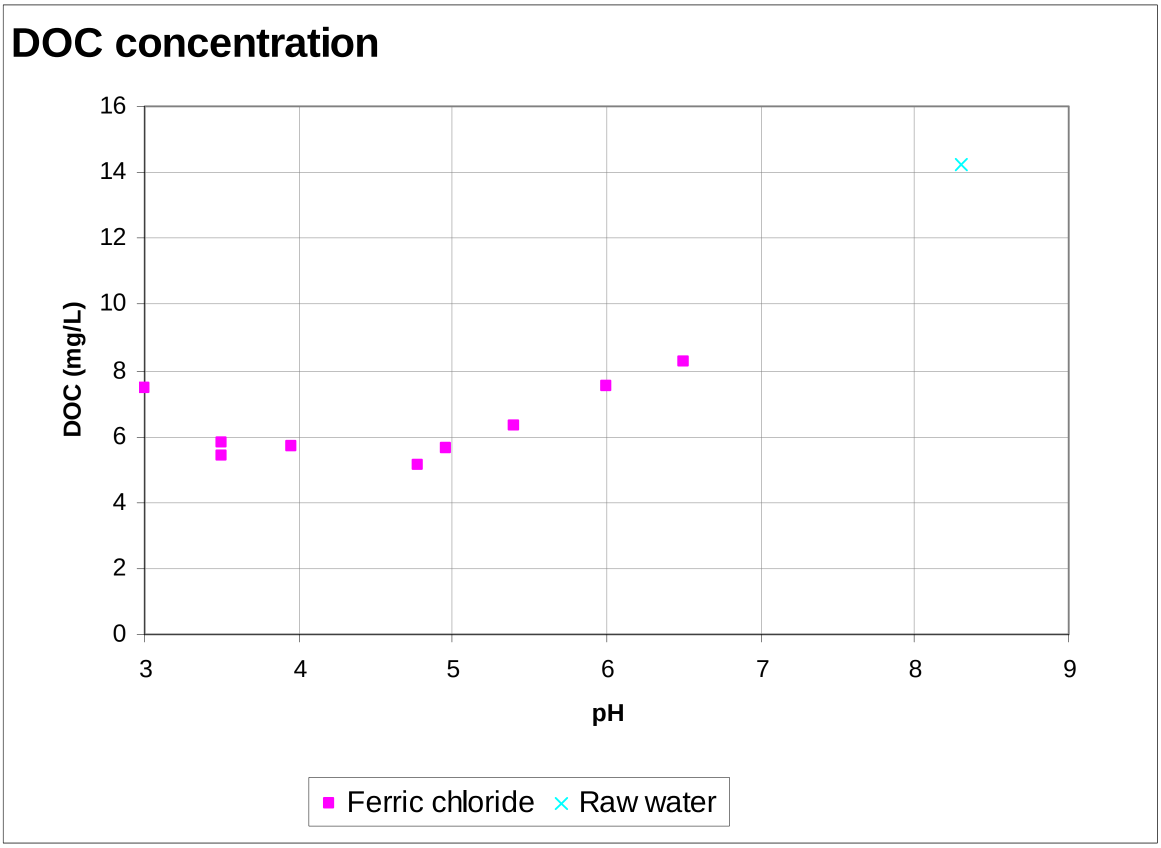
pH
Ferric chloride
Raw water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8
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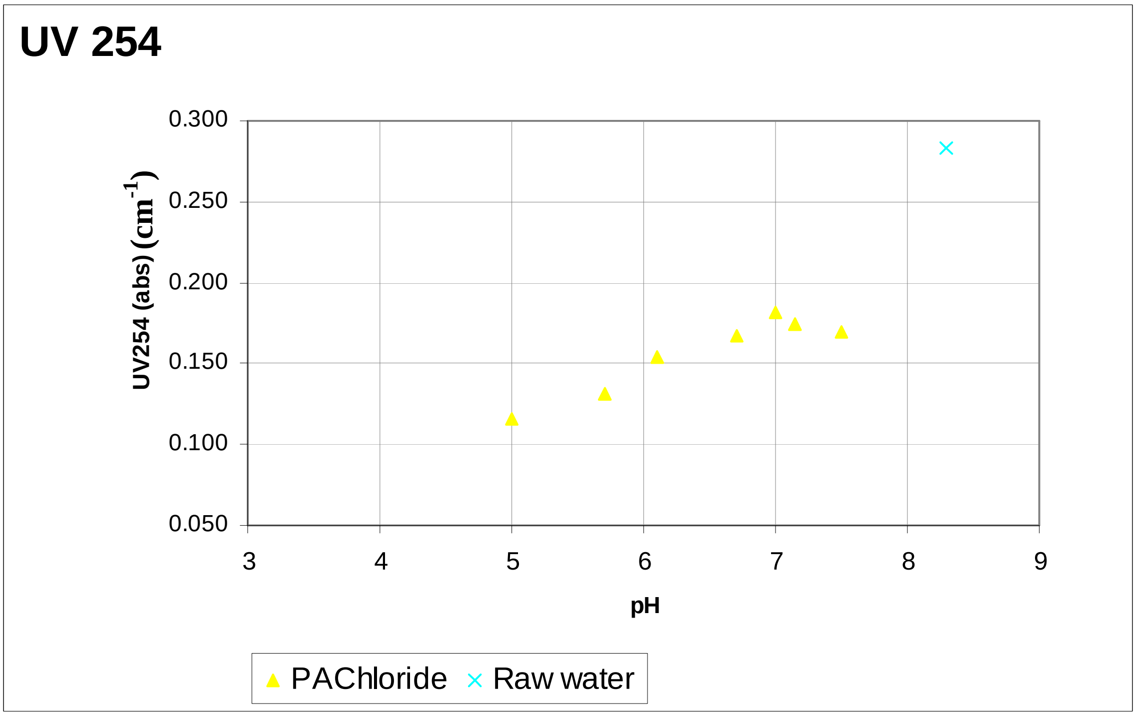
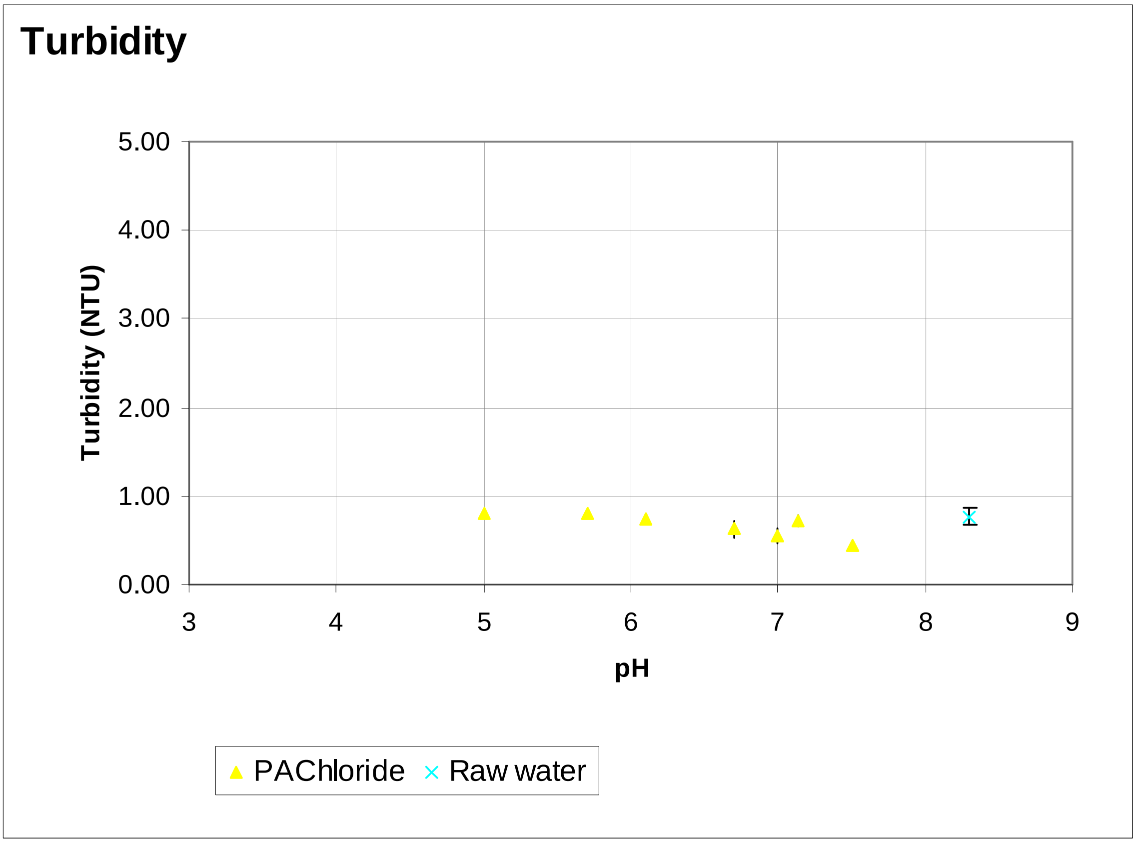
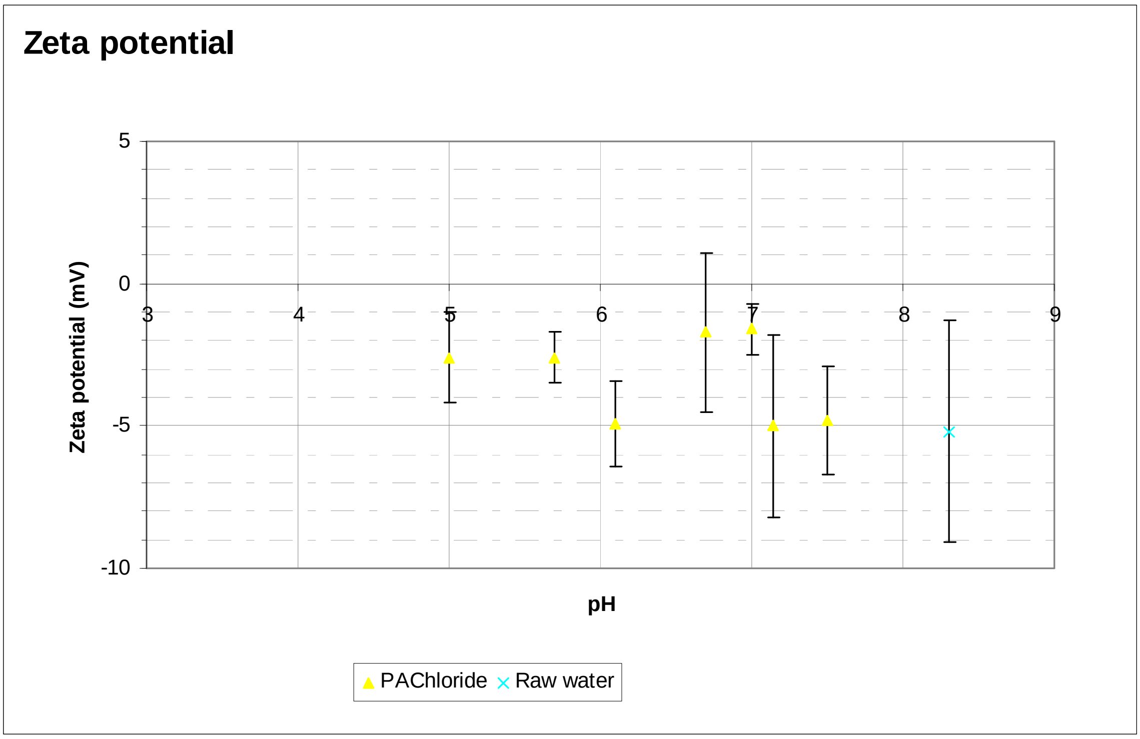
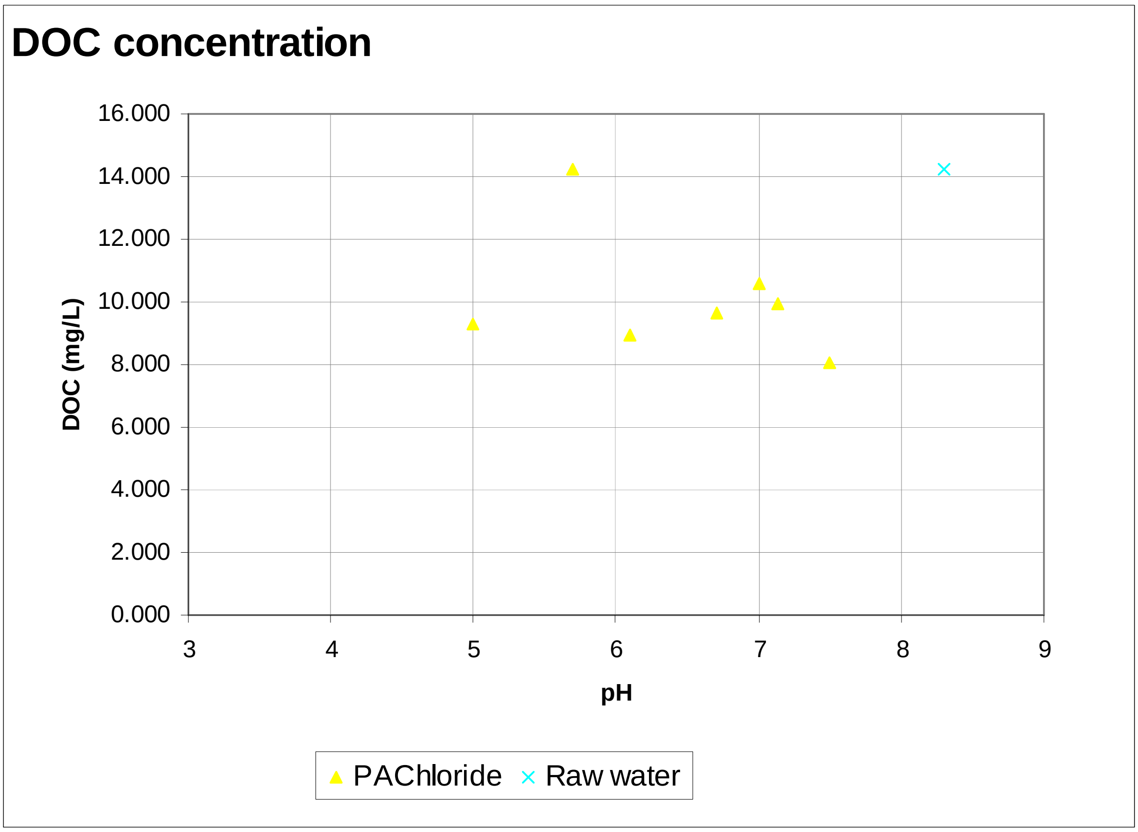
pH
Ferric chloride
Raw water

Polyaluminium chloride

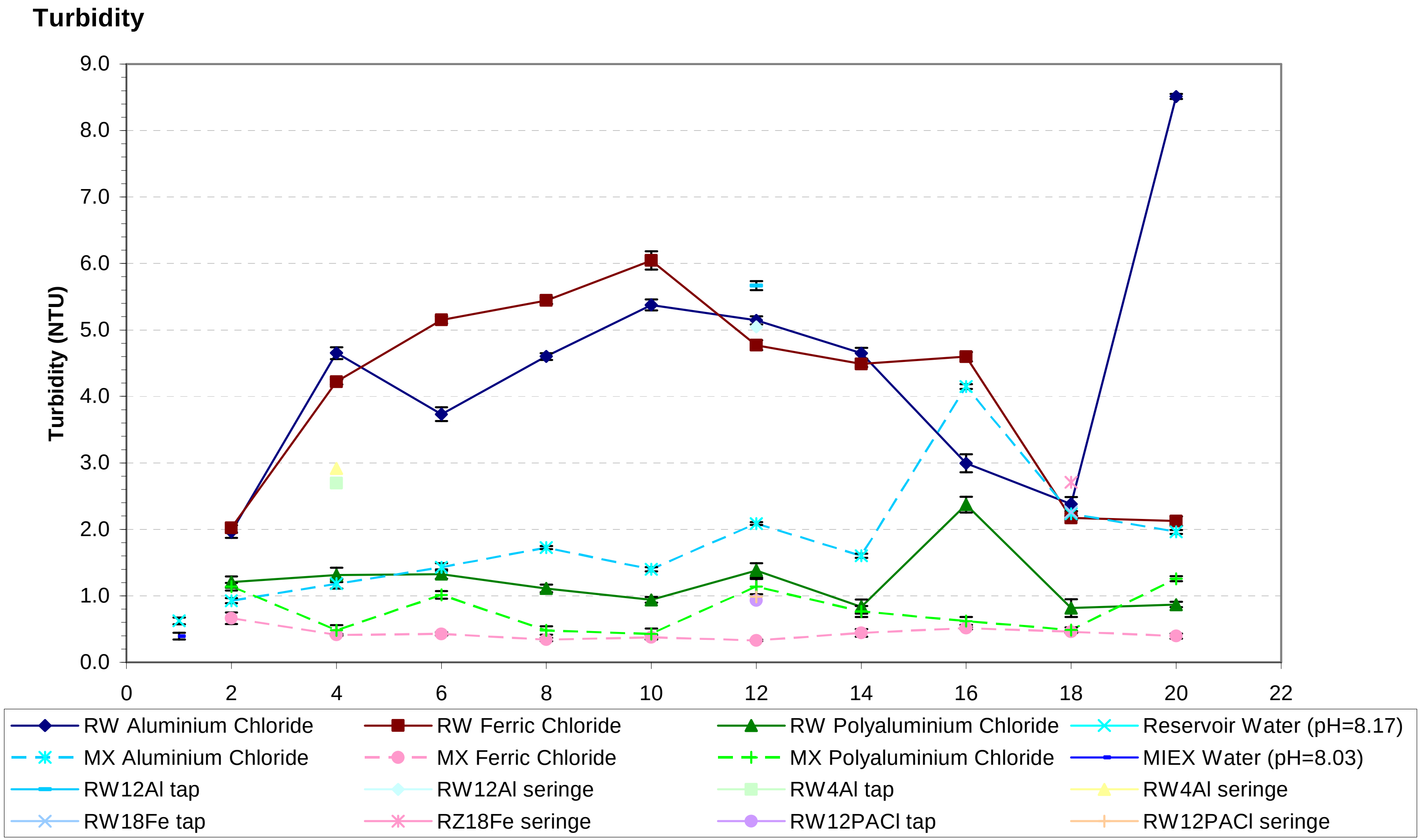




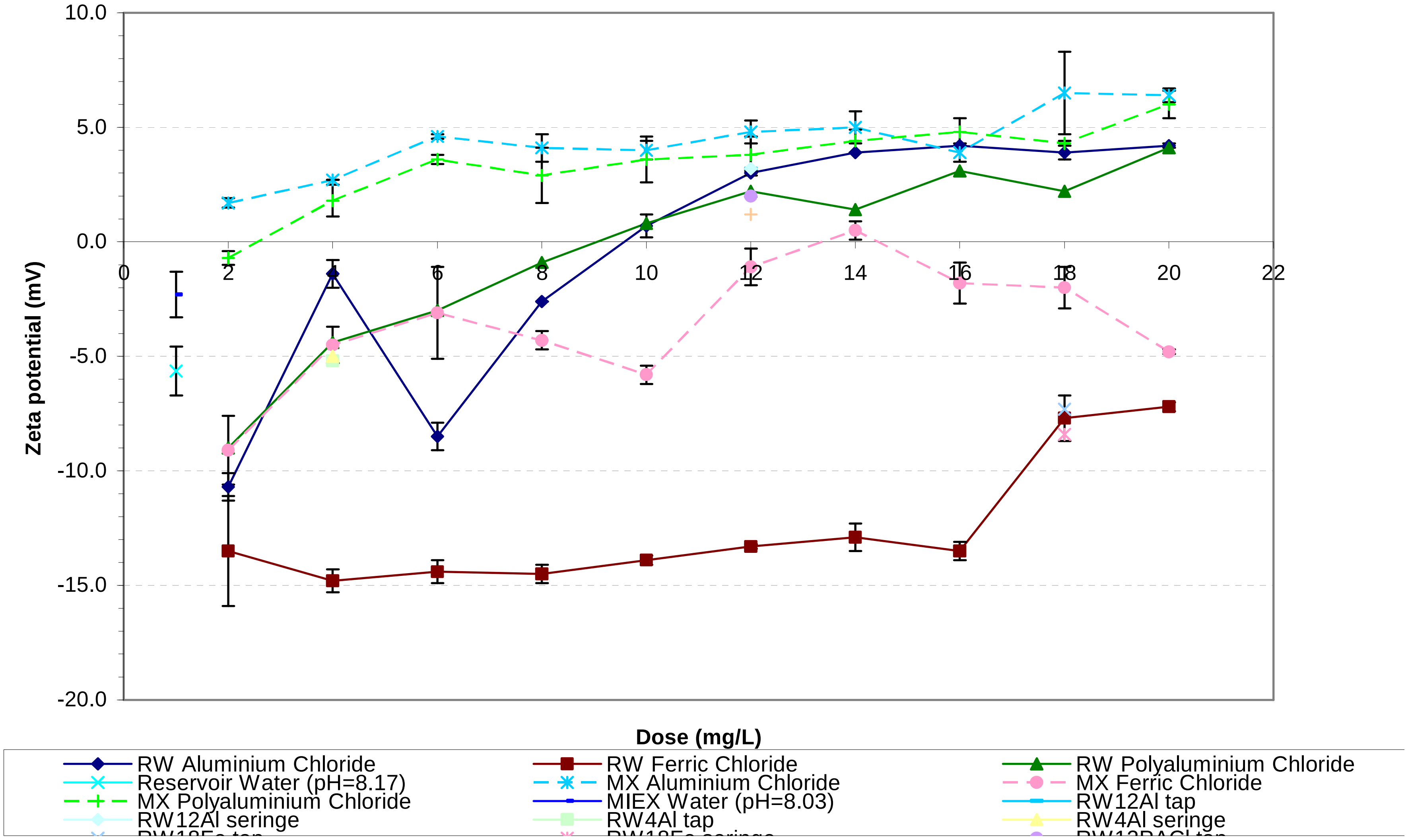

Zeta potential
5
0
-5
-10
Zeta potential (mV)
3
4
5
6
7
8
9
pH
PAChloride
Raw water


DOC concentration
16.000
14.000
12.000
10.000
8.000
6.000
4.000
2.000
0.000
DOC (mg/L)
3
4
5
6
7
8
9
pH
PAChloride
Raw water

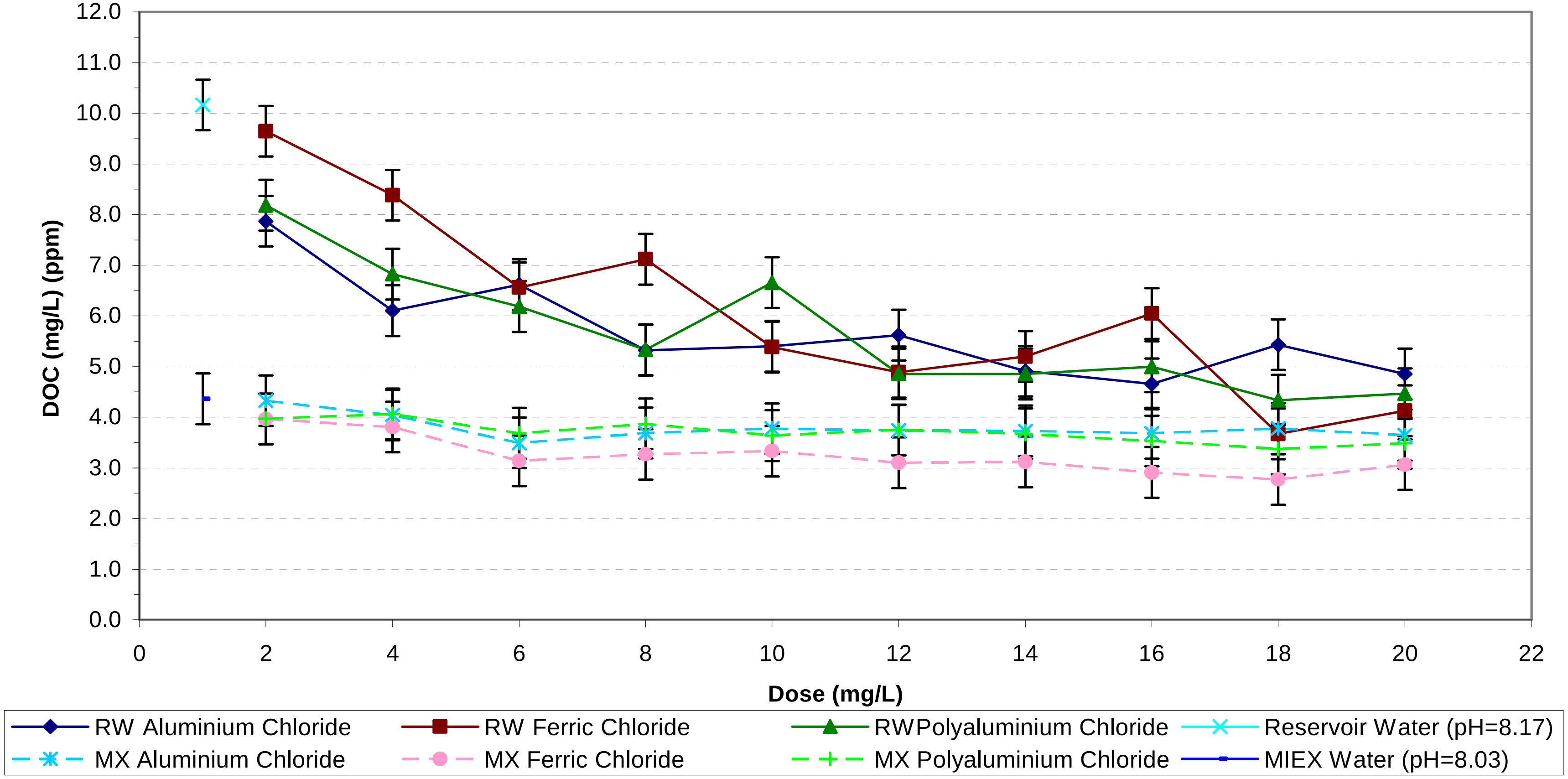
B.2. Dose optimisation

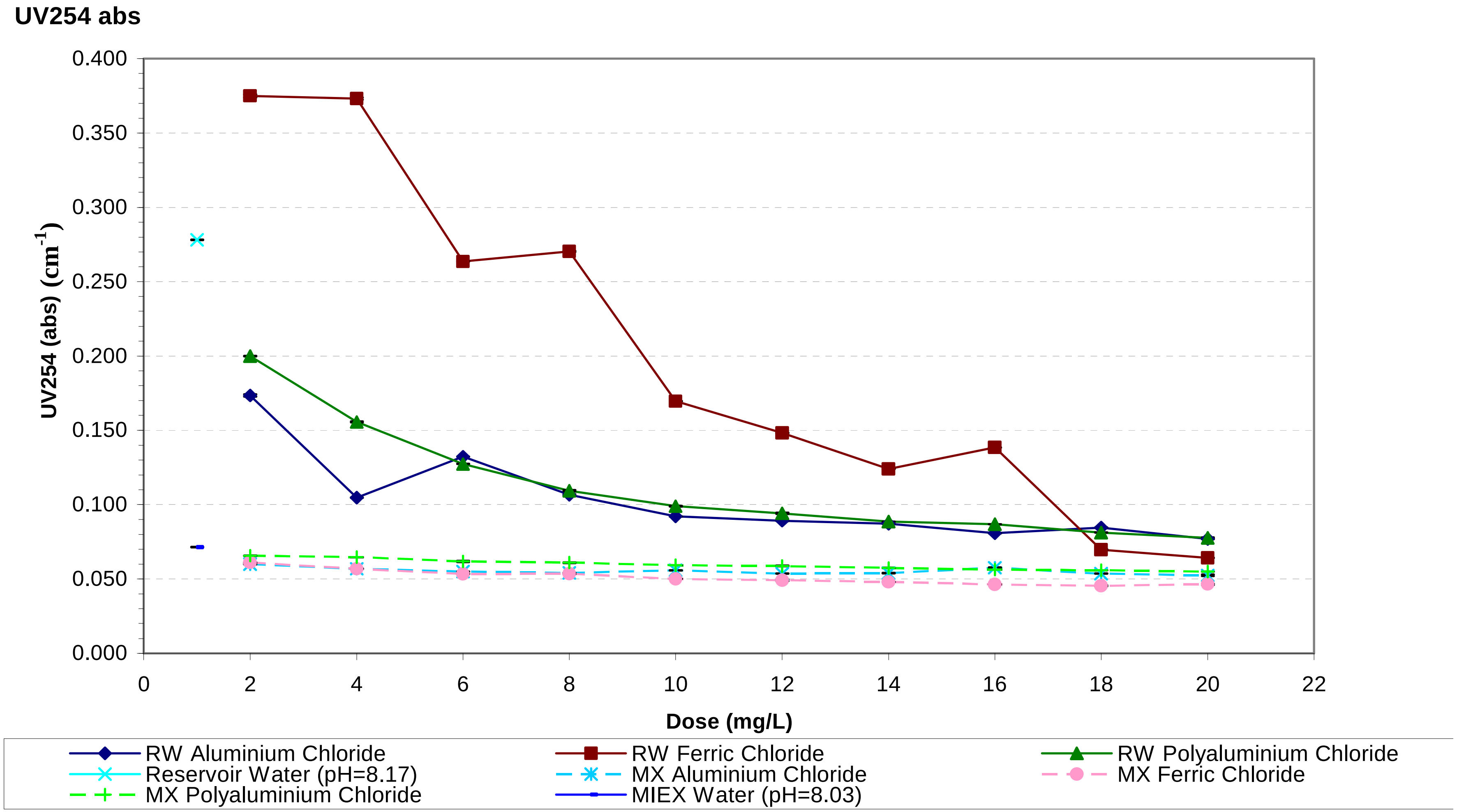


Zeta potential



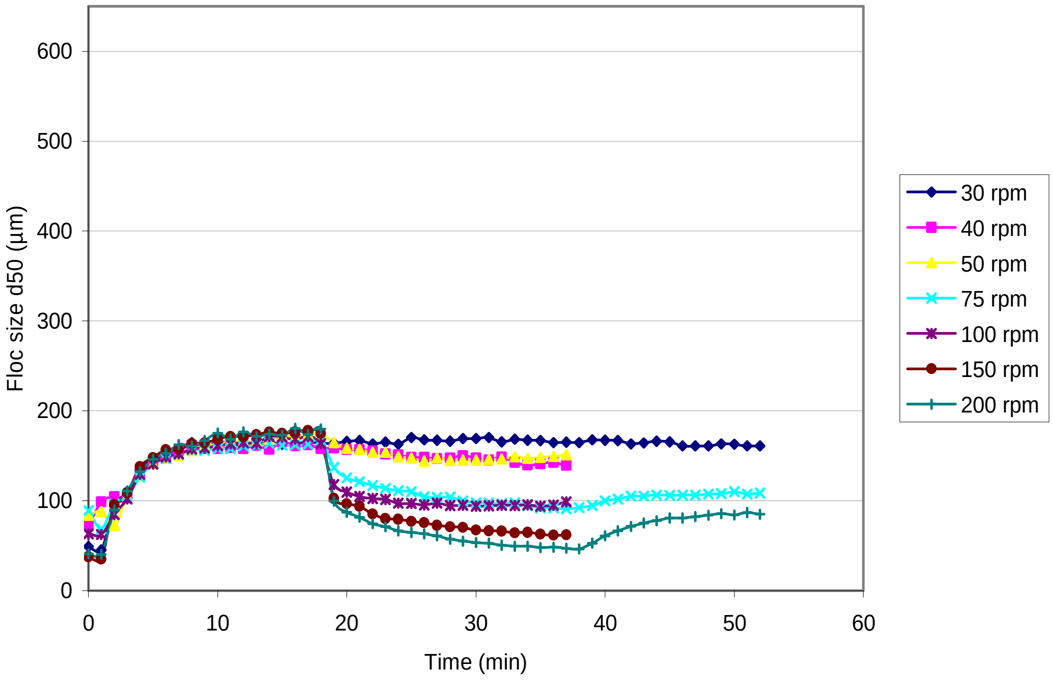
DOC concentration



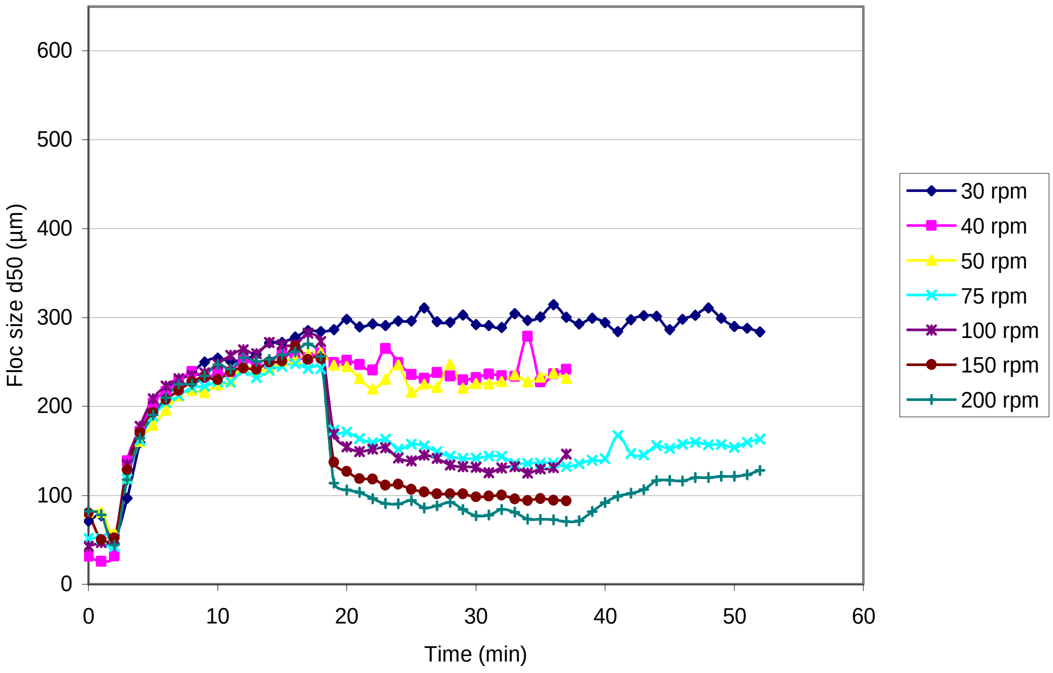

UV254 abs
UV254 (abs) (cm^{-1})
0.400
0.350
0.300
0.250
0.200
0.150
0.100
0.050
0.000
0
2
4
6
8
10
12
14
16
18
20
22
Dose (mg/L)
RW Aluminium Chloride
RW Ferric Chloride
RW Polyaluminium Chloride
Reservoir Water (pH=8.17)
MX Aluminium Chloride
MX Ferric Chloride
MX Polyaluminium Chloride
MIEX Water (pH=8.03)

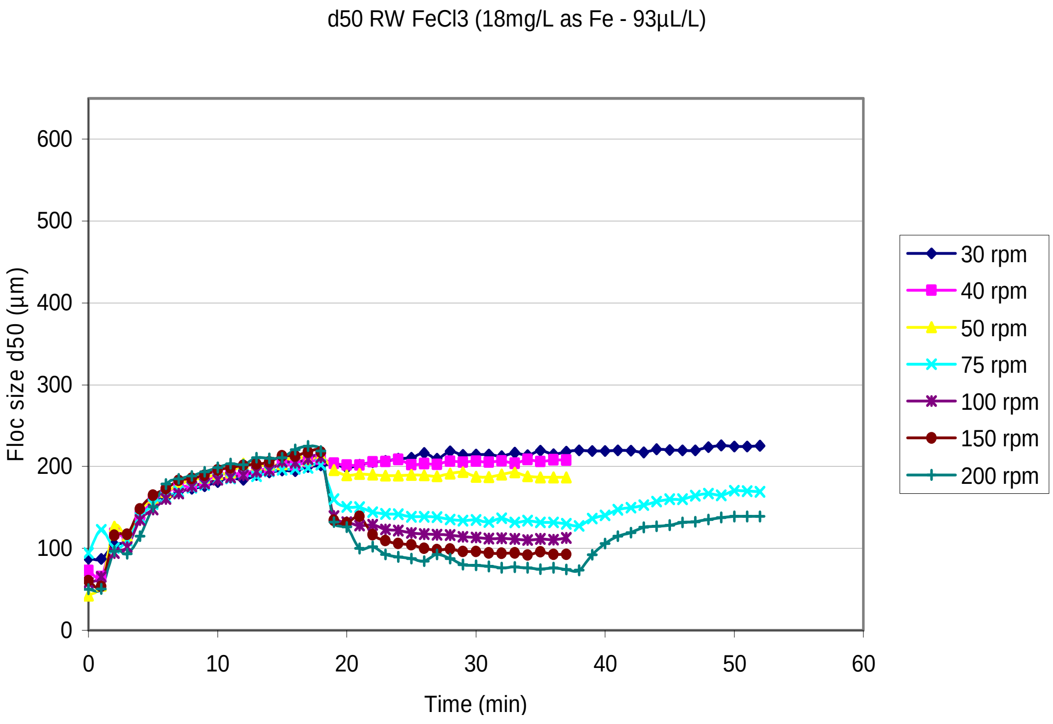
Appendix C: Size measurements for the different treatment options

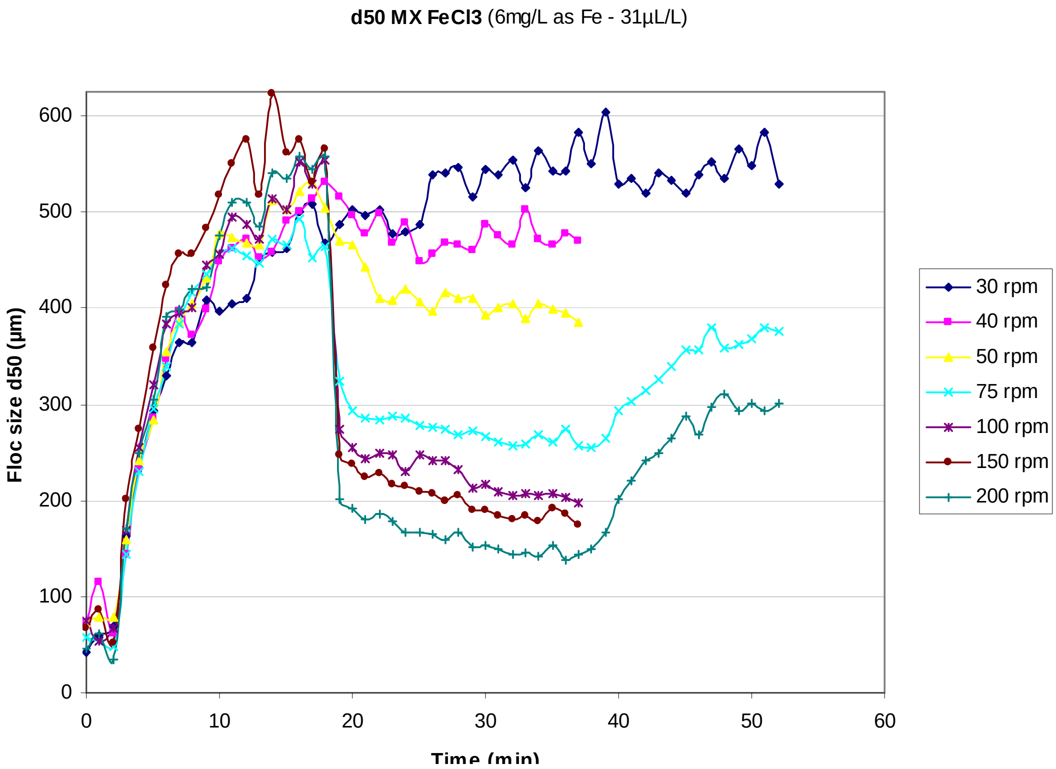
d50 RW AlCl3 (12mg/L as Al - 154µL/L)

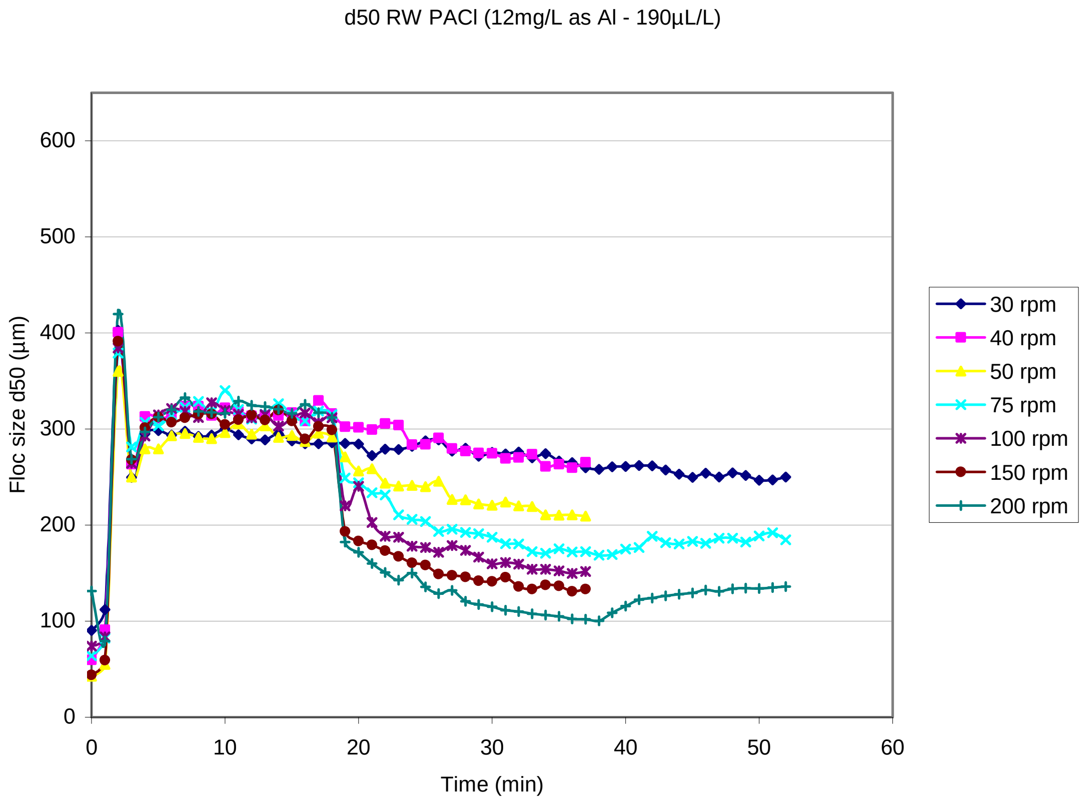


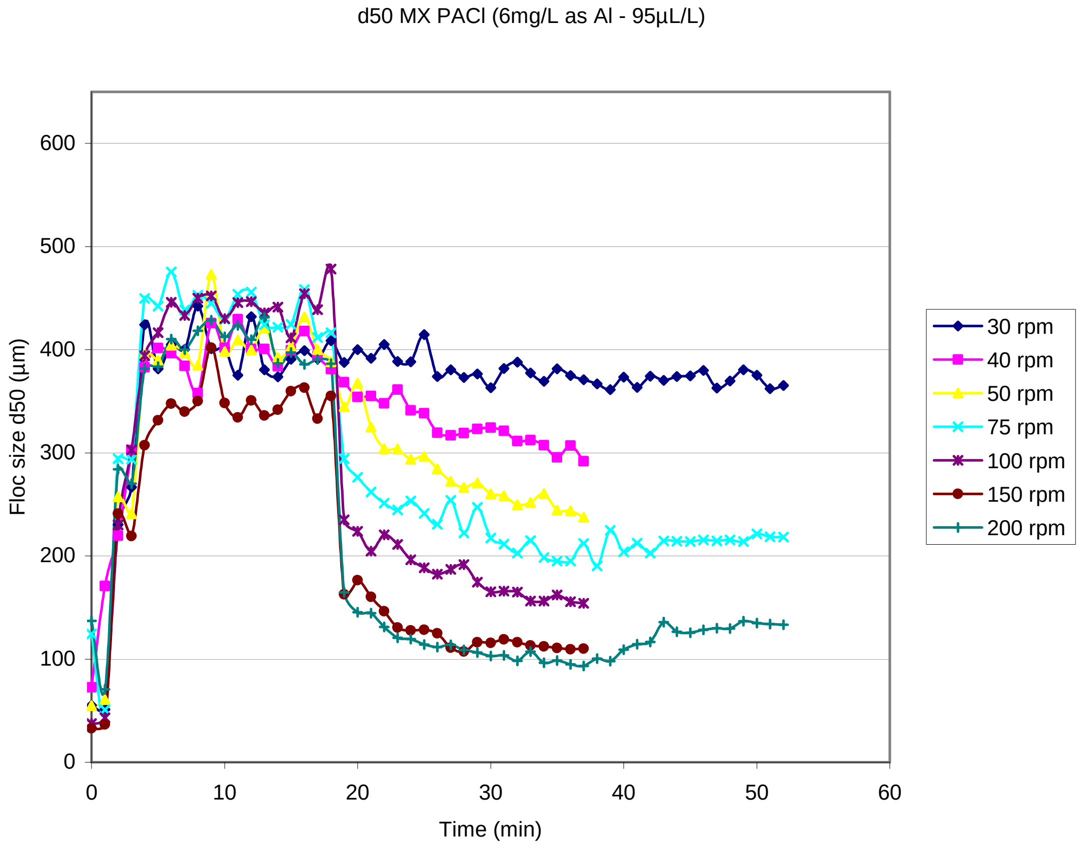
d50 MX AlCl3 (6mg/L as Al - 77µL/L)




d50 RW FeCl3 (18mg/L as Fe - 93µL/L)


d50 MX FeCl3 (6mg/L as Fe - 31µL/L)


d50 RW PACl (12mg/L as Al - 190µL/L)


d50 MX PACl (6mg/L as Al - 95µL/L)

Appendix D: Strength and recovery factor calculations

Strength factor: (d2/d1)*100 and Recovery factor ((d3-d2)/(d1-d2))*100

MIEX $AlCl_3$

rpm	d_1 (µm)	d_2 (µm)	d_3 (µm)	Strength factor (%)	Recovery factor (%)
30	277	303	290	110	49
40	255	235		92	
50	252	232		92	
75	244	135	159	55	21
100	273	133		49	
150	256	95		37	
200	261	72	124	28	27

MIEX $FeCl_3$

rpm	d_1 (µm)	d_2 (µm)	d_3 (µm)	Strength factor (%)	Recovery factor (%)
30	482	559	557	116	2
40	491	471		96	
50	517	396		77	
75	470	265	371	56	52
100	524	203		39	
150	558	183		33	
200	549	144	297	26	38

MIEX PACl

rpm	d_1 (µm)	d_2 (µm)	d_3 (µm)	Strength factor (%)	Recovery factor (%)
30	397	374	371	94	-14
40	398	300		75	
50	407	247		61	
75	428	200	218	47	8
100	446	157		35	
150	353	111		31	
200	390	96	135	25	13

Raw $AlCl_3$

rpm	d_1 (µm)	d_2 (µm)	d_3 (µm)	Strength factor (%)	Recovery factor (%)
30	164	166	162	101	183
40	162	141		87	
50	173	149		86	
75	164	93	109	57	22
100	169	96		57	
150	176	63		36	
200	177	48	85	27	29

Raw $FeCl_3$

rpm	d_1 (µm)	d_2 (µm)	d_3 (µm)	Strength factor (%)	Recovery factor (%)
30	198	217	225	109	-46
40	205	208		102	
50	210	187		89	
75	199	132	169	66	55
100	208	112		54	
150	215	93		43	
200	219	76	139	35	44

Raw PACl

rpm	d_1 (µm)	d_2 (µm)	d_3 (µm)	Strength factor (%)	Recovery factor (%)
30	286	266	249	93	-91
40	318	262		83	
50	292	210		72	
75	314	173	187	55	10
100	312	152		49	
150	300	135		45	
200	318	104	135	33	14

Appendix E: Floc fractal dimension

$FeCl_3$			D_2					
			30 rpm		75 rpm		200 rpm	
MX Fe	**d_1**	Growth	R^2=0.9871	2.044 ± 0.022	R^2=0.9871	2.044 ± 0.022	R^2=0.9871	2.044 ± 0.022
	d_2	Breakage	R^2=0.9873	2.035 ± 0.024	R^2=0.9673	1.898 ± 0.034	R^2=0.9447	1.720 ± 0.040
	d_3	Re-growth	R^2=0.9916	2.007 ± 0.020	R^2=0.9778	1.919 ± 0.027	R^2=0.9767	1.945 ± 0.027
			30 rpm		75 rpm		200 rpm	
RW Fe	**d_1**		R^2=0.9642	1.902 ± 0.033	R^2=0.9642	1.902 ± 0.033	R^2=0.9642	1.902 ± 0.033
	d_2		R^2=0.9760	1.881 ± 0.027	R^2=0.9142	1.719 ± 0.044	R^2=0.9608	1.708 ± 0.035
	d_3		R^2=0.9754	1.941 ± 0.031	R^2=0.9520	1.776 ± 0.039	R^2=0.9760	1.838 ± 0.028

$FeCl_3$			**D_3**					
			30 rpm		75 rpm		200 rpm	
MX Fe	**d_1**	Growth	R^2 = 0.9985	2.480 ± 0.025	R^2 = 0.9985	2.480 ± 0.025	R^2 = 0.9985	2.480 ± 0.025
	d_2	Breakage	R^2=0.9986	2.406 ± 0.020	R^2=0.9990	2.623 ± 0.020	N/A	
	d_3	Re-growth	R^2=0.9993	2.456 ± 0.014	R^2=0.9985	2.567 ± 0.022	R^2=0.9976	2.452 ± 0.028
			30 rpm		75 rpm		200 rpm	
RW Fe	**d_1**	Growth	R^2=0.9979	2.485 ± 0.040	R^2=0.9979	2.485 ± 0.040	R^2=0.9979	2.485 ± 0.040
	d_2	Breakage	R^2=0.9970	2.545 ± 0.031	R^2=0.9959	2.579 ± 0.044	N/A	
	d_3	Re-growth	R^2=0.9978	2.583 ± 0.028	R^2=0.9975	2.556 ± 0.031	R^2=0.9978	2.482 ± 0.031

$AlCl_3$			**D_3**					
			30 rpm		75 rpm		200 rpm	
MX Al	**d_1**	Growth			R^2 = 0.9989	2.446 ± 0.021		
	d_2	Breakage			R^2=0.9977	2.697 ± 0.036		
	d_3	Re-growth			R^2=0.9988	2.634 ± 0.027		
			30 rpm		75 rpm		200 rpm	
RW Al	**d_1**	Growth			R^2=0.9986	2.498 ± 0.025		
	d_2	Breakage			R^2=0.998884	2.919 ± 0.033		
	d_3	Re-growth			R^2=0.9979	2.710 ± 0.038		

PACl			**D_3**					
			30 rpm		75 rpm		200 rpm	
MX PACl	**d_1**	Growth			R^2 = 0.9990	2.397 ± 0.020		
	d_2	Breakage			R^2=0.9985	2.673 ± 0.030		
	d_3	Re-growth			R^2=0.9983	2.596 ± 0.031		
			30 rpm		75 rpm		200 rpm	
RW PACl	**d_1**	Growth			R^2=0.9983	2.362 ± 0.025		
	d_2	Breakage			R^2=0.9981	2.733 ± 0.040		
	d_3	Re-growth			R^2=0.9983	2.570 ± 0.034		