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Optimising powdered activated carbon dosing procedures for removal of natural organic matter

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Abstract.

The performance of three different types of PAC was analysed for the efficiency at which they remove natural organic matter (NOM) from untreated (raw) water, with the objective of ultimately reducing disinfection bi-product (DBP) formation. The treatment of raw water by PAC was also examined in conjunction with the addition of iron salts in the form of ferric sulphate, for coagulation and flocculation of NOM.

The optimum dosing of PAC was achieved at pH 3 and at a dose of around 20mgl^{-1} which gave 32.7% removal. Coagulation could be seen to give 88% removal and when used together PAC and coagulant gave between 93.6% and 97% removal of NOM.

The dosing sequence of PAC and coagulant was investigated whereby it was found that optimum removal was achieved by dosing PAC prior to dosing coagulant, although if the delay between dosing PAC and coagulant was more than 30 seconds it was found to impair NOM removal and increase turbidity.

Scale up trials of the dosing strategy were implemented at both Ewden water treatment works, in Yorkshire, and at the Pilot Hall in Cranfield University.

The greatest reduction in DBP formation could be seen using Norit SA Super and coagulation. Dosing this activated carbon at 20mgl^{-1} resulted in a decrease of DBP formation by 86% in raw water and by 78.7% using coagulation alone. Dosing PAC before coagulant produced the lowest levels of DBPs, which were 27.2μgl-1. This is much lower than the 80μgl-1 limit to which water treatment works must adhere.

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Key to Abreviations

AC	Activated carbon
BET	Brunauer, Emmett, and Teller
CO_2	Carbon Dioxide
DAF	Dissolved air flotation
DBP	Disinfection by-product
DEFRA	Department for environmental, food, and rural affairs
DOC	Dissolved organic carbon
DWI	Drinking water inspectorate
DWQS	Drinking Water Quality Standards
EPA	Environmental protection agency
FA	Fulvic acid
FAF	Fulvic acid fraction
GAC	Granular activated carbon
GCECD	Gas chromatography electron capture device
HA	Humic acid
HAA	Halo-acetic acid
HAF	Humic acid fraction
HAPAC	High activity powdered activated carbon
HP-A	Hydrophilic acid fraction
HP-NA	Hydrophilic non-acid fraction
HPSEC	High performance size exclusion chromatography
IC	Inorganic carbon
IUPAC	International Union of Pure and Applied Chemistry
Kf	Freundlich constant
NOM	Natural organic matter
O_2	Oxygen
PAC	Powdered activated carbon
PSD	Particle size distribution
RW	Raw water
TAA	Tri-halo acetic acid
TC	Total carbon

THM	Tri-halo methane
TOC	Total organic carbon
YW	Yorkshire water
WHO	World health organisation
WTW	Water treatment works

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1. Introduction

Water treatment is a multi-billion pound industry (Cave, 2009). While there has been some form of water management from as early as Roman times the 10 main water authorities were set up in England and Wales in 1974. All water treatment works (WTW's) have strict legislation which governs the standard and quality of the water that they produce. Legislation of drinking water in the United Kingdom is strictly controlled and fines can be imposed on the water treatment companies if drinking water fails to meet the drinking water quality standards (DWQS) set by the regulatory agencies.

Water is as an essential molecule because it is essential to life on this planet. Almost 70% of the planet is covered by water and the human body comprises 60-70% water. In addition, it is an important factor in many biochemical processes, such as the Krebs cycle (Gutman, 1999). Provision of high quality drinking water for public consumption requires the source water to pass through a number of treatment processes before it is of the right quality for drinking. In the UK, the Drinking Water Inspectorate (DWI) is the regulatory body that stipulates which components of the water must be removed and to what concentration. This includes controlling a range of microbial, physical and chemical (organic and inorganic) parameters. In order to kill and prevent microbes growing in the water, a disinfection stage is incorporated into the treatment process. This is normally achieved through the addition of chlorine, which is a powerful oxidant and anti-bacterial agent.

In moorland source waters that contain high concentrations of natural organic matter (NOM), (UV < $50m^{-1}$, TOC <$12mgl^{-1}$), one of the key requirements is to remove as much of the organic content from the water as possible. This is principally to prevent the formation of disinfection by-products (DBPs) from the reaction between chlorine and residual NOM. Trihalomethanes (THMs) are the DBP of primary concern for most water utilities in the UK because they are currently the only regulated organic DBP. The DWQS for total THMs is $100\mu gl^{-1}$ in the UK, whereas the USA has limits of $80ugl^{-1}$. If the UK legislation changes to lower THM levels to that of the USA then potentially a lot of water treatment works could struggle to meet the standards.

The conventional mechanism for bulk removal of NOM is by using metal salts as coagulating agents. Here, NOM is incorporated into a floc aggregate that can be separated from the water by flotation or sedimentation. Additional NOM removal is often required to ensure that the DWQS for DBPs are met. To achieve this, coagulation is used in conjunction with a second process such as an adsorption or ion-exchange stage. Powdered activated carbon (PAC) is one of the most commonly used adsorbents for enhanced NOM removal because it has an incredibly large (up to $1500m^2$) surface area which is the key factor that makes it suitable to aid in NOM removal. It is because of the high surface area and the high number of available adsorption sites that PAC is used as an adsorbent in many other industries for organic compound removal such as in alcoholic distillation, gas purification and the medical industry to remove impurities.

The effectiveness of PAC for NOM removal in water treatment is dependent on a number of factors such as the type and dose of PAC, the nature of the organic molecules in the water and the dosing sequence of the PAC with respect to the coagulant. This project focuses on the application of PAC at a specific WTW in the Yorkshire Water region, Ewden WTWs, in order to understand how PAC may be used most effectively to achieve optimum NOM removal and low DBP formation.

1.1. Aims and Objectives

This project will examine the performance of three different types of PAC with respect to adsorption and in particular the removal of NOM. These PAC were Norit SA Super (Norit, UK), Pulsorb C (Chemviron, UK) and Pulsorb 207 CP-90 (Chemviron, UK). Pulsorb C is a standard activity carbon currently used by Yorkshire Water at Ewden WTW. Pulsorb 207 CP-90 is a high activity PAC from the same supplier, and Norit SA Super is a competitors high activity PAC. NOM removal will be assessed by TOC and absorbance at UV_{254} which will illustrate the difference between aromatic and aliphatic NOM removal. The performance of the three PACs will be assessed with respect to concentration (mgl^{-1}) and pH. The optimum dosing strategies for PAC will then be tested in conjunction with ferric sulphate coagulant at a concentration of $12mgl^{-1}$ as Fe, which will be tested in a series of jar tests with different contact times for both coagulant and PAC during the rapid mix stage. The optimum dosing strategies will then be tested at Ewden WTW and on the pilot-scale water treatment facility at Cranfield University.

At the end of the project it is anticipated that the optimum dosing strategy for a combination of PAC and ferric will be found. Upon completion of this project the key deliverables will be:

1. Empirical proof of which of the 3 PACs is the most efficient.
2. The optimum dose at which to add the PAC to remove NOM.
3. The best pH at which to dose the PAC.
4. The best sequence in which to dose PAC and Ferric.

5. The best dosing strategy to implement that gives the lowest THM formation.

2. Literature review

2.1. Aims and objectives

The aim of this review is to examine the performance of absorbents in removing organic compounds, of which the main focus will be the removal of natural organic matter (NOM). The review focuses on NOM characteristics in source waters, the components of NOM which are removed by conventional treatment methods used in water treatment and which components of NOM are removed by adsorption as well as the key factors that influence adsorption. The data in this review will also be used to demonstrate which are the controlling parameters that improve NOM removal with respect to adsorption in order to lower disinfection by-product (DBP) formation.

2.2. Natural organic matter (NOM)

Certain sources of raw water, such as lowland and upland reservoirs, have a distinctive yellow/brown colour due to containing a high concentration of NOM. It is important that water treatment works (WTWs) remove NOM from water in order to obtain high quality potable water. The amount of NOM present in drinking water is not currently legislated but it is the legislation connected with the disinfection of the water that means that NOM must be removed because toxic DBPs can form from reactions between NOM and the halogenated disinfectant (Fearing *et al*., 2004).

The source of NOM in the raw waters is from soil, plant material, both living and decaying and in some cases animal material (Goel *et al*., 1995). NOM is a heterogeneous mixture of numerous organic carbon compounds such as humic acids, fulvic acids, amino acids, carbohydrates and lipids (Richardson, 2001). The exact composition and ratio of NOM and its constituent components varies between different water sources depending on the origin of the water. This is because raw water comes from a number of different geographical locations and from different environmental niches. This results in significant changes to the quality of the raw water that must be treated between different water treatment works as well as changes in the NOM composition for a particular water source as environmental conditions change. In many source waters this is evidenced by an increase in NOM concentrations in the water at certain times of the year, such as the first heavy runs of late summer and autumn (Figure 1).

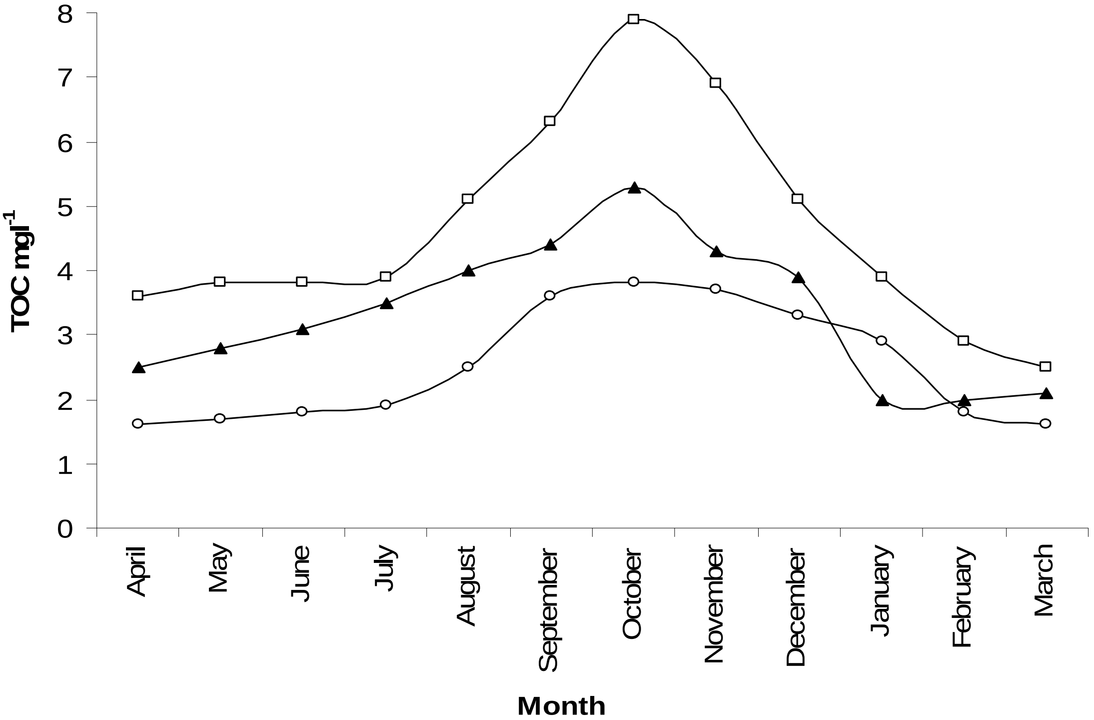


Figure 1. The change in NOM levels, measured by TOC, over a year, adapted from (□)Zanardi-Lamardo *et al*. 2004; (▲)Sasaki *et al*. 2005; (○)Chen *et al*. 2008.

NOM is essentially the biological remnants of living, dying and dead flora and fauna. It is because NOM originates from flora and fauna that a distinct cycle is often seen such as that shown in figure 1. In many cases, particularly in northern Europe the spike in NOM results from heavy rains after dry periods which flushes accumulated NOM from the soil into receiving water bodies. Any WTWs that treats this type of water must be prepared and able to treat high spikes of NOM loading at certain times of the year. It is of paramount importance that the treatment regime that is employed is flexible enough to treat both heavily ladened NOM waters and waters containing lower concentrations of NOM.

2.2.1. Characterisation

It is possible, and useful for treatment purposes, to categorise the components of NOM in to fractions dependent on the hydrophobicity of the fractions. The fractionation of NOM can be achieved using resins and a process of sorption and desorption at different pHs. The most common method for fractionation is using a styrene divinylbenzene polymer and an acrylic ester polymer (Malcom & McCarthy, 1992). These fractions are segregated by phobicity into 2 fractions, either hydrophobic or hydrophilic (Aiken *et al.*,1992) The hydrophobic fraction contains aliphatic carboxylic acids (C5-C9), 1-2 ring aromatic carboxylic acids and 1-2 ring aromatic phenols whereas the hydrophilic fraction contains poly functional organic acids, aliphatic acids as well as more complicated carbohydrates and proteins.

NOM can also be fractionated by acidity (Malcolm and McCarthy, 1992). NOM can therefore be separated into acidic, basic or neutral fractions. Combining these two fractionation methods gives a total of six possible fractions present in NOM with each fraction having different carbon compounds present; for example sugars in the hydrophilic acid fraction compared to proteins that can mainly be found in the hydrophobic basic fraction. Table 1 shows examples of the chemical compounds that can be observed in each of these fractions of NOM and how easily they can be removed by conventional water treatment. This effectively shows that hydrophobic fractions of NOM are well removed and hydrophilic fractions are poorly removed by water treatment.

Table 1. The categorisation of chemical compounds found in NOM by the presence in each fraction (adapted from Edzwald, 1993) and the ease of removal of these fractions.

	Hydrophobic		**Hydrophilic**	
	Compound	**Ease of Removal**	**Compound**	**Ease of Removal**
Acidic	Humic Acid	+	Hydoxyl acids	-
	Fulvic Acid	+	Sugars	-
	Aromatic Acids	+		
	Phenols	+		
	Tannins	+		
Basic	Proteins	+/-	Amino Acids	-
	Aromatic Amines	+	Purines and Pyrimidines	+/-
Neutral	Hydrocarbons	+	Polysaccharides	-
	High mwt Aldehydes	+	Low mwt alcohols	-
	Ethers	+	Aldehydes	-
			Ketones	-

Key + Easy to remove, - Not easy to remove, +/- removal not documented.

Table 2 shows a summary of the relative proportion of each fraction from a number of different upland source waters in order to show approximately how much each fraction contributes to the overall composition of NOM. For this type of water, the major fraction of NOM is in the hydrophobic fraction. This fraction contains the humic and fulvic substances. These fractions are of significant interest to WTWs as they tend to produce the greatest amount of colour change in raw water, can adversely affect taste and odour and can also contribute to DBP formation. However, this fraction is also easier to treat by conventional methods than more hydrophilic compounds. Just as NOM is a heterogeneous mixture containing numerous fractions so is the term ‘humics’. In fact, humics and fulvics can be best described as an “umbrella term” for numerous chemical substances that affect the colour of the fraction based upon their relative abundance.

Table 2. The suggested composition of NOM based on characterisation by fractionation. Adapted from Zularisam *et al.*, (2007); Goslan *et al*., (2002), Ratnaweera *et al*., (1998); Sharp *et al*., (2006).

NOM Characteristic	**Percentage range (min – max)**
Humic Acid	7 - 37
Fulvic Acid	27 - 68
Hydrophilic Acid	1 - 21
Hydrophilic Non Acid	11 - 36

Humic substances are “macromolecular structures” with a molecular weight (MW) greater than 2000Da (Richardson, 2001). The exact structure of humic substances can change but it is generally agreed that they are large molecules with numerous aromatic rings and carboxyl and hydroxyl functional groups. Figure 2 shows a suggested model for a humic substance according to Stevenson (1982) showing that it is a very large and complex molecule. Fulvic substances are generally smaller molecules with structures similar to that in Figure 3.

It can be seen in both figures 2 and 3 that there are three things to note regarding the chemical structure of both humic and fulvic acids. Firstly there are a number of aromatic rings: more so in humic acid (HA) than fulvic acid (FA). This is an important point to consider as aromatic rings fluoresce at λ=254nm. The second aspect regarding FA and HA structure is the high number of functional groups attached to the main molecule that are, or have the potential to be, polar. The two most noticeable groups are carboxylic acids (COOH) and alcohols (OH). The third aspect to note with regards to the chemical structure of these two compounds is that they both contain a rich abundance of electrons that are prone to attack from electrophiles such as chlorine. The electron rich sites on the molecules are in the aromatic rings and the double bonds, for example C=O.

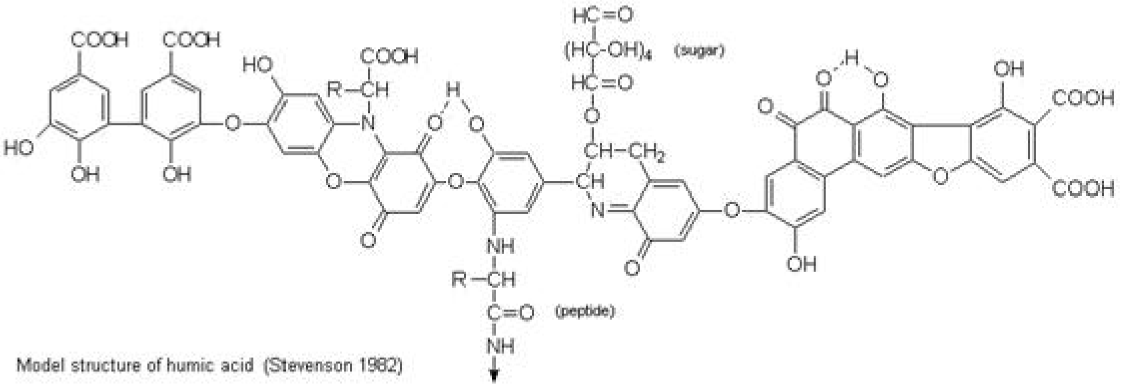


Figure 2. A suggested model of Humic acid, taken from Stevenson (1982).

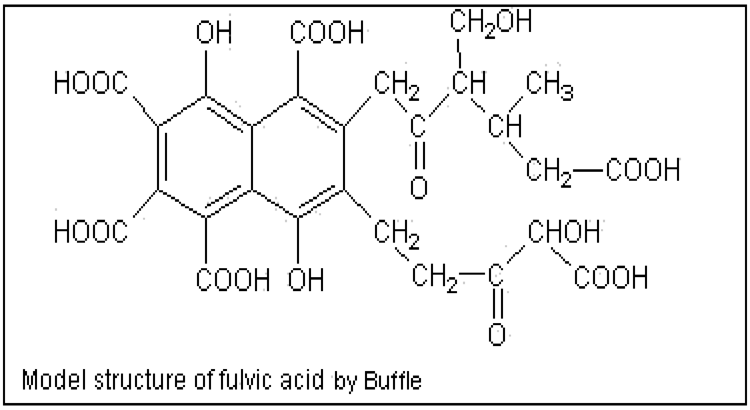


Figure 3. The structure of Fulvic acid, from Buffle (1977).

Although much work has been carried out on the characterisation of NOM (such as spectroscopy (see for example: Bortiatynski *et al*., 1996; Cook *et al*., 2003) chromatography (e.g. Chin and Gschwend, 1991; Namjesnik-Dajanovic and Cabaniss, 2004), or mass spectrometry (Brown and Rice, 2000; Klaus *et al*., 2000)) it is still only possible to generally categorise NOM rather than identify individual molecules that are present. However the characterisation of NOM that has been carried out provides a greater understanding of how it reacts with disinfection compounds. It is generally considered that aromatic rings and double bonds are more reactive to electrophiles than single bonds. It can therefore easily be seen why HA (Figure 2) and FA (Figure 3) are more susceptible to electrophilic attack from oxidising agents, not only from chlorine that is used as a disinfectant, but also bromine that may be naturally present in water **(**Adin *et al*., 1991; Cowman and Singer, 1996; Krasner, 1999; Croué *et al*., 2000). The reaction of residual NOM with oxidising agents, in particular chlorine, leads to the formation of DBPs. In order to produce high quality potable water that does not contain DBPs, WTWs must ensure that as much NOM is removed as possible.

2.2.2. NOM removal

Removal of NOM is very important in water treatment. This is because incomplete NOM removal may cause bacterial growth in the water treatment distribution system because incomplete removal of NOM leads to the presence of an exploitable energy source by the microorganism (Croué *et al*., 1999). Residual NOM can also interfere with downstream treatment, such as fouling of membranes which can drastically reduce their overall effectiveness (Morran *et al*., 1996), as well as provide unpleasant taste and odour issues for the consumer.

However, the biggest problem with incomplete removal of NOM is the formation of DBPs. DBPs form from the reaction of residual NOM with disinfection chemicals. DBPs have been shown to be carcinogenic under in *vivo* conditions (Singer, 1999; Rodriguez *et al*., 2000). The most reactive constituent of NOM that is responsible for DBP formation is the hydrophobic humic and fulvic acid fractions, however DBPs can form from the lower molecular weight hydrophilic fraction (Rook, 1977; Christman *et al*., 1983). The most widely documented and the most frequently regulated DBPs are the trihalomethanes (THM) and haloacetic acids (HAA) (including the trihaloacetic acids (TAA) (Uyak *et al.*, 2007)). Both THMs and HAAs have been shown to be carcinogenic under in *vivo* conditions, (Dalvi *et al*., 2000; Kimbrough and Suffet, 2002) particularly in the liver (Kleiser and Frimmel, 2000).

The hydrophobic fractions of NOM, mainly the humic and fulvic acids can be relatively easily removed by conventional water treatment. However it is worth noting that even the most efficient removal process does not produce 100% removal. The problem compounds with regards to removal by conventional treatment are the hydrophilic fractions that tend to be largely uncharged and smaller in molecular weight. Such compounds may include sugars, amino acids, even peptides and alcohols. While these compounds have a lower DBP formation potential compared with humic and fulvic compounds, they can still be a significant group of DBP pre-cursors.

In order to maximise NOM removal (and hence minimise DBP formation) WTWs use a number of different strategies to treat the water. The strategy used can vary between sites and is largely governed by the raw water quality and the variability of the source water. There are a number of options available to the WTWs in order to remove NOM from raw water, such as coagulation, membrane filtration, adsorption, ion-exchange and oxidation (Table 3). While coagulation is the main method used for bulk NOM removal, NOM can be physically removed using membranes of a low pore size, or utilisation of adsorption or ion-exchange of NOM onto the surface of an adsorbate or ion-exchange material. A less used technology is to use oxidation processes to change the chemistry of NOM into less reactive species, or provide complete mineralisation to carbon dioxide. Alternative options for the removal of NOM often have a number of associated disadvantages (Table 4). Membrane filtration as removal method can be prone to fouling of the membrane by organic compounds and can be expensive to operate. An ion-exchange process, such as the magnetic ion exchange resin (MIEX), still requires coagulation in order to achieve appropriate levels of NOM removal. Dosing an adsorbent often produces large quantities of sludge because it is often used in conjunction with conventional coagulation. Often these alternative processes are used with coagulation in instances where high NOM removal is required to prevent excessive DBP formation.

The conclusion that can be drawn from this analysis is that coagulation still remains the favoured process for removing the largest part of NOM for full-scale treatment systems. Coagulation is the process whereby small particles, colloids and dissolved components are aggregated into larger particles to facilitate their removal (Amirtharajah and O'Melia, 1990). Dennett *et al*. (1995) develops this further by stating that coagulation involves adding a chemical, usually a metal salt such as aluminium or iron, to the water. This chemical then destabilises contaminants in order to aid in the removal of them. Perhaps the best definition of coagulation is suggested by Jiang and Graham (1998) who postulate that coagulation is the process of adding a chemical to the water in order to combine colloids and small particles into larger aggregates. Dissolved organic matter can also be adsorbed and incorporated into the aggregates. The aggregates, or flocs, can then be removed downstream using a combination of flotation or sedimentation and sand filtration.

With respect to coagulation of NOM, the success of the process hinges on factors linked to the properties of NOM such as the charge present on functional groups of the NOM molecules. NOM generally contains a high number of negatively charged carboxylic ($COOH^-$) and hydroxyl (OH^-) functional groups (Owen *et al*., 1993; Stevenson, 1982; Buffle 1977). Due to the electronegativity of these functional groups, NOM exhibits a distinct anionic character making them extremely susceptible to attraction to cationic species such as metal salts (Sharp *et al*., 2005). They are therefore very amenable to removal by coagulation.

The process that occurs during coagulation of NOM is generally considered to be a two stage process of 1) charge neutralisation and 2) adsorption onto hydroxide species (Cheng *et al*., 1995; Dennett *et al*., 1995; Gregor *et al*., 1997; Bell-Ajy *et al*., 2000). In order for successful coagulation to occur, the charge on these species must effectively be neutralised so that flocs can be formed. This occurs from the formation of positively charged aqueous species from the addition of the charged metal salts of the coagulant (Cornwell and Bishop, 1983). The destabilised coagulated colloids then need to interact and collide with one another and, with the aid of intermolecular forces, bond together to form larger aggregates or flocs in a process known as flocculation (Klimpel and Hogg, 1991; Gregor *et al*., 1997). Once flocculation has occurred it is necessary to further treat the water to remove the flocs. There are a number of options available to WTWs in order to remove flocs. One option is to use simple sedimentation, but one of the most commonly used methods for separation of NOM-coagulant flocs is dissolved air flotation (DAF). DAF involves dissolving air into water under pressure and then releasing the saturated water into a flotation tank at atmospheric pressure. The saturated water forms tiny bubbles that attach to the flocs and these bubble-floc aggregates rise to the surface of the flotation tank. The floated flocs form a sludge on top of the clarified water that can be periodically skimmed off.

Table 3. Summary of common treatment methods employed by water treatment works and the efficacy they exhibit for removing NOM, based on DOC values.

Treatment method	**Percentage NOM removed (min – max)**	**References**
Coagulation	10 – 85	Croué *et al*., 1993; Owen *et al*., 1993; Dennett *et al*., 1995; Edzwald, 1993; Crozes *et al*., 1995; Volk *et al*., 2000; Bolto *et al*., 2001; Matilainen *et al*., 2002; Wang *et al*., 2002.
Membrane filtration i.e. MF, UF, NF (with pre-treatment)	80 – 100	Jacangelo *et al*., 1995; Amy and Cho, 1999; Fu *et al*., 1994; Lin *et al*., 1999; Judd and Hillis, 2001; Pikkarainen *et al*., 2004.
Adsorption & ion-exchange	60 - 80	Fu and Symmons, 1990; Owen *et al*., 1993; Newcombe *et al*., 1997; Summers and Roberts, 1998; Bolto *et al*., 2002.
Advanced oxidation processes	25 - 75	Goel *et al*., 1995; Graham, 1999.

Table 4. The advantages and disadvantages of many of the common water treatment processes for removing NOM from raw water.

Treatment method	**Advantages**	**Disadvantages**
Coagulation	• Dose can be changed to respond to changing water quality • An established process	• Increasing cost of coagulant • Poor removal of hydrophillic NOM • Has a narrow "optimum dosing" window
Membrane filtration i.e. microfiltration, ultrafiltration or nanofiltration (with pre-treatment)	• Multiple filters can be used ensuring high level of removal • Robust process	• Filters may become clogged • Usually require a coagulation pre-treatment stage • Problems with pressure and flow • Expensive to operate and install
Adsorption & ion-exchange	• Can be modified prior to dosing • Can be turned on or off easily. • Resin is re-usable. • Can reduce quantity of coagulant and disinfection required. • Very high levels of removal when combined with coagulation. • Lower risk of bromate formation in waters containing Br.	• Difficult to remove from water after dosing. • Increases volume of waste sludge • Needs a long contact time to achieve maximum adsorption. • Requires coagulation as well as adsorbent/ion-exchange material • Initial high cost of installation.
Advanced oxidation processes	• Can remove a number of other impurities in addition to NOM	• May require further treatment • Unproven technology • AOP often require a number of different reagents.

2.3. Adsorbents

NOM removal using coagulation can be improved using a range of additional processes. One of these options is adsorption. The following sections of the review will concentrate on the principles of adsorption, with particular focus on application for NOM removal. During adsorption, the process takes advantage of the chemistry of the component that is to be removed, by adding a solid state material to the solution that will interact with the chemical to be removed. It is worth noting that adsorption can also occur in the gaseous phases, but for the purpose of this review only the adsorption in the aqueous phase shall be discussed.

There are a number of adsorbents that are widely used for commercial adsorption purposes. These include zeolites, silica gels and activated carbons, each of which has associated advantages and disadvantages (Table 5) but the reaction process is essentially the same for each type of adsorbent. The key characteristic of any absorbent is the requirement for a large surface area that allows for the sorption of the adsorbate to the adsorbent. It is possible to categorise adsorbents in a number of different ways but the most useful way is to class them by their material composition. The main types of adsorbent are:

- **Silica gels:** are usually comprised of sodium silicate and are small granular vitreous beads. The highly porous nature of their structure gives them a large surface area. Although it can be used in a number of different capacities the most common use is as a desiccant.

- **Zeolites:** encompass a wide range of substances that are generally described as aluminosilicate minerals. Although a few synthetic zeolites have been made, the majority of them are naturally occurring. Zeolites are often referred to as molecular sieves due to the variable porous structure that they have, which can attract various cations. Zeolites have a number of different uses such as in cat litter which can absorb feline urine and adsorb ammonia. Zeolites can also adsorb detergents and are used in animal feeds where the material is pre-adsorbed with nutrients that are then released during digestion. Clotting agents that adsorb moisture which then triggers platelet action are used in medicine. Finally, in water treatment processes, zeolites are used for purification and softening.
- **Ion exchange resins:** have a highly porous matrix structure that have numerous charged functional groups which allow for oppositely charged ions to attach to the ion exchange resin through electrostatic attraction. During ion-exchange, these ions are exchanged with the target contaminant to enable its removal. The type of ions exchanged depends on the nature of the resin, which falls into four categories based on the functional groups of the polymer, which are strongly acidic, strongly basic, weakly acidic and weakly basic. Ion exchange resins have a number of different uses but most commonly they are used for water purification, water softening, and metal separation.

- **Graphite**: an allotrope of carbon, is often used as an adsorbent in the form of graphite fibre or carbon nanotubes. As with other adsorbents, the large surface area of the adsorbent is the key characteristic that governs its use. Graphite derived adsorbents are commonly used as air filters for example removing CO_2, but can also be used for water purification.
- **Activated carbon (AC)** is derived from different carbon sources such as coconut, bitumen coal or wood. It is carbonaceous material that has been pyrolised at 600-1200°C and then activated using steam or oxygen for physical activation, or acids and salts for chemical activation. There are two distinct types of AC; powdered (PAC) and granular (GAC). These are distinguished by particle size, with PAC being <1mm in diameter and the granular forms being defined by being >1 mm. AC has a number of uses such as gas purification and water purification, treatment of poisonings and overdoses, and clean-up of environmental spillages.

Table 5. The advantages and disadvantages of commonly available adsorbents.

Adsorbent	**Advantages**	**Disadvantages**
Silica Gel	• Very high rate of adsorption	• Limited adsorption, mainly used as desiccant
Zeolites	• Natural and readily available • Cheap	• Removal very dependent on size of the adsorbate
Ion Exchange Resin	• Resin can be easily regenerated	• Expensive • Requires 2 stages sorption/ desorption • Requires extra waste stream
Graphite	• Easy to modify surface activity	• Harder to remove than PAC • Often disposable
Activated Carbon	• Relatively cheap • Surface activity can be easily modified	• Is combustible • Difficult to remove after dosing

2.4. Adsorption

As has been shown, there are many different types of adsorbents with a wide range of physical and chemical properties, but all of them work on the same premise: that is the availability of a high surface area, and that this surface area can be used to adsorb target molecules on to it usually by weak inter-molecular forces such as van der Waals forces or London dispersion forces. Some adsorption can involve direct chemical reaction with functional groups on the adsorbent. In general, adsorption is considered to occur if it is more energetically favourable for the solute to adsorb to the adsorbent than to remain in solution, i.e. the adsorbent has a lower energy state and thus adsorption occurs according to Gibb’s free energy:

Equation 1:

$$G = H - TS$$

Where: G = Gibbs free energy

H = Enthalpy (Joules)

T = Temperature (Kelvin)

S = Entropy (Joules/Kelvin)

Equation 1 shows is the relationship between Gibbs free energy and enthalpy, entropy, and temperature. The equation is useful in establishing an equilibrium point for a closed system. If $G = < 0$ then the reaction will likely occur spontaneously (i.e. without the need for a catalyst or an input of energy). If $G = > 0$ then the reaction is unlikely to occur, as the activation energy would be too high. Of particular interest is in the equation is if $G = 0$ as this suggests the reaction is in equilibrium. There are a number of components in the equation 1 that affect the equilibrium rate of adsorption. Of particular interest is temperature (T), as this needs to be constant when $G = 0$ for the system to be at equilibrium. For many adsorption reactions temperature is an important factor that affects the rate that a reaction reaches the point of equilibrium at which the concentration of adsorbate that is adsorbed is equal to the concentration of contaminant remaining in solution. It is therefore possible, according to equation 1, to shorten the equilibrium time by altering other factors that affect adsorption, for example enthalpy, entropy or free energy available to the system, as altering the temperature, for example would increase the kinetic energy of the molecules.

The amount of free energy that is needed to determine if a reaction, such as adsorption, occurs needs to be applied to all components of the system. A more suitable equation for the enthalpy of the system as a whole is given by Newcombe & Drikas (1997) and Bjelopavlic *et al*. (1998). Both studies show that adsorption can only occur if the free energy (ΔG_{ads}) is less than zero. The equation for calculating this is given as follows:

Equation 2:

$$\Delta G_{ads} = \Delta G_{elec} + \Delta G_{spec}$$

Where: ΔG_{ads} = Free energy of adsorption

ΔG_{elec} = Electrical contribution to adsorption

ΔG_{spec} = Specific interactions that affect adsorption.

There are a number of factors that effect each component of equation 2, and hence the rate at which adsorption reaches equilibrium. ΔG_{elec} is most likely to be affected by hydrophobic interactions and surface-adsorbate interactions (Hough and Rendall, 1983). This attraction may manifest itself when the pH of the solution is altered as the polarity of the surface charge of the carbon may be altered (Newcombe & Drikas., 1997; Bjelopavlic *et al*., 1998). The polarity of the adsorbate may affect adsorption in other ways, such as the repulsion between adsorbate molecules in solution or even interactions between adsorbate molecules on the surface of the adsorbent and molecules still in solution (Muller *et al*., 1985; van de Steeg *et al*., 1992). There may also be repulsion between molecules that have been adsorbed, in other words, “lateral electrostatic” repulsion, (Newcombe and Drikas, 1997). This interaction will impede the adsorption process.

All other interactions are encompassed in $\Delta G_{spec,}$ which is used to quantify factors that are unique to the adsorption system. Although mentioned in more detail later in the review, it is generally considered that four main factors contribute to changes in $\Delta G_{spec.}$

- Adsorbent pore size.
- Hydrophobic reaction between adsorbent surface and adsorbate.
- π-interactions between aromatic compounds and the adsorbent.
- Hydrogen bonding between functional groups and the adsorbent.

The change in each of these factors can affect the extent of adsorption particularly ΔG_{elec}, and the electrical (ionic) components of ΔG_{spec}. The kinetics of adsorption is extremely complex and requires a working knowledge of thermodynamics to appreciate the complexity of reactivity as there are a number of different factors affecting it. Temperature affects the rate of adsorption in a closed system. Given that adsorption can either produce or require energy (an enthalpy change) then this will affect the temperature of the system. The equilibrium constant K will change with temperature according to Van’t Hoffs equation:

<u>*Equation 3:*</u>

$$(\eth \ln K / \eth\ {}^{1}/_{T}) = -\Delta H^{\square}/R$$

Where: K = Equilibrium constant

T = Temperature

$\Delta H^{\square}$ = Enthalpy change

R = Gas constant (8.314472$JK^{-1}mol^{-1}$)

ð = Inexact differential.

Equation 3 shows that both enthalpy and temperature are important factors in determining methods of obtaining maximum adsorption. Temperature has two facets that relate to this equation. Firstly there is the external temperature, i.e. the temperature of the environment and secondly the internal temperature or the temperature of the molecules contained within the system. Enthalpy can be linked to the internal temperature if the adsorption process is exothermic. The temperature of the system as a whole relates to the kinetic energy of the molecules and hence the chance of interaction and therefore intermolecular interactions as discussed in equation 2. There are numerous mathematical models that attempt to describe the mechanism of adsorption. The three most common mathematical models according to Öztürk and Ennil Köse (2008), are pseudo-first order, pseudo-second order, and interparticle diffusion model, which can all be used to work out which is the limiting factor for adsorption.

According to Lagergren (1898), and Ho (2004), the equation for pseudo-first order adsorption can be expressed as:

Equation 4:

$$Dq_t/dt = k_1(C_e - C_t)$$

Where: C_e= Concentration of adsorbate that is adsorbed

C_t = Concentration of adsorbate at equilibrium

t = Equilibrium time (mins)

k_1 = Rate constant of pseudo-first order adsorption

The pseudo-second order, according to Ho (2003; 2006), can be written as follows:

Equation 5:

$$Dq_t/dt = k_2(C_e - C_t)^2$$

Where: C_e= Concentration of adsorbate that is adsorbed

C_t = Concentration of adsorbate at equilibrium

t = Equilibrium time (mins)

k_2 = Rate constant of pseudo-second order adsorption

The adsorption kinetics of the second order adsorption assumes that a monolayer has previously been formed and that the first order adsorption has reached equilibrium point. Mathematical modelling of adsorption is carried out using isotherms that describe the relationship between the concentration of adsorbate that is adsorbed as a function of mass of adsorbent. Although discussed in more detail later the three main adsorption models are the empirical Freundlich isotherm, and two theoretical models of adsorption: the Langmuir and BET isotherms.

In equations 4 and 5 the main factor that effects adsorption is the concentration of the adsorbate, both in solution and that which has been adsorbed. Once these two values are effectively balanced the next determining factor is the interparticle diffusion rate calculated by the interparticle diffusion model (equation 6). Incorporating intraparticle diffusion helps to model the adsorption process more accurately, which is not always easy because it is a multi-step process. In general, it is considered that the solute must pass from the aqueous phase to the solid phase of the pore structures within the adsorbent (Bhattacharyya and Sharma, 2004), providing that it is energetically viable to do so according to Gibb's energy as mentioned earlier. According to Lin and Wu (1996), the interparticle diffusion model can be described using the following equation:

Equation 6:

$$C_t = k_i t^{1/2}$$

Where: C_t = Concentration of adsorbate at equilibrium

t = Equilibrium time (mins)

k_i = intraparticle diffusion rate

The three mathematical models presented can be used to determine the limiting factor in adsorption and are used as a holistic tool to model the adsorption process.

In terms of mechanisms of adsorption it is generally considered that 3 major steps can explain the process (Chingombe *et al*., 2006). Behera *et al*., (2008) describes the three mechanisms of adsorption as:

1. Film diffusion.
2. Particle diffusion.
3. Surface sorption.

In the first mechanism there is a movement of the adsorbate out of solution and onto the peripheral surface of the adsorbent. The second stage involves absorption towards the inner pores of the absorbent, with the final mechanism involving sorption onto the inner surfaces of the adsorbent.

Equations 4, 5 and 6 tell us that the rate of adsorption is initially higher at the start of a reaction compared to that at the end. This is because much of the adsorbate is in solution at the start and not attached to the surface of the adsorbent. As the system approaches equilibrium point then the limiting factor will be the diffusion rate. It is at this point that the system and the remaining molecules in solution need to be altered to achieve a greater level of diffusion and hence more adsorption onto the surface of the adsorbent. The charge of the molecules, or the kinetic energy that the molecules have can be altered by increasing the temperature. The charge of the molecules can be altered by adding salt or changing the pH.

2.4.1. Measuring adsorption

Adsorption or more specifically the rate of adsorption can be measured and expressed using an isotherm. The first isotherm was developed in 1894 by Freundlich and Küster, although Küster is not normally accredited and the isotherm is just referred to as the Freundlich isotherm. The Freundlich isotherm relates the concentration of a solute on the surface of an adsorbent to the concentration of solute remaining in solution. It can be expressed as follows:

Equation 7:

$$q_e = k\,P^{1/n}$$

Where: q_e = mass of adsorbate that is adsorbed per mass of adsorbent

P = Pressure of adsorbate

k and 1/n = Empirical constants.

For liquids the equation can be written:

Equation 8:

$$q_e = k\,C_e^{1/n}$$

Where: q_e = mass of adsorbate that is adsorbed per mass of adsorbent

C_e = equilibrium concentration of adsorbate in solution

The Freundlich isotherm is developed by plotting log C on the X-axis and log $^{x}/_{m}$ on the Y-axis. A straight-line relationship suggests that the data follows the Freundlich model with the Freundlich constant, k, the intercept and the magnitude of adsorption, 1/n, obtained from the slope of the line. The adsorption constant k is an indication of the capacity that the adsorbent has for adsorption. A higher k value indicates that the adsorbent can adsorb a greater amount of adsorbent. The slope of the line 1/n is an indication of the magnitude of adsorption, where a higher value indicates a stronger adsorption force.

There are, however, limitations to the Freundlich isotherm as it makes a number of assumptions about the system. The main limitation of the Freundlich isotherm is that it makes no allowance for an adsorption limit. It does not assume that a monolayer is formed, which in most instances is thought to be what occurs in real systems. The Freundlich model does not deal very well with multi-adsorbate systems. While this may not be a problem for single component adsorption models, systems containing different chemical species such as NOM would be poorly reflected using the Freundlich model. To this end, a modified form of the equation has been developed which has been shown to be very effective for multi-adsorbate systems such as is the case for most sources containing NOM:

Equation 9:

$$q_e = k\,(C_e/m)^{1/n}$$

Where: q_t = The concentration of the adsorbate adsorbed at equilibrium

m = concentration of adsorbent added

The Langmuir isotherm model has also been widely used to model adsorption which when rearranged into the most commonly used form is referred to as the Lineweaver-Bark regression and is expressed as follows:

Equation 10:

$^{1}/_{qe} = {}^{1}/_{qmax} + {}^{1}/_{qmax\ K\ Ce}$

Where: k = Constant

q_e = mass of adsorbate absorbed per mass of adsorbent

q_{max} = Theoretical maximum amount of adsorbate that can be absorbed.

C_e = Equilibrium concentration of adsorbate remaining in solution

The assumptions of the Langmuir equation are:

- The surface containing the adsorbing sites is a perfectly flat plane with no corrugations, i.e. no single site is preferentially absorbed to compared to other adsorption sites.
- The adsorbent adsorbs in an immobile state.
- All adsorbent sites are equivalent.
- Each site can hold at most one molecule of A.

Based on these assumptions there are a number of limitations to the Langmuir model. Firstly the surface of the adsorbent is unlikely to be perfectly symmetrical and without corrugations. It is also assumes that only a monolayer of adsorbate can adsorb onto an adsorbent. In reality, this is not normally the case, where adsorbates can absorb onto already adsorbed molecules.

2.4.2. Adsorption of NOM

An ionic charge or weak intermolecular charge on the adsorbate is generally considered more favorable to adsorption. The chemical properties of an adsorbate can be altered by changing the ionic nature of the solute either by changing the pH or by the addition of salts such as sodium chloride. Carboxylic acid species such as those present in NOM can be made more susceptible to adsorption when the pH is decreased as the bond length between carbon and oxygen is increased, causing a greater degree of electronegativity (Yost *et al*., 1990; Stevenson *et al*., 1994; Hadzija and Spoljar, 1995; Celi *et al*., 1997; Kubicki *et al*., 1997; Dupuy and Dounay, 2001). Electronegativity governs the bonding and the polarity of the molecule(s), and an increase in electronegativity causes the molecule to become more polar and hence more disposed to ionic bonding. As the adsorption of NOM to the surface of PAC uses electrostatic forces such as hydrogen bonds, a more polar compound will adsorb better.

Altering the electronegativity of NOM can be beneficial for both adsorption and coagulation as a treatment option for removal. Dong *et al*., (2005) showed that NOM removal using coagulation and UF increased from 23% to 42% when the pH was dropped from 7.5 to 5.5. The optimum pH for adsorption varies considerably between studies depending on the treatment method and the adsorbent that is dosed. It is worth noting that pH affects not only the chemistry of the NOM but also affects the chemistry of the adsorbent dosed. An example of this is polyacrylonitrile (PAN), which has smaller pore sizes at pH 10 compared with larger pore sizes at pH 4 (Oak *et al*., 1997).

There is no set pH at which maximum NOM adsorption can occur as the chemistry of the feed water can vary drastically and contain many different types of substances (Teixeira and Rosa, 2002). Although it is dependent on the specific matrix, the most suitable pH for the removal of NOM it is generally considered a low pH (Ivancev-Tumbas *et al*., 1999: Specht *et al*., 1999). Tiller and O'Melia, (1993) showed that pH 4 was the optimum, while Edwards *et al*. (1995) found that pH 3 was optimum whilst Fairhurst *et al*. (1995) demonstrated maximum efficacy as low as pH 2. Jucker and Clark (1994) reported that maximum adsorption of humic substances occurred at pH 3.2.

Figure 4 shows the removal of NOM from raw waters with DOC ranging from 8.2 – 12.6 mgl^{-1} using PAC dosed over an eight hour period at 15-25 mgl^{-1} at different pH. A lower pH can be seen to increase NOM removal. This is due to an increase in the rate of deprotonation of the carboxylic acids on the NOM molecules resulting in a greater concentration of charged organics that are easier to remove by coagulation and adsorption than uncharged organics.

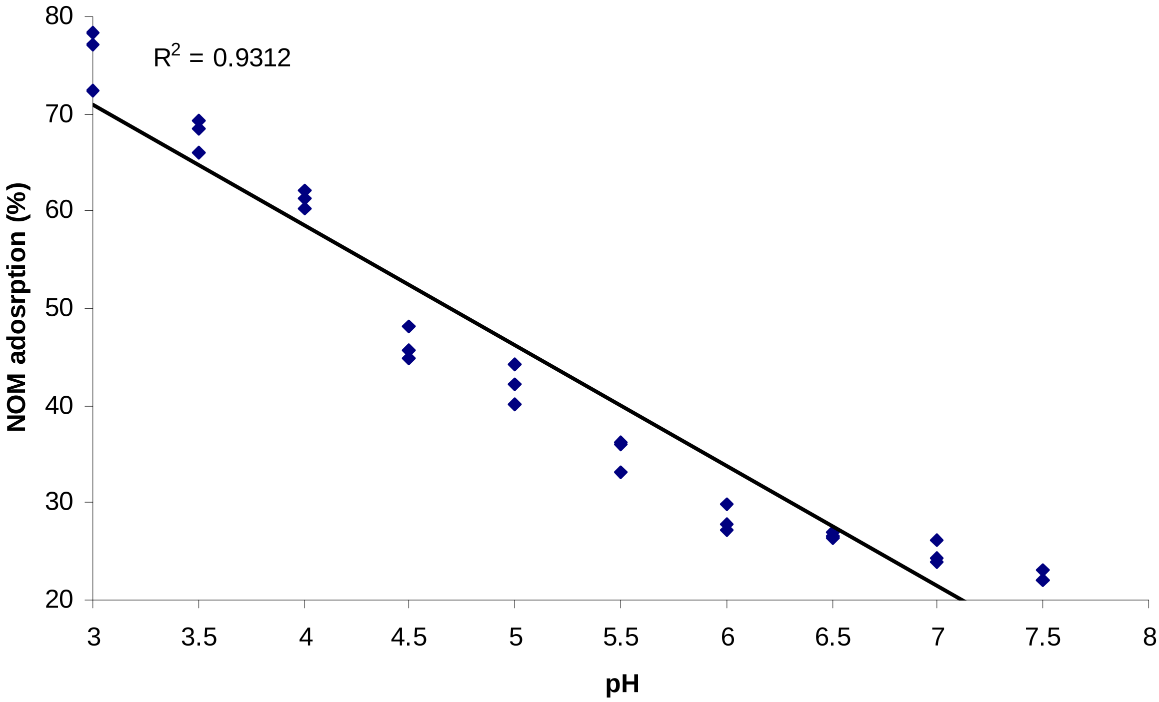


Figure 4. The increase in NOM removal using PAC dosed at a lower pH. (Adapted from Reed and Matsumoto *et al*., 1991; Duan *et al*., 2002; Tomaszewska *et al*., 2003)

It can be seen in figure 4 that as pH decreases the removal of NOM by adsorption becomes more efficient. Statistical analyses in the form of a Spearman rank correlation shows a significant negative correlation between pH and the amount of NOM removed (r_{s26} = -15.37, p= 0.0036).

The main conclusion that can be drawn for NOM removal by adsorption is that a lower pH results in more NOM removal, with a pH of <4 generally suggested for optimum NOM removal.

2.5. Powdered Activated Carbon

PAC is an AC that exists in a powderised form. It is usually derived from charcoal or another carbon source that has been activated using heat and gas or by heat and chemical addition. Heat and steam activation involves 2 stages, firstly the carbon is exposed to temperatures of 600-900°C in an inert atmosphere such as nitrogen or argon, and then it is activated by oxidisation using steam, O_2 or CO_2 at temperatures of 600-1200°C. With chemical activation the carbon is impregnated with acids or salts and then exposed to temperatures of 450-900°C. Chemical activation provides the advantage of being cheaper and quicker than physical activation due to the difference in temperatures (450-900°C as opposed to 600-1200°C). Chemical activation is a quicker process than physical activation and it allows chemical modification of the AC surface to be made .

Adsorption on PAC is dependant on a number of factors such as the pore size, adsorbent density, relative surface area and the type of molecule being absorbed. The activation process can drastically alter the ability of PAC to adsorb material, mainly because it changes the pore size, density or surface area. The source of the carbonaceous material can also affect the end activity of the PAC.

2.5.1. PAC Pore Size

Pore size can affect the overall efficiency of the PAC in removing the adsorbate. However, pore size should not be examined in isolation because the size of the adsorbate will have an effect on the efficacy of removal for any given size of pore. Pore size of PAC is usually split into 4 distinct size classes, each with a definite exclusion size. The International Union of Pure and Applied Chemistry (IUPAC) define the pore sizes as follows (Table 6):

Table 6. The types and sizes of pores with a PAC molecule (taken from Pelekani and Snoeyink, 1998).

Pore type	**Size range**
Macropore	500 Å
Mesopore	20-500 Å
Secondary Micropore	8-20 Å
Primary Micropore	<8 Å

The relative abundance of each type of pore is important. For example if a certain type of PAC has a high abundance of micropores then theoretically it could have a larger surface area (relative to density), however this PAC is more prone to pore blockage because the micropores can more easily become blocked. This makes large parts of the adsorbent unavailable for adsorption. Therefore this makes choosing an adsorbent with the correct pore size important for removal of different sized target adsorbates. A PAC that has a mixture of macropores and micropores can remove a much broader range of compounds than one with more uniform pores.

Indicator substances are used to test the ability of the PAC to adsorb different molecules. These are usually iodine for micropores, methylene blue for mesopores, and molasses for macropores. It is also possible to use tannin to measure the ability of the PAC to adsorb a mixture of different sized molecules. Using these compounds it is possible to provide some standardised information on the ability of a specific proprietary PAC to be able to remove small, medium or large molecular weight (MW) compounds.

It is worth noting that not only is pore size and abundance important, the size of the molecule being adsorbed relative to the pore size is important. As previously mentioned large molecules can block the pores but it has been suggested that there is an optimum ratio between pore size and adsorbate size. Kasakoa *et al*., (1989) suggested that optimum absorption occurred when the (micro) pore diameter was 1.7 times greater than the absorbates second widest diameter. On a similar theme the pore diameter to adsorbate size ratio is linked to adsorption due to the thermodynamic availability of Gibbs free energy. Pelekani and Snoeyink, (1998) suggested that "compounds are preferentially adsorbed into pores that are similar in size to the adsorbate" in order to satisfy this criteria. The explanation that they proposed was due to an increase in the number of contact points, indicating that an increase in these would lead to greater adsorption. Using this theory, it is therefore rational to explain the adsorption of small MW halogenated organics by Ebie *et al*., (1995), in which they found that absorption mostly occurred in pores of width less than 15 Ǻ . PAC is therefore best at removing small MW compounds given that the majority (90%) of the total surface area of PAC is composed of micropores (Walker, 1965; Sontheimer *et al*., 1988) (Figure 5). If a molecule has a particular affinity for a specific pore size then mixtures of compounds results in competition for the favoured pores. Competitive adsorption has been documented on numerous occasions (see for example: Najm *et al*., 1991; Smith and Weber, 1985; Zimmer *et al*., 1989; Newcombe *et al*., 1997).

Newcombe *et al*. (1997) looked at competitive adsorption between NOM and 2-methylisoborneol (MIB). The main findings were that a greater level of competition was observed between the smaller NOM fractions and MIB compared to the larger NOM molecules. This conclusion was also reached by Jain and Snoeyink, (1973) who also studied MIB and NOM competition for PAC pores. Both studies attributed the increase in competition to the fact that compounds with a similar size will actively compete for pores within the PAC. Neither Newcombe *et al*. (1993) or Jain and Snoeyink (1973) looked at the effect that the change in polarity or the aromaticity of the molecule has on competition and Jain and Snoeyink (1973) acknowledged that it is difficult to identify a “dominant competitive mechanism” between molecules due to heterogeneity.

2.5.2. PAC pore quantity

It is generally accepted that the higher the surface area of the PAC the greater the number of pores and in particular the greater the number of micropores. This can have a serious implication on the effectiveness of the PAC if the correct pore distribution has not been selected. Figure 5 shows the (BET) surface area of a number of commercially available activated carbons and shows the distribution of primary and secondary micropores and mesopores.

As previously noted, the pore size to adsorbent size ratio is extremely important for adsorption. If the mesopores become blocked by the absorbent then it is possible that access to the micropores is greatly reduced lowering the overall effectiveness of the PAC. Also, as previously noted, there is an optimum adsorption ratio of 1.7 between pore size and absorbent size, therefore a PAC with a high prevalence of primary micropores will not be suitable for the adsorption of larger molecules such as NOM. In general the volume of micropores is normally higher in a "high activity" PAC (HAPAC) and is more suited to remove the smaller MW uncharged organics that coagulation does not remove. Typically, the Iodine number of a HAPAC is between 900 and 1200 mg/g with standard PAC ranging from 500-1100 mg/g.

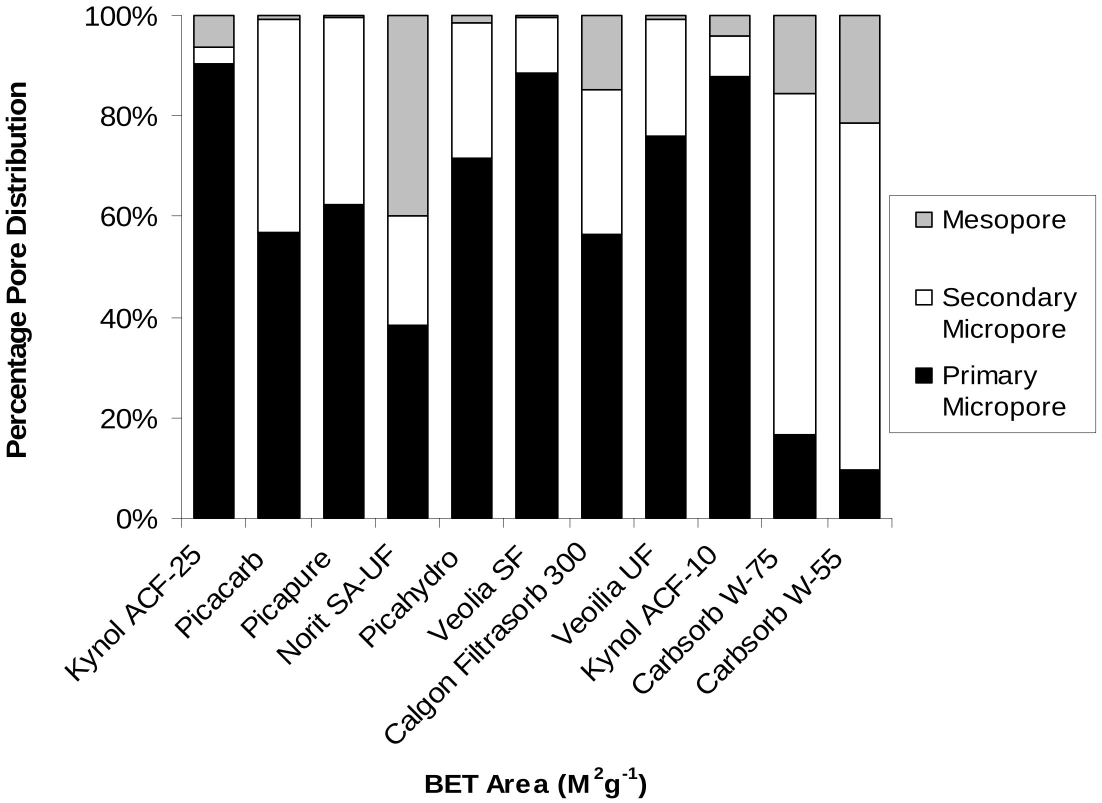


Figure 5. The percentage pore distribution of a number of commercially available carbons in relation to total (BET) surface area (adapted from Pelakani & Snoeyink, 1998; Li *et al*., 2003a; Daifullah *et al*. 2004; Treguer *et al*., 2006).

2.5.3. PAC dosing

PAC dosing is used to remove a number of impurities, including NOM, from water. In order to be cost effective it is necessary to dose only as much PAC as is needed. The dose is usually established by generating adsorption isotherms or carrying out empirical mixing tests. It can be seen from table 7 that the concentration of PAC dosed plays an important part in the amount of NOM removed. PAC is not usually a viable method for treatment of NOM alone due to the long time needed to reach the maximum achievable adsorption due to pore diffusion. Typical adsorption experiments for PAC show that the time to reach equilibrium ranges from 2 hours up to 24 hours (Uyak *et al*., 2007; Humbert *et al*., 2008). This illustrates the point that a PAC only dosing strategy is unsuitable for NOM removal in WTWs.

PAC is therefore often used in conjunction with coagulation for increased removal of NOM. As well as achieving higher levels of NOM removal, dosing with the coagulant enables a removal route for the PAC. This is because one of the primary issues with dosing PAC is the problem of how to remove it after dosing. In the case of dosing with the coagulant the PAC is incorporated into the flocs and is therefore removed in the sludge during the dissolved air flotation stage.

Currently documented literature often scrutinises the efficacy of NOM removal just by dosing PAC alone and various efficiencies have been reported ranging from 4% up to 75% for PAC alone (Uyak *et al*., 2007). If PAC is dosed in conjunction with a coagulant then the removal of NOM can be as high as 90% which is typically 5-10% more than that which can be removed by just coagulation (Chiemchaisri *et al*., 2008). The most efficient removal of NOM currently documented was achieved using 25mgl^{-1} of PAC combined with nanofiltration in which removal efficiencies of 94.7% were observed (Kazner *et al*., 2008).

2.6. Summary

This review has addressed a number of issues regarding NOM removal and PAC adsorption. It is generally considered that coagulation is the most cost effective method to remove NOM from raw water. The most commonly used coagulants are either aluminium or iron (Gregory, 1989). The larger MW NOM that is charged, mainly the humic and fulvic acids, are the easiest to remove leaving smaller uncharged molecules such as sugars and amino acids after coagulation. Humic and fulvic acids are also more prone to oxidation/attack form chlorine or other disinfectants. PAC when dosed with coagulation can augment the coagulation process providing a greater level of NOM removal, hopefully removing the NOM that coagulation does not effectively remove. This review has shown that decreasing the pH can provide a greater level of removal by PAC due to increased polarisation of NOM.

Table 7. A summary of the success at various doses of PAC of removing NOM from raw water.

Percentage removal	**PAC dose**	**Reference**
0-9	Aquasorb 20mgl^{-1}, Norit SA-UF 20mgl^{-1}	Uyak *et al*., 2007.
10-19	Norit 40mgl^{-1}, Aquasorb 40mgl^{-1} Norit 60mgl^{-1}, Aquasorb 60mgl^{-1}.	Ha *et al*., 2004; San Miguel *et al*., 2006; Uyak *et al*., 2007; Chiemchaisri *et al*., 2008; Ho & Newcombe, 2005.
20-29	Norit 80mgl^{-1}, Norit 100mgl^{-1}, Kemisorb 10 mgl^{-1}	Uyak *et al*., 2007; Ho & Newcombe, 2005; San Miguel *et al*., 2006; Humbert *et al*., 2008; Tian *et al*., 2008; Choi *et al*., 2008.
30-39	Kemisorb 40mgl^{-1}, Filtrasorb F400 60mgl^{-1} Aquasorb 100mgl^{-1}.	Humbert *et al*., 2008; Uyak *et al*., 2007; Ho & Newcombe, 2005; San Miguel *et al*., 2006; Chiemchaisri *et al*., 2008.
40-49	Aquasorb 80mgl^{-1} Kemisorb 20mgl^{-1} Kemisorb 40mgl^{-1}	Ha *et al*., 2004; Uyak *et al*., 2007; Tian *et al*., 2008; Ho & Newcombe, 2005.
50-59	Kemisorb 60mgl^{-1} Norit SA-UF 100mgl^{-1} Aquasorb 100mgl^{-1}	Cathifaud *et al*., 1997; Ho & Newcombe, 2005; Chiemchaisri *et al*., 2008; Ates *et al*., 2007; Uyak *et al*., 2007; San Miguel *et al*., 2006; Humbert *et al*., 2008
60-69	Kemisorb 80mgl^{-1}, Filtrasorb F400 80mgl^{-1}	Uyak *et al*., 2007; Ho & Newcombe, 2005.
70-79	Kemisorb 100mgl^{-1} Filtrasorb F400 100mgl^{-1}	Chiemchaisri *et al*., 2008; Uyak *et al*., 2007; Choi *et al*., 2008; Cathifaud *et al*., 1997.

3. Methods

3.1. Analytical techniques.

The following analytical techniques will be used to analyse both treated water and the untreated controls:

- Total organic carbon (TOC) analysis.
- UV_{254} absorption.
- Trihalomethane (THM) analysis using gas chromatography. electron capture device (GC-ECD).
- High Performance Size Exclusion Chromatography (HPSEC).

3.1.1. TOC analysis

TOC analysis was carried out on raw and treated samples using a Shimadzu TOC 5000A TOC analyser with TOC control v 1.02.01 analysis software.

Standards of total carbon (TC) and inorganic carbon (IC) were made up to 20ppm from an initial stock solution of 1000ppm. The stock solution for TC was made by dissolving 2.125g potassium hydrogen phthalate in 1L RO water. The stock solution for IC was made by dissolving 1.750g sodium hydrogen carbonate in 500 mL deionised water and adding it to 2.205g sodium carbonate in 500mL deionised water.

The TOC was cleaned using two rinse samples to clean the machine and piping. The accuracy of the TOC machines calibration was tested using a

TC and IC standard of 20ppm and an ultra-pure water blank sample, The acceptance level for calibration was accepted as ± 2.5ppm. If values beyond this range were observed then the machine was recalibrated. These three controls were used at the start of the calibration sequence, and after running samples, to determine if the calibration drifted over the sampling period. Quality control was also implemented by randomly selecting 3 unknown samples and diluting them by 50%. If the TOC machine was measuring carbon levels accurately then these samples should be half of the original sample.

An example of this can be seen in table 8, which shows the actual values and diluted values of 3 random samples.

Table 8. The quality control measures taken by showing the TOC concentration (ppm) of three random unknown samples at original and 50% concentration.

Sample ID.	Original concentration	50% concentration.
Norit Raw pH 3, 15mg	10.86	5.19
Norit Raw pH 5.5, 4mg	14.22	7.22
Pulsorb 207 CP-90 DAF, 2mg.	1.506	0.801

The TOC analyser took up to five replicates per sample and reported an average on the three closest matched values out of five, given that the coefficient of variance was not greater than 2%,

3.1.2. UV$_{254}$ analysis

Each sample was analysed for absorbance at λ=254 in a Jenway 6506 UV/Vis spectrophotometer. A quartz cuvette measuring 4cm x 1cm was used for analysis. The cuvette was first rinsed with distilled water and then rinsed with a small volume of sample, which was then discarded. The cuvette was then filled with the sample and analysed for absorbance at 254nm. The absorbance was measured per 4cm and was then multiplied by 25 to give the final absorbance per m, giving units of m^{-1}. Each sample was analysed in triplicate and the mean of all three results was used.

3.1.3 THM analysis of treated water

50ml of sample was allowed to equilibrate to room temperature. A 10mL aliquot was removed to check that the pH was within the range 4.5-5.5. This was to ensure that a true representation of THM levels was obtained, as THMs are stable in water at sampling/storage conditions of pH 4.5 and 4°C, but will degrade in water at increased pH and temperature, ((LeBel et al., 2002; Koudjonou and LeBel, 2003). If the pH was not within range, a new sample was collected, or the pH was adjusted. The universal containers with contents were weighed to the nearest 0.1 g and the weights recorded for subsequent volume determination.

Three mL of MTBE (Fisher Scientific, UK) with internal standard was added to the sample using a dispenser (internal standard was bromoflurobenzene at 1µg/mL). Approximately 10±0.5 g sodium chloride (Fisher Scientific, UK) was added into vial, the cap replaced and was shaken for approximately 4 minutes, and all layers were allowed to separate for 2 minutes.

Approximately 1 ± 0.1 mL of MTBE top layer was transferred to a GC vial and analysed for THM formation. Four THMs were measured: trichloromethane, dichlorobromomethane, dibromochloromethane, tribromomethane using a GC-ECD (Agilent 6890 GC-ECD). A capillary column (Rtx-1MS – 15m × 0.25mm id × 0.25µm) was used with helium carrier gas at a constant linear velocity of 25cm/second. The split ratio was set at 10:1. A volume of 1 µl was injected. The initial oven temperature was 35°C held for 0 minutes followed by a 2°C per minute temperature ramp to 50°C and held for 10 minutes. The temperature was increased to 225°C at a rate of 10°C/minute and held for 15 minutes followed by an increase to 260°C at a rate of 10°C/minute and held for 30 minutes. The temperature of the injector was set at 200°C and the detector at 290°C. The rate of data collection was 20Hz.

3.1.4. HPSEC analysis

Samples were analysed using a high performance liquid chromatogram (HPLC) (Shimadzu VP Series, Shimadzu, Milton Keynes, UK) with UV detection set to 254nm. The mobile phase was 0.01M sodium acetate that had been ultra-sonicated at room temperature at 25mhz for 15 minutes. The flow rate of the mobile phase was set at 1mL min^{-1}. The column used was a BIOSEP-SEC-S3000 7.8 mm (ID) × 30cm and the guard column was a ‘Security Guard’ fitted with a GFC-3000 disc 4.0mm (ID) × 3.0mm (Phenomenex UK, Cheshire, UK). For each sample a chromatogram of UV_{254} absorbance (milli-absorbance units) against time (minutes) was produced.

3.2. Water collection and location of on-site trials

Two different types of water were used in this analysis, which were raw water (RW) that had not been treated, and water from post dissolved air flotation (DAF) that had been treated with ferric sulphate coagulant. 150L of RW and 150L of DAF water was collected from Ewden water treatment works (WTW), Sheffield, (53°27' N, 1°33'W) February 7th 2008. 350L of RW was collected from Ewden on 14th April 2008.

All water collected for analysis was measured for pH using a Jenway 3150 pH meter, TOC and UV_{254} absorbance (section 3.1). Ewden WTW was the location used for on-site trials, which took place between the 28th July 2008 and the 5th September 2008. The experimental protocol implemented for the on-site trials is described in detail in section 3.6.

3.3. Adsorption of natural organic matter onto powdered activated carbon

3.3.1 Adsorbents

Three different PAC were tested in these trials. The first PAC was Chemviron Pulsorb C which is the PAC that is currently being used on site at Ewden WTWs. Two other PAC were also used: Norit SA Super, and Pulsorb 207 CP-90. The high activity carbons (Norit SA Super and Pulsorb 207 CP-90), have a higher surface area and are therefore capable of a greater level of adsorption. This can also be seen by the iodine number, methylene blue, and phenol adsorption. Which are all greater in the high activity carbons (Norit SA

Super, & Pulsorb 207 CP-90) compared to the standard activity carbon (Pulsorb C), (Table 9).

Table 9. The physical properties of the three activated carbons tested.

	Norit SA Super	**Pulsorb 207 CP-90**	**Pulsorb C**
Surface area (m^2/g)	1150	1050	950
Density (kg/m^3)	250	200	210
Iodine Number (g/kg)	1050	1000-1100	900-1000
Methylene Blue Adsorption (g/kg)	2.2	2.5-2.8	2.0-2.2
Phenol number (g/Kg)	0.5	0.4	0.3
Micropore volume (cc/g)	n/a	0.31	0.48
Mesopore volume (cc/g)	n/a	0.11	0.20
Macropore volume (cc/g)	n/a	0.11	0.25
Ash content (%)	10	<4	<14
Moisture (%)	3	10	5

3.3.2. Measurement of particle size of PAC

The particle sizes of the PAC were measured using a laser diffraction particle size instrument (Malvern Mastersizer, Malvern, UK). This was achieved by dispersing 10mg of PAC in 500mL of deionised water, which was then pumped through the optical unit of the Mastersizer. Each PAC particle size measurement was repeated in triplicate.

3.3.3. Determination of Equilibrium point for NOM adsorption onto PAC

All water samples were stored at 4±1°C until needed for experimentation. 9L of RW and 9L of DAF water were removed from storage and left for 18 hours overnight at room temperature to acclimatise. The RW and DAF water were divided into separate 1L aliquots. Three of the RW aliquots and

3 of the DAF aliquots were adjusted to pH 7. Three aliquots of both RW and DAF were adjusted to pH 1 and the final 3 aliquots of each adjusted to pH 14. One aliquot from each of the pH adjustments was dosed with 40mgl^{-1} of each different PAC. All of the samples, once treated, were stirred continuously for 24 hours using a Phipps and Bird jar tester. 50ml aliquots of each sample were removed at 60, 120, 240, 360 480, and 1440 minutes. Each of the aliquots was filtered using a KNF Neuberger VP series pump and a sidearm flask with Munktell BMC Ø70mm glass microfiber disc with pore size of 1.2µm. The elute was analysed for absorbance at λ=254 and TOC (section 3.1). The equilibrium point (E_p) was determined by the lowest reading achieved during the experiment, i.e. the point at which no more NOM would be adsorbed onto the PAC.

3.3.4. Assessment of the performance of the PAC

Once the equilibrium time had been established for the PAC, the adsorption performance of each of the PAC were analysed at a range of doses from 0-80mgL^{-1} and at six different pHs ranging form 3–5.5 using the equilibrium time established in section 3.3.3. 250mL of raw water collected on the 07/02/08 was added to a conical flask. Each dose and pH condition was carried out in triplicate. There were 10 PAC doses per pH condition which were 0, 2, 4, 6, 8, 10, 15, 20, 40 and 80mgl^{-1}. The 6 pH variables used were pH 3, 3.5, 4, 4.5, 5, and 5.5. The whole procedure was then repeated for DAF water.

After the pH had been adjusted and the PAC added, the conical flasks were placed on two-Ikamag RO 15 place magnetic stirrers (Fisher Scientific, UK). The conical flasks each had a 45x8mm PTFE magnetic stirrer bar (Patterson Scientific, UK) added to them and were sealed with Parafilm (Pechiney plastic packaging, Chicago, USA) and stirred for 6 hours to reach equilibrium as determined in section 3.3 The treated water was then filtered as detailed in section 3.3 and analysed for UV_{254} and TOC content as described in section 3.1.

Isotherms were created using Microsoft Excel 2003 (v 11.8169.8172) to compile data and represent it graphically, The natural log (l_n) of all data was used and was expressed graphically using log-log axes (x and y). Three different isotherms where used in order to determine which one gave the best data fit, which was determined using a straight line of best fit transecting the most data points. The three isotherms used were Freundlich, modified Freundlich and Langmuir. Figures 6 a-c show the three isotherms for one experimental treatment set (Norit in raw water), where it can be seen only the modified Freundlich isotherm produces a straight line.

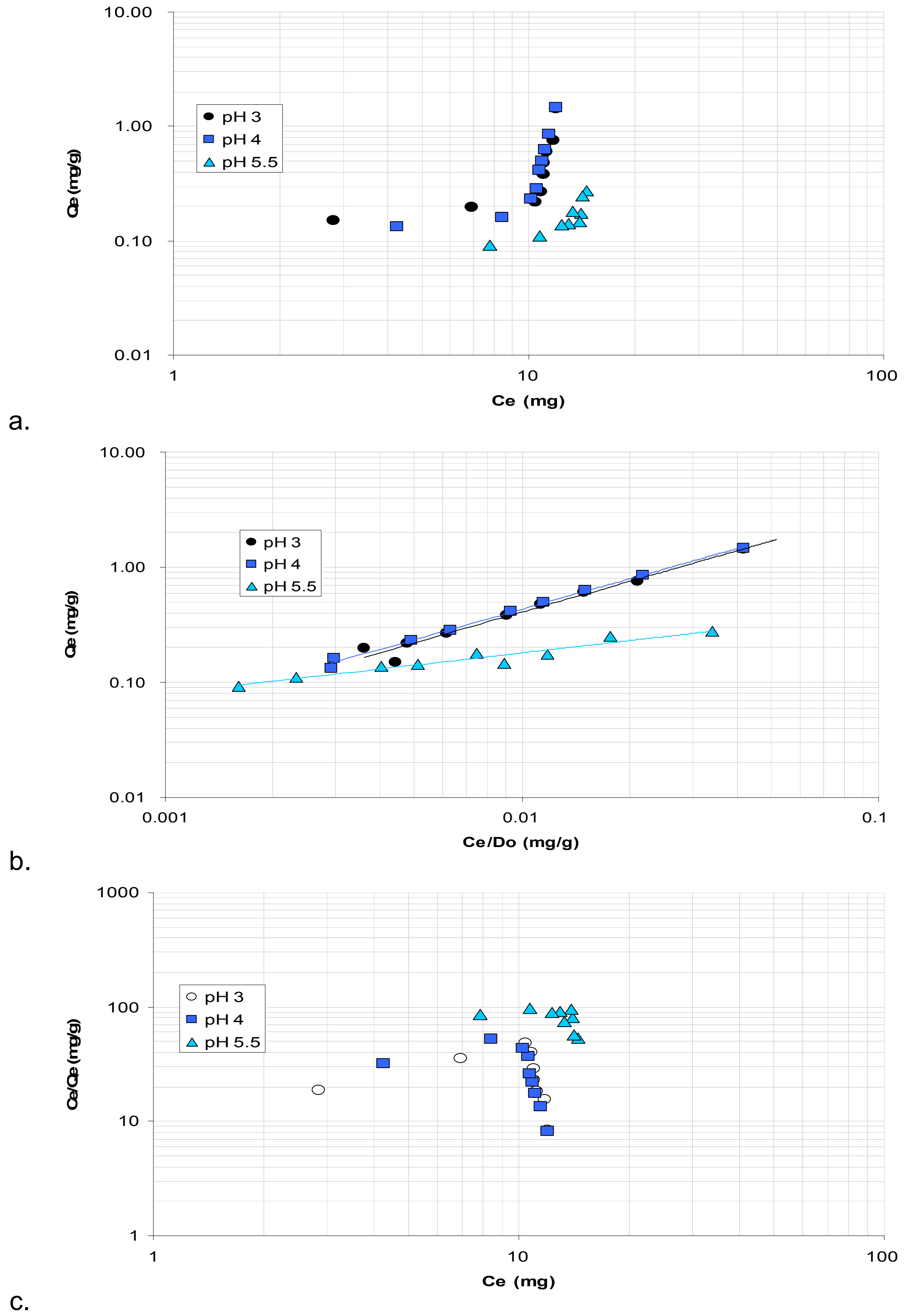


Figure 6. Comparison of isotherms for Norit SA Super in raw water. The three isotherms are Freundlich (a), modified Freundlich (b) and Langmuir (c).

3.3.5. Determination of coagulation and PAC Interaction for the removal of NOM

After the adsorption assessment of the PAC had been carried out, experiments were performed to understand the interaction of PAC with coagulant at bench scale. 109L of raw water collected on 14/04/08 was analysed 3L at a time and divided into three 1L aliquots for triplicate analysis. Each L of raw water was adjusted to pH 4 and had 20mg of carbon and 11.5 mg/L of ferric sulphate (Fe) coagulant added at different intervals during the rapid mix stage of a jar test.

The jar test was carried out using a Phipps and Bird jar tester (Camlab, UK), and six 1L beakers each filled with 1L of raw water. The four memory slots of the jar tester were programmed with different times and speeds and were run sequentially. The first memory slot had a slow mixing at 30 rpm for 90 seconds. The second slot was a rapid mix stage at 200rpm for 90 seconds. It was during this stage that all the treatments were added as can be seen in table 10. The third memory slot was a slow mix at 30 rpm for 15 minutes to allow flocculation. The fourth memory slot had no stirring (0 rpm) for 15 minutes to allow the flocs to settle.

Thirteen dosing condition experiments were carried out during the rapid mix stage of the jar test to look at dosing sequence and contact time for PAC and coagulant. The rapid mix stage was always 90 seconds and the pH was adjusted at the start. The rapid mix stage, although continuous was hypothetically divided into three separate sections as dictated by the dosing times. The dosing times were 0 seconds, 30 seconds and 60 seconds. These dosing times dictated the contact time for the experiment which was 90 seconds 60 seconds and 30 seconds respectively. Experiments 1-3 show a decrease in contact time for coagulant and that the coagulant was dosed after the PAC. Experiments 4 and 5 show decreasing contact times for PAC and that the PAC was dosed after the coagulant. Experiments 6-9 show decreased contact times for both PAC and Fe, experiments 10 and 11 show a split dose for PAC. Experiments 12 and 13 are the controls of PAC and Fe respectively. Six 1L beakers were used and the experiments were conducted in pairs with beakers 1, 2, and 3 followed the odd numbered dosing experiments (Table 10) and beakers 4, 5, and 6 following the even numbered dosing experiments (Table 10).

Table 10. An overview of the experimental protocol followed to examine the optimum dosing sequence to achieve maximum NOM removal.

Experiment Number	Rapid mix time (seconds)								
	0 – 30			30 60			60 - 90		
1	pH	PAC	Fe						
2	pH	PAC		Fe					
3	pH	PAC					Fe		
4	pH	Fe		PAC					
5	pH	Fe					PAC		
6	pH			Fe	PAC				
7	pH						Fe	PAC	
8	pH			Fe			PAC		
9	pH			PAC			Fe		
10	pH			1/2 PAC	Fe		1/2 PAC		
11	pH			1/2 PAC			1/2 PAC	Fe	
12	PAC								
13	Fe								

Once the jar test had finished the unfiltered sample was analysed for turbidity by placing a syringe 3cm below the top of the water level in the jar and removing a $50cm^3$ aliquot. The aliquot was placed in a Hach 2100N Turbidimeter (Camlab, UK) and analysed for 15 seconds to stabilise. After 15 seconds, one measurement was read every second for 5 seconds and the average of all five measurements was used.

The remainder of the water used in the jar test was filtered and were analysed for TOC, UV_{254}, HP-SEC, and THM formation (section 3.1).

3.3.6. Floc analysis

To establish how well the PAC was incorporated into the floc during coagulation depending on the dosing sequence of the PAC, image analysis was carried out. Approximately 1.5ml of sample was removed from experiments 1, 3, and 5 (section 3.4) immediately after the flocs had settled and just before a sample was removed for turbidity analysis. The sample was added to a concave glass slide and analysed using a Qimaging Fast 1394 Qicam microscope and digital camera equipped with Image-Pro Plus v6.3 software (Media Cybernetics, UK). Approximately 50 flocs were analysed at a dose of $11.5mgl^{-1}$ of Fe, 20mg PAC and pH 4. The area and number of PAC particles per floc was counted by setting the light intensity threshold to 75. This was established to be the point at which PAC particles could be distinguished from the background floc, allowing the image analysis software to count the total number of PAC particles in the floc. The floc projected area was also measured using the image analysis software. The number of particles counted was divided by the area of the flocs to give the ratio between area and PAC content per floc.

3.3.7. Fractionation

XAD fractionation of raw and treated water was carried out using XAD4 and XAD8 adsorption columns (Kinesis, UK). The XAD-4 column retains hydrophilic acid compounds and the XAD-8 column retains hydrophobic acid compounds (Malcolm and McCarthy 1992). XAD-8 has since been discontinued although Goslan *et al*., (2002) report XAD-7HP to be a suitable substitute. Both columns were filled with resin (approximately 60 mL). The columns were rinsed through using 0.5% HCl for approximately 20 minutes. The fractionation process was exactly the same as Goslan *et al*., (2002) who used a modification of the original method by Malcolm and McCarthy (1992). Figure 7 shows a schematic overview of the fractionation process.

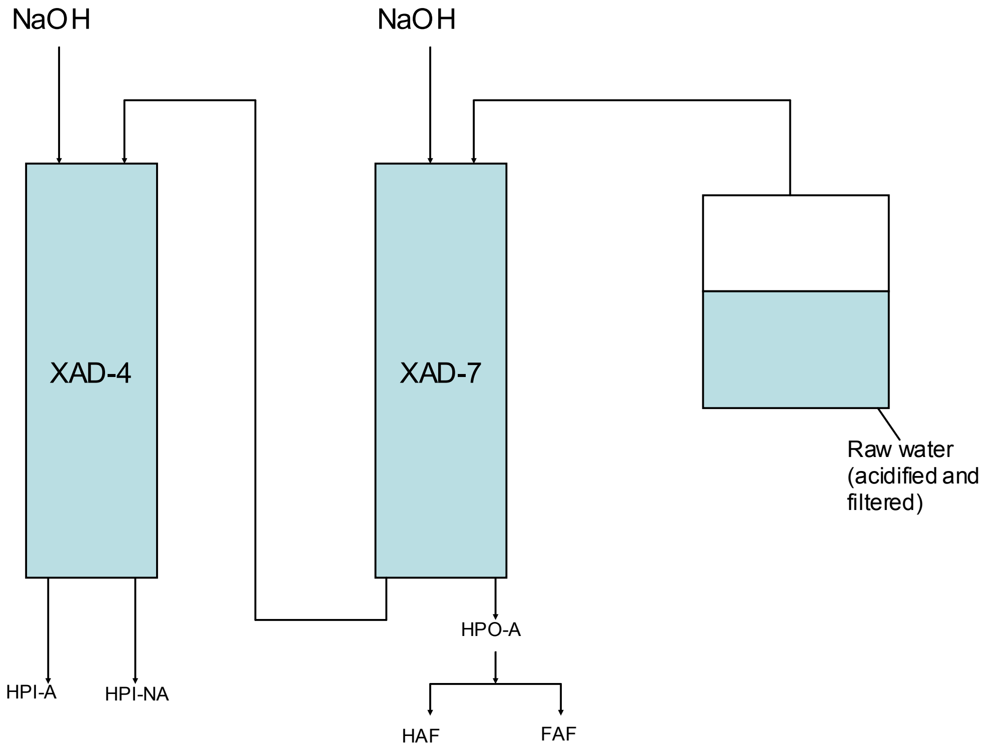


Figure 7. An overview of the fractionation procedure as used by Goslan *et al.*, (2002).

Two peristaltic pumps were used and set at a velocity of 5 and 6 rpm. The sample was adjusted to pH 2 using concentrated HCL and then passed through both columns, then 120 ml of 0.1m NaOH was passed through the first column (XAD-7HP) to give the hydrophobic acid fraction (HPO-A). The XAD 4 column was also back eluted with NaOH to give the hydrophilic acid fraction (HPI-A). The pH of the HPO-A fraction was adjusted to 1 (+/- 0.2) by adding concentrated HCl and left to settle for 24 hours and centrifuged. The supernatant (which contains fulvic acid) was decanted (FAF). The residue (HAF: humic acid fraction) was dissolved in the minimum required volume of NaOH (0.1M, around 50 ml). The HPI-A elute was re-passed through a smaller set of columns and desorbed with 0.1m NaOH in order to obtain the hydrophilic non-acid fraction (HPI-NA).

3.4. Full-scale PAC trials.

3.4.1 Ewden WTWs

On-site trials were conducted at Ewden WTW's as detailed in section 3.1. Figure 8 shows a diagrammatical overview of the treatment process which illustrates both the sampling process as well as the PAC dosing strategies that were implemented on site. The treatment plant at Ewden consisted of three identical mixing tanks before the flocculation tank, as can be seen in figure 8. Yorkshire water had a rapid mixer in tank 1 and tank 3. The normal dosing strategy employed by Yorkshire water is to adjust the pH of the raw water in the first tank and to add the coagulant in the third tank. When water quality deteriorates (UV_{254} ~$100m^{-1}$) the treatment process is augmented using PAC which is also dosed into the third tank. Although Yorkshire Water would not permit any change to the way the coagulant was dosed there was an opportunity to change the dosing of the PAC. By adding PAC into either tank 1 or tank 2 it would be possible to increase the contact time that the PAC has with the NOM in the raw water.

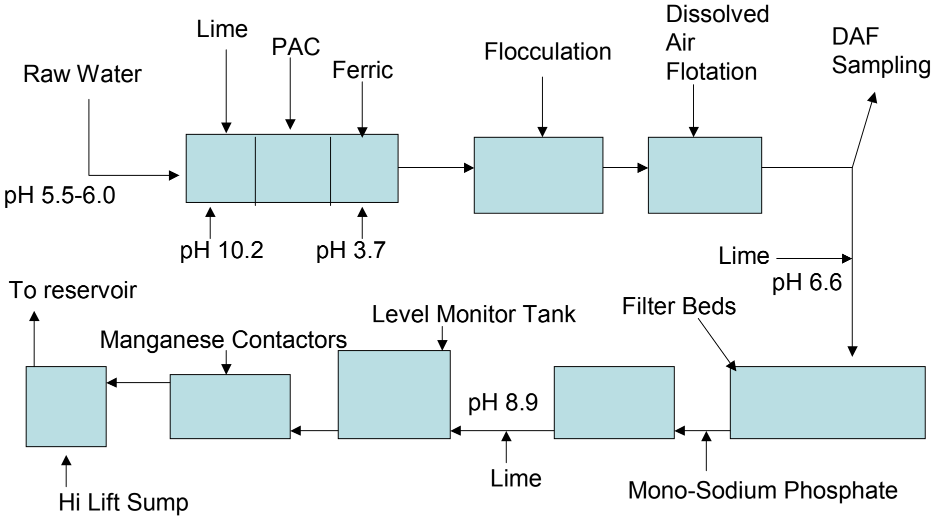


Figure 8. An overview of the dosing procedure used at Ewden water treatment works.

There were a total of three PAC dosing strategies that were tested on site and a series of baseline readings. Sampling was conducted every hour for 8 hours a day over a 4 day period giving 32 samples for each dosing strategy that was implemented. The first two weeks of sampling consisted of establishing a baseline reading for the level of NOM removal for just coagulation. After the baseline readings were established the PAC dosing was started. The first dosing strategy was dosing into the third tank at the same point that the coagulant was dosed. The second dosing strategy looked at the effect of dosing into the middle tank and the final week looked at dosing into the first mixing tank at the same point that the pH is adjusted.

Samples of both RW and DAF water were collected and analysed for UV_{254} and TOC as described in sections 3.3.1. In line instrumentation was also used to measure the RW pH, turbidity and UV absorbance. In line instrumentation also showed the UV, pH and turbidity of water leaving the DAF as well as the turbidity and pH of water post-filtration.

3.4.2. Pilot Hall trials

In order to test some alternative PAC dosing strategies, continuous scale testing of PAC dosing and coagulation were tested at the Pilot Hall at Cranfield University (Figure 9).

Figure 9. The Pilot-scale WTWs at Cranfield University.

The pilot rig was used for comparing the effectiveness of the Norit SA Super high activity PAC against the standard Pulsorb C. The pilot studies were also used to test dosing PAC before filtration.

The pilot plant consisted of three separate mixing tanks in a similar manner to those observed at Ewden (figures 8, 9). There was a large reservoir of water below the rig, as well as a pressurised container and pump for dissolved air flotation. The water was pumped from the reservoir up to the mixing tanks and then into the DAF tank. The flow rate of the water was set at 200L an hour, and coagulation was achieved by adjusting the pH to 4.0±0.2 using 0.1M NaOH. The NaOH coagulant and PAC were all added into the first mixing tank with the exception of the final run.

Figure 10 shows a schematic of the DAF rig at the Pilot Hall, and it can be seen that the rig has three separate tanks. All three tanks had mixers but only the first tank was used as a rapid mixing stage. The mixers on the second and third tanks were set to a low rpm and used as flocculators similar to the dosing strategy of Ewden WTW. A total of six runs were carried out at the Pilot Hall each lasting for 5 hours, with pH measurements being taken every 15 minutes. The first run was dosing coagulant at 12mgL^{-1} as Fe, the second was dosing coagulant at 12mgL^{-1} as Fe and Chemviron Pulsorb C at 20mgL^{-1}, the third run was coagulant at 12mgL^{-1} as Fe and Norit SA Super at 20mgL^{-1}. The fourth run dosed just coagulant at 12mgl^{-1} as Fe for two hours and then coagulant and Chemviron Pulsorb C at 20mgL^{-1} for 3 hours. The fifth run dosed just coagulant at 12mgl^{-1} as Fe for two hours and then coagulant and Norit SA Super at 20mgL^{-1} for 3 hours. The final run dosed coagulant at 12mgL^{-1} as Fe into the first tank and Norit SA Super at 20mgL^{-1} as Fe into the last tank.

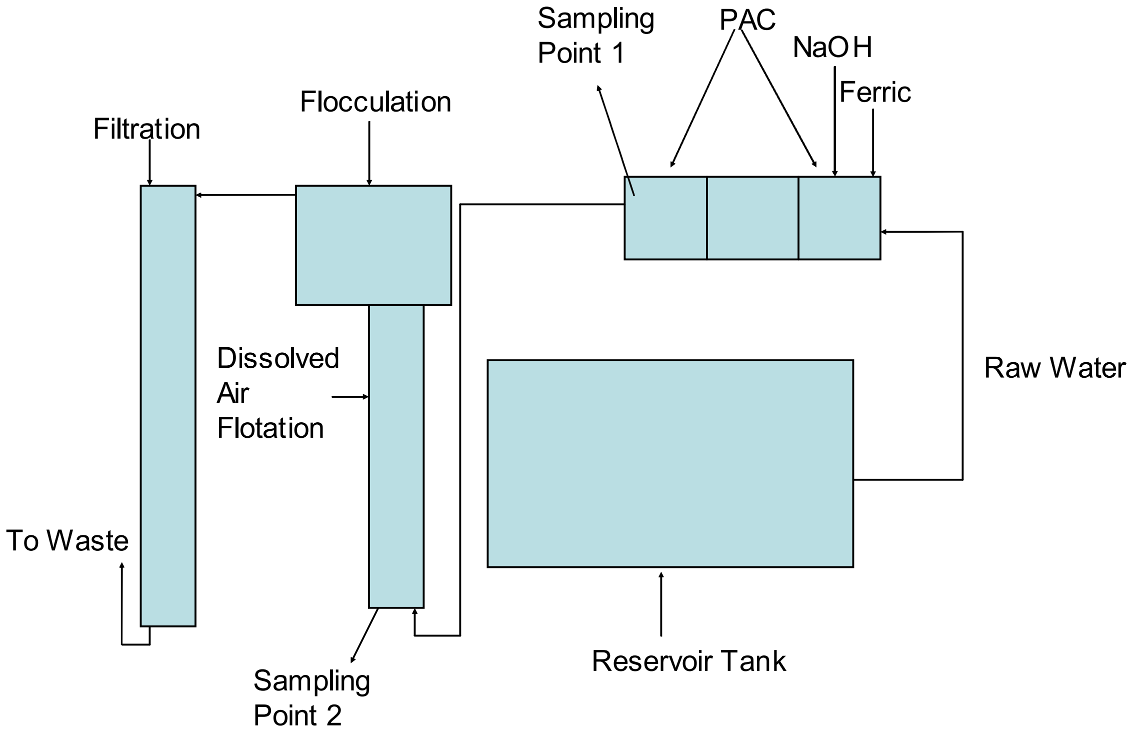


Figure 10. An overview of the dosing procedure used at the Pilot Hall in Cranfield University.

The water was sampled at the points indicated at the same time pH measurements were taken. The water was analysed for TOC, and UV_{254} as described in section 3.1. A second sample was taken from sampling point 1 and was allowed to settle. Once the sample had settled the unfiltered sample was analysed for turbidity by placing a syringe 3cm below the top of the water level and removing a $50cm^3$ aliquot. The aliquot was placed in a Hach 2100N Turbidimeter, (Camlab, UK) and analysed for 15 seconds to stabilise. After 15 seconds, one measurement was read every second for 5 seconds and the average of all five measurements was used.

3.5. Data handling and analysis

All data was analysed with Minitab v 15.1.1.0 statistical analysis software. Data was imported from Microsoft Excel 2003 (v 11.8169.8172), which was used for graphical representation of data. Microsoft Excel was also used for the compiling and organisation of the raw data.

All data imported into Minitab was analysed for normal distribution using an Anderson-Darling normality test. The level of significance for acceptance for normality and all other statistical analyses was $p = <0.05$.

Descriptive statistical analyses were performed that gave the mean ± standard deviation (SD) for normally distributed data, or median ± stand error of the mean (SE) for non-normally distributed data.

Significant differences between two data sets, was tested for using Two-Sample T-Tests for parametric analyses or Mann-Whitney for non-parametric analysis. For analysis of significant differences between three or more data sets a one-way analysis of variance (ANOVA) was used for parametric analysis or a Kruskal-Wallace test for non-parametric data.

Correlations were tested for using a Pearson correlation for normally distributed data and a Spearman-rank correlation for non-normal data. Advanced regression analyses were performed by using a general linear model regression analysis with post hoc testing in the form of a Tukey analysis.

4. Results

4.1. Water characteristics

The characteristics of both untreated raw water and water that had been coagulated was analysed in order to determine a baseline reading with which to compare NOM removal for all further experimentation. The untreated raw water was collected before the hydrogenerator and the coagulated water from after the DAF at Ewden WTW.

The untreated water had a high TOC, UV_{254}, and turbidity, which were 15.3 mgl^{-1}, 60.1 m^{-1} and 3.6 NTU respectively (Table 11). Treatment with coagulation resulted in 88% of the TOC being removed and the UV_{254} absorbance being lower by 90%. This was because the TOC in this water contains a large portion of humic and fulvic acids that fluoresce at $\lambda = 254$nm, and these molecules were subsequently well removed during coagulation. The change in pH from 6.0 to 4.0 was a reflection of the optimum conditions that are required for NOM removal during coagulation of the water.

Table 11. The physical characteristics of untreated and coagulated water obtained from Ewden WTW on February 7th and April 14th 2008.

	Untreated water	**Coagulated water**
TOC	15.3 ± 0.5 mgl^{-1}	1.8 ± 0.3 mgl^{-1}
pH	5.5-6.0	3.9-4.0
UV_{254}	60.1 ± 0.5 m^{-1}	4.9 ± 0.3 m^{-1}
Turbidity	3.5-3.7 NTU	2.5-2.6 NTU

4.2 Powdered activated carbon characterisation

The mean particle size distribution of all three PAC were analysed using a laser diffraction instrument. The results in Figure 11 show that Norit SA Super had the smallest average particle size of 10.9 μm and narrowest particle size distribution (PSD). Pulsorb 207 CP-90 had the next smallest particle size of 27.2 μm but the PSD was wider than that of Norit. Pulsorb C had the largest particles of all of the PAC (37.6 μm) and also had the widest PSD showing that this PAC was much more coarsely graded than the other types.

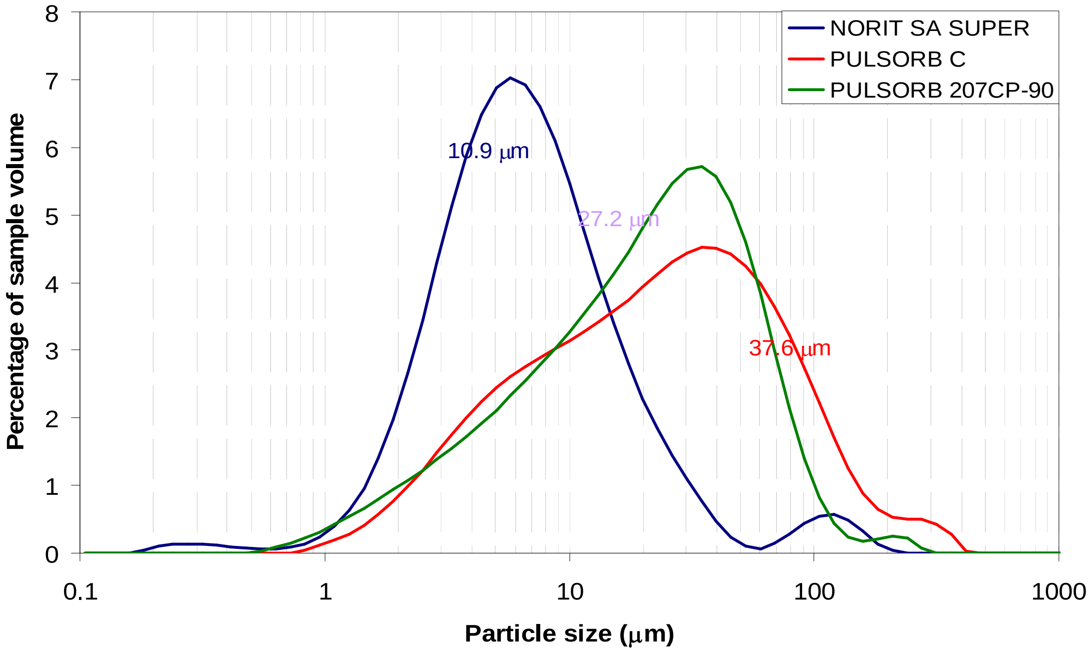


Figure 11. Comparison of particle size distribution for Norit SA Super, Chemviron Pulsorb C and Pulsorb 207 CP-90.

4.3. PAC adsorption of NOM

4.3.1 Equilibrium results and pH effect

Before adsorption isotherms were developed for adsorption of NOM onto the different PAC, the first stage was to understand how long was required before equilibrium was reached between the two components. The equilibrium point of adsorption based on UV_{254} removal for all 3 PAC was found to be 6 hours at pH 1, 7 and 14 for NOM removal from both raw and coagulated water (Figures 12 and 13). This was accepted to be the equilibrium time for the adsorption of NOM from raw water using PAC.

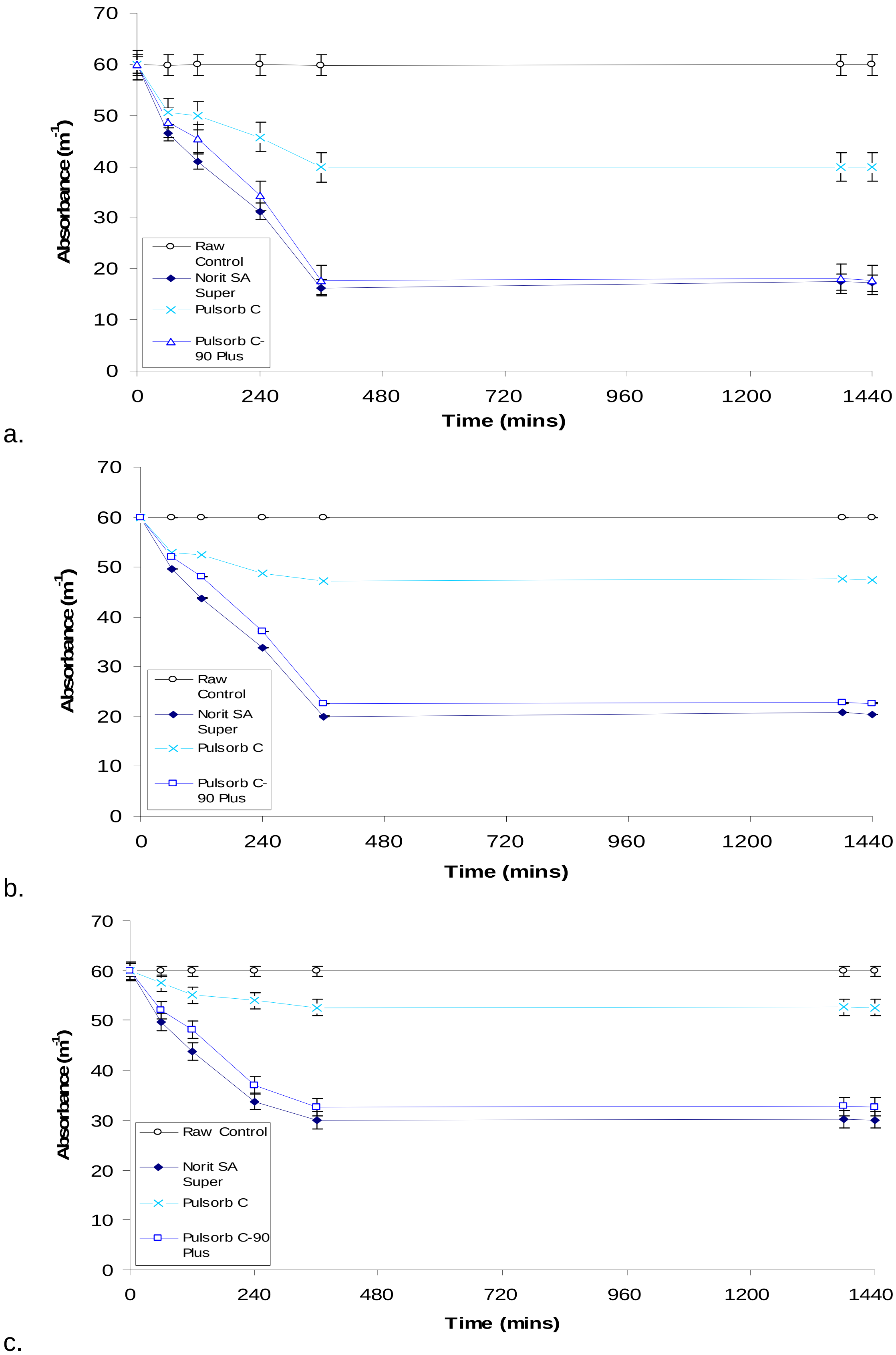


Figure 12. Mean ± S.D UV_{254} absorbance showing the equilibrium of PAC at pH 1 (a) ph 7 (b) and pH 14 (c) from raw water at a PAC dose of $40mgl^{-1}$.

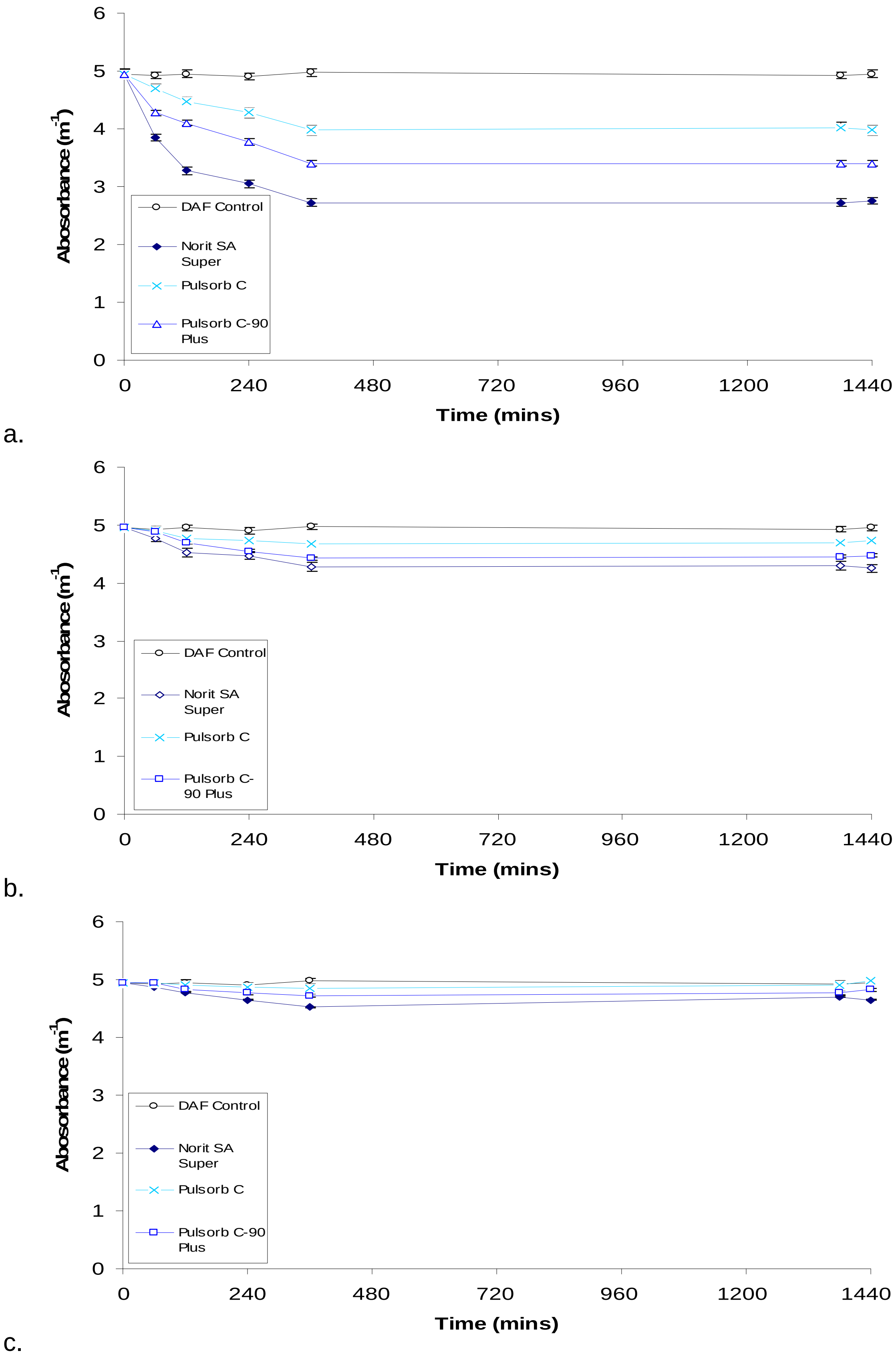


Figure 13. Mean ± S.D UV$_{254}$ absorbance showing the equilibrium of PAC at pH 1 (a) ph 7 (b) and pH 14 (c) from coagulated water at a PAC dose of 40mgl^{-1}.

Further tests were carried out to understand the change in NOM adsorption at pHs that were more likely to be experienced at a full scale WTWs (Figures 14-17). Figures 14-17 show a summary of the UV_{254} removal with pH and PAC dose. The full data can be seen in appendix 1. NOM removal based on removal of UV_{254} absorbance showed that lowering adsorption pH increased the amount of NOM that was removed from the raw water. In these tests, raw water had a UV_{254} absorbance of 60.1 ± 0.5 m^{-1} (table 11). Figures 14-17 shows the difference between the UV removal before and after adsorption (ΔUV_{254} value), with a greater change in UV_{254} absorbance being taken as indicative of a greater amount of NOM removal. It can be seen that adsorption at pH 3, irrespective of which PAC was dosed, produced the greatest change in UV_{254}. Adsorption at pH 5.5 was the least effective at removing NOM.

It can be seen from the differences between NOM removal in Figures 14-15 and between Figures 16-17 that increasing the dose of PAC from 20 to 80 mgl^{-1} increased the amount of NOM that was removed. In raw water (Figures 14, 15) increasing the PAC dose from 20 mgl^{-1} to 80 mgl^{-1} resulted in an increase in removal of between 19.6% and 32.7% depending on which PAC was used. In coagulated water (Figures 16, 17) increasing the PAC dose resulted in an increase in removal of between 3.5% and 36%. Irrespective of pH and PAC concentration, the most effective PAC was Norit SA Super, and the least effective was Pulsorb C.

Norit SA Super was most efficient for adsorption of NOM at pH 3, where 66% and 88% of TOC was removed from the raw water using 20 mgl^{-1} or 80 mgl^{-1} respectively whilst 83% and 97% was removed from the coagulated water using the high and low doses. The least effective dosing regime was observed when dosing Pulsorb C at pH 5.5 where only 6.9% and 14.7% of NOM was removed from raw water using either 20 mgl^{-1} or 80 mgl^{-1} respectively and11% and 14.5% from coagulated water.

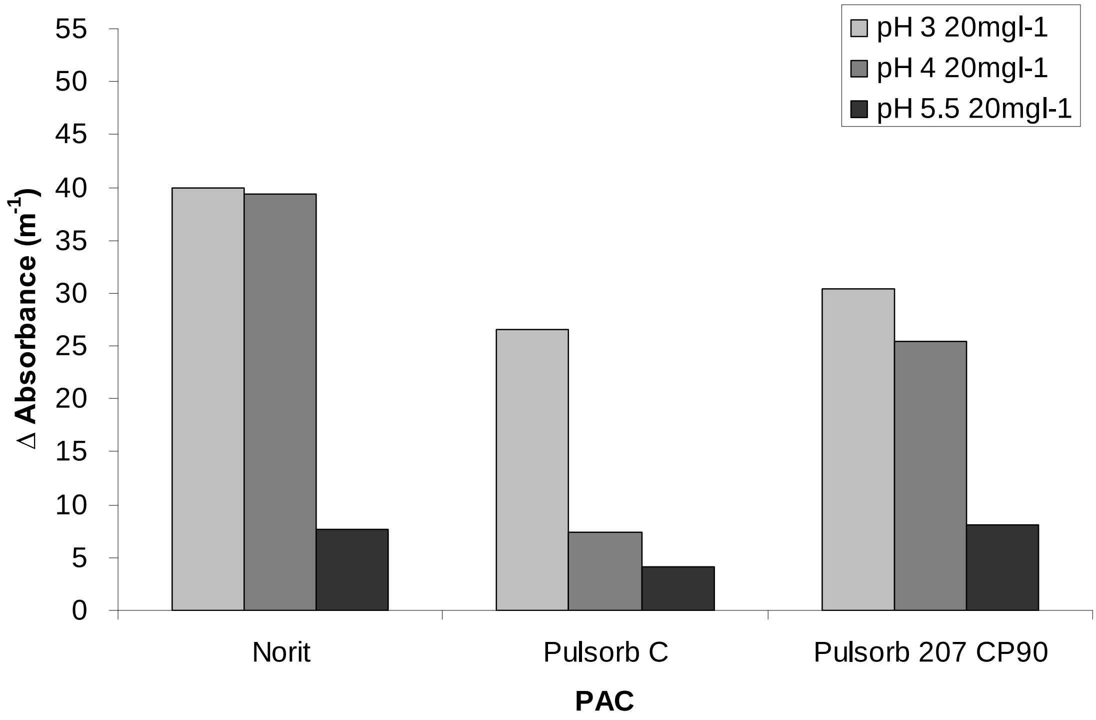


Figure 14. Summary of the amount of removal of NOM from raw water, based on the reduction in absorbance at UV_{254} for pH 3, 4, and 5.5 for Norit SA super, Pulsorb C, and Pulsorb 207 CP90 dosed at $20mgl^{-1}$.

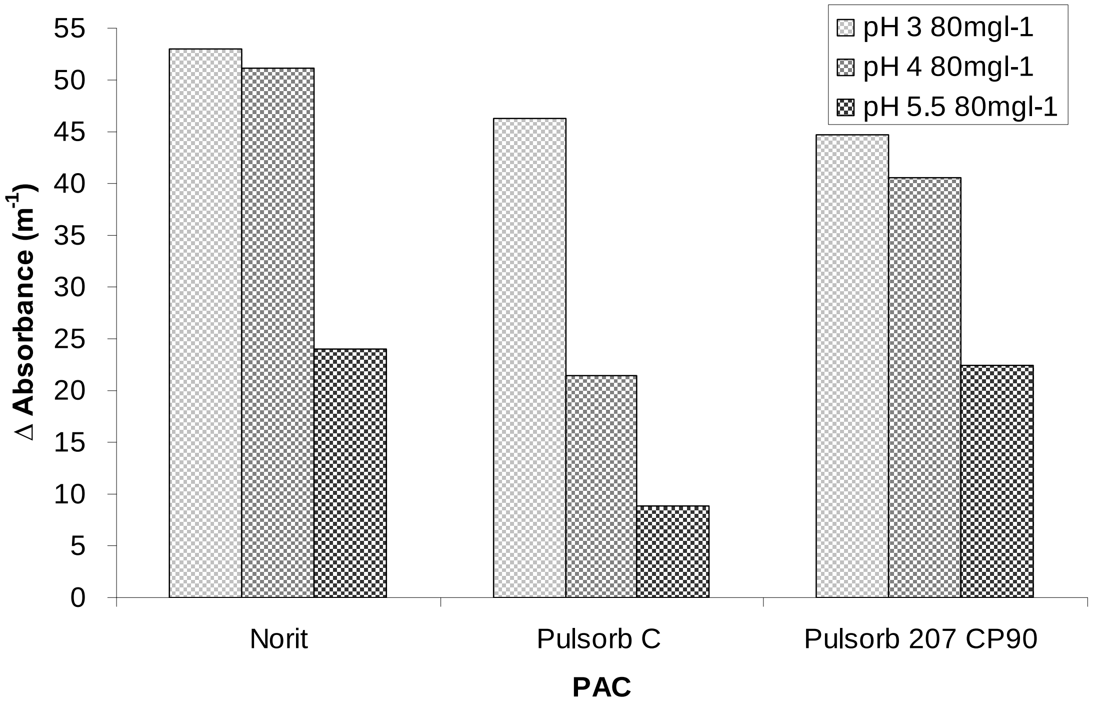


Figure 15. Summary of the amount of removal of NOM from raw water, based on the reduction in absorbance at UV_{254} for pH 3, 4, and 5.5 for Norit SA super, Pulsorb C, and Pulsorb 207 CP90 dosed at 80mgl^{-1}.

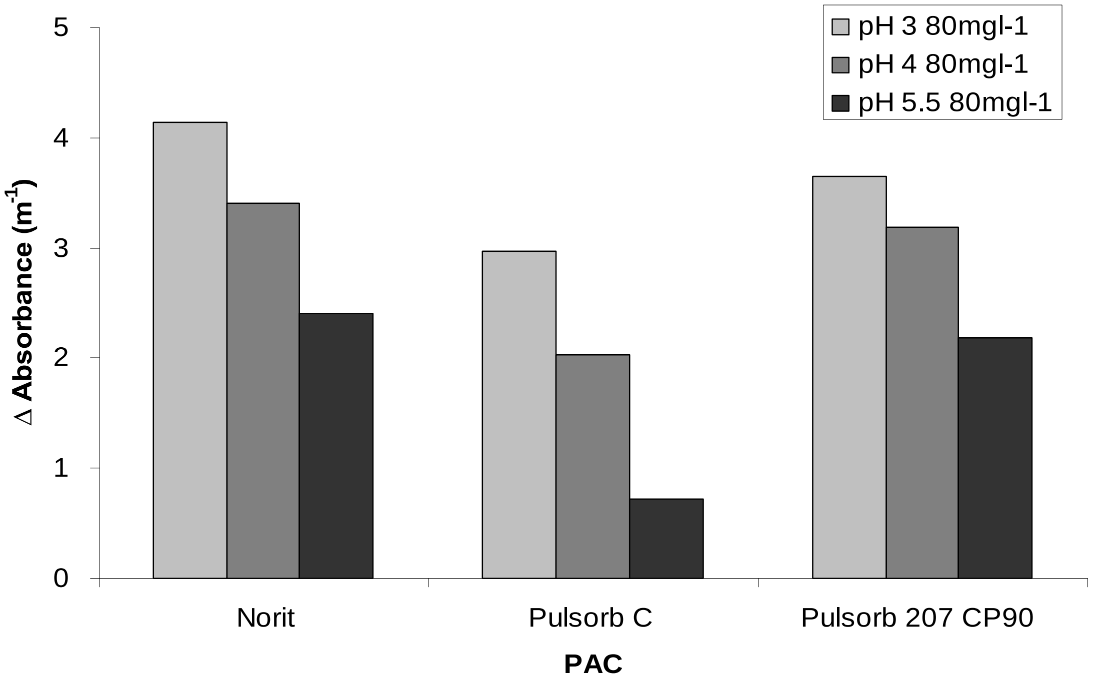


Figure 16. Summary of the amount of removal of NOM in DAF water, based on the reduction in absorbance at UV_{254} for pH 3, 4, and 5.5 for Norit SA super, Pulsorb C, and Pulsorb 207 CP90 dosed at 20mgl^{-1}.

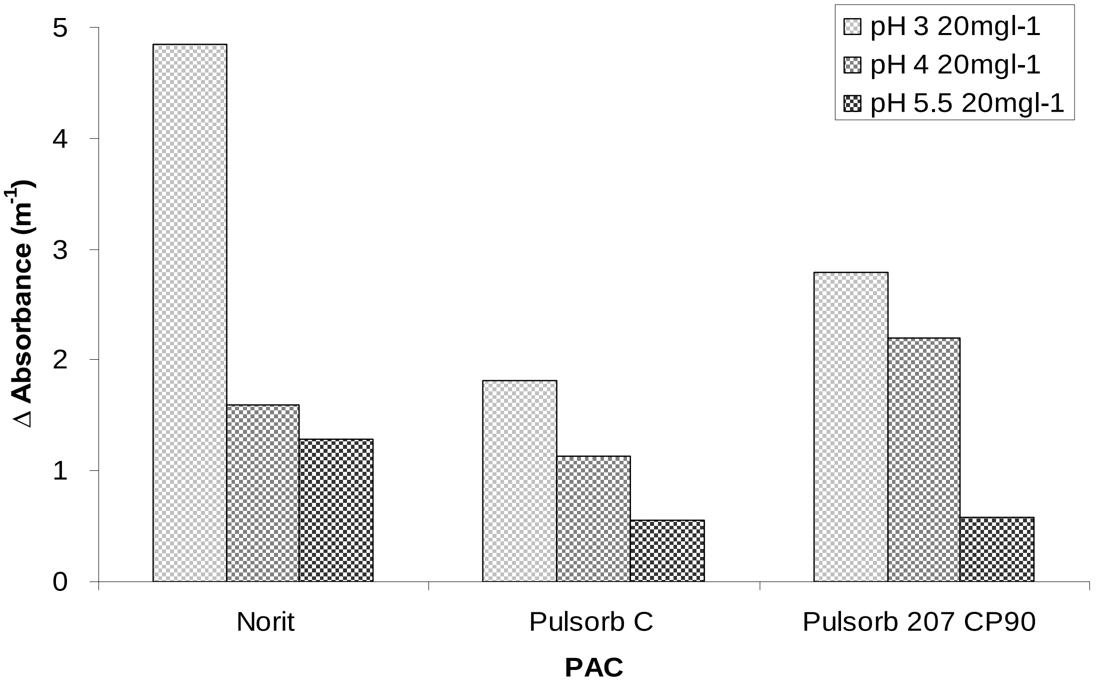


Figure 17. Summary of the amount of removal of NOM in DAF water, based on the reduction in absorbance at UV_{254} for pH 3, 4, and 5.5 for Norit SA super, Pulsorb C, and Pulsorb 207 CP90 dosed at $80mgl^{-1}$.

4.3.2 Adsorption isotherms

Once the equilibrium conditions and pH conditions had been established, adsorption isotherms were developed for the three PAC at pH of 3-5.5 for adsorption from raw and coagulated water. Data was fitted to the modified Freundlich isotherm (Figures 18-23). The value for the modified Freundlich constant k was taken from the intercept and 1/n from the slope of the line from log transformed data. These values were compared in order to determine the best performing PAC. In general, for most adsorption systems, individual regression correlation co-efficients (R^2) for each pH ranged from 0.88 – 0.97 (n = 6) showing that the data fitted the modified Freundlich adsorption model very well. The highest values of k and 1/n were observed at pH of less than 4 for all types of PAC.

A summary of the performance of the PAC for NOM removal was carried out by comparing the modified Freundlich adsorption constants (Tables 12 and 13). Table 12 shows the benefit of changing the pH from 4, which is the optimum coagulation pH down to pH 3 in raw water and table 13 shows the same for adsorption from coagulated water. Data for all of the isotherms can be seen in appendix 2. Norit SA Super is shown to perform best as it has the highest K value in both raw water and coagulated water. Pulsorb C displayed the worst performance as it has the lowest values for K. It can be seen that lowering the pH to 3 in raw water increases the capacity for adsorption (K) . However, the exception is Norit SA super, which is most effective at pH4 rather than 3 as the K value for pH 4 was greater than that of pH 3 in both raw and coagulated water. Tables 12 and 13 show the best and worst conditions of pH 3 and 5,5 respectively as well as the optimum pH for coagulation (pH4). Norit SA Super is the only PAC that performs best at an optimum coagulation pH of 4 instead of pH 3. In general, when 1/n values are between 0.1 and 1, adsorption is considered favourable (Tseng and Wu, 2008). As can be seen, most of the 1/n values met this criteria for PAC for adsorption from both raw and coagulated water (Tables 12 and 13).

Table 12. Summary of the performance of the three PACs at removing NOM from raw water at pH 3, 4 and 5.

	k (mg/g)			**1/n**		
	pH 3	pH 4	pH 5.5	pH 3	pH 4	pH 5.5
Pulsorb C	17.85	14.76	4.93	0.82	0.80	0.67
207 CP90	21.56	18.36	8.46	0.86	0.83	0.71
SA Super	23.85	24.11	0.92	0.88	0.87	0.35

Table 13. Summary of the performance of the three PACs at removing NOM from coagulated water at pH 3, 4 and 5.

	k (mg/g)			**1/n**		
	pH 3	pH 4	pH 5	pH 3	pH 4	pH 5
Pulsorb C	0.13	0.41	0.01	0.56	0.40	-0.13
207 CP90	0.32	0.23	0.17	0.74	0.69	0.67
SA Super	0.60	22.31	0.12	0.93	1.74	0.69

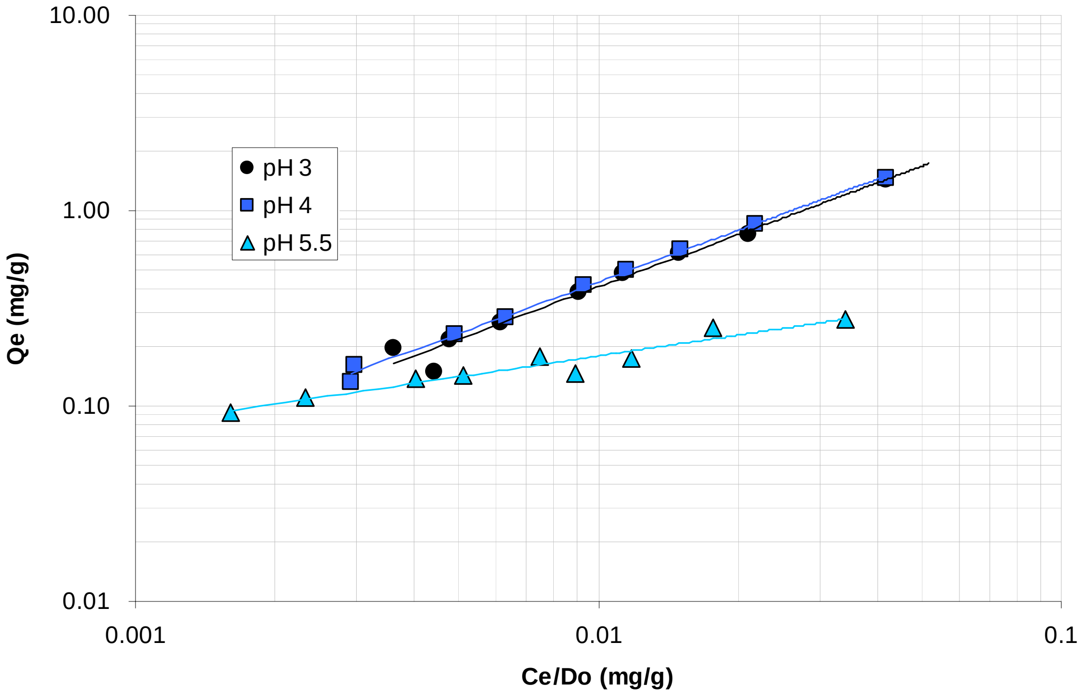


Figure 18. The modified Freundlich isotherm showing the amount of TOC in raw water at equilibrium per g of Norit SA Super against the amount of TOC adsorbed per gram of PAC.

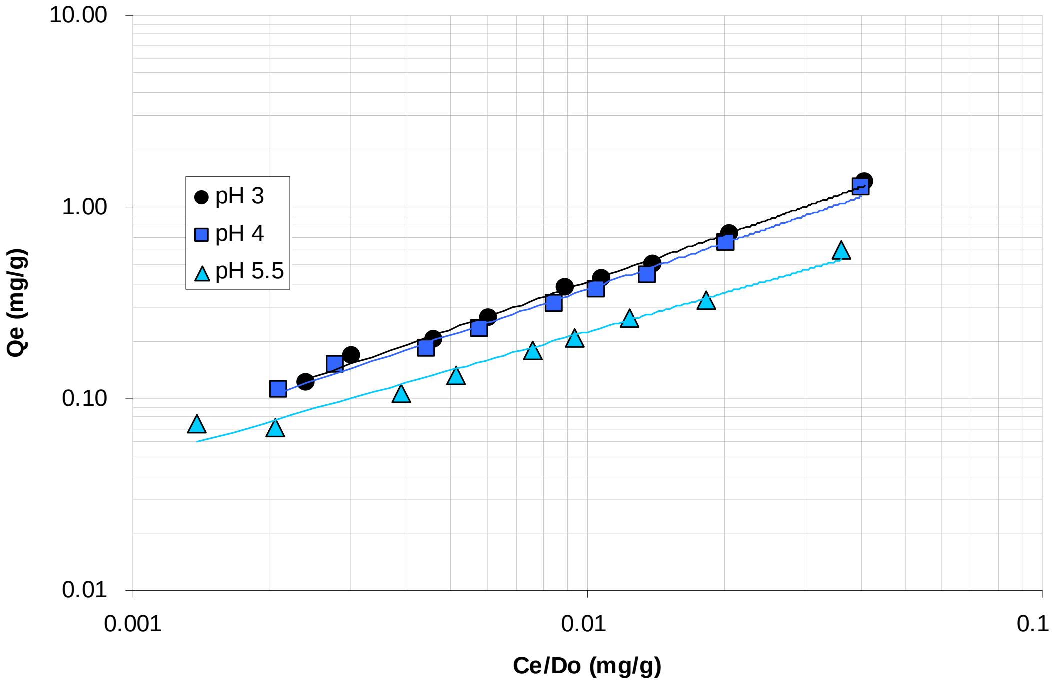


Figure 19. The modified Freundlich isotherm showing the amount of TOC in raw water at equilibrium per g of Pulsorb C against the amount of TOC adsorbed per gram of PAC.

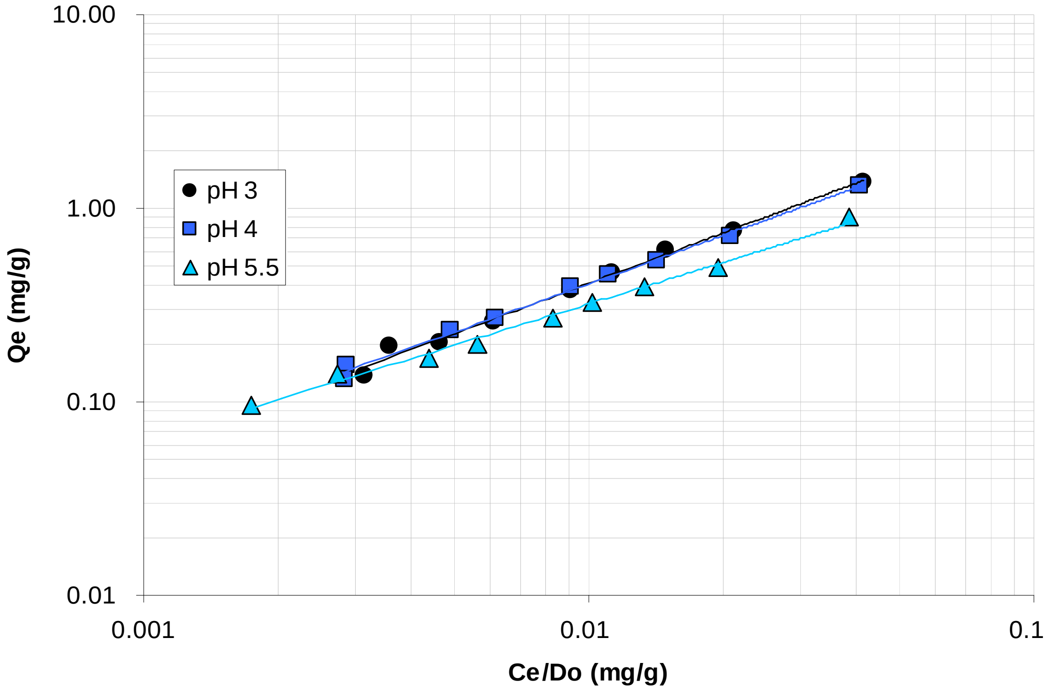


Figure 20. The modified Freundlich isotherm showing the amount of TOC in raw water at equilibrium per g of Pulsorb 207 CP-90 against the amount of TOC adsorbed per gram of PAC.

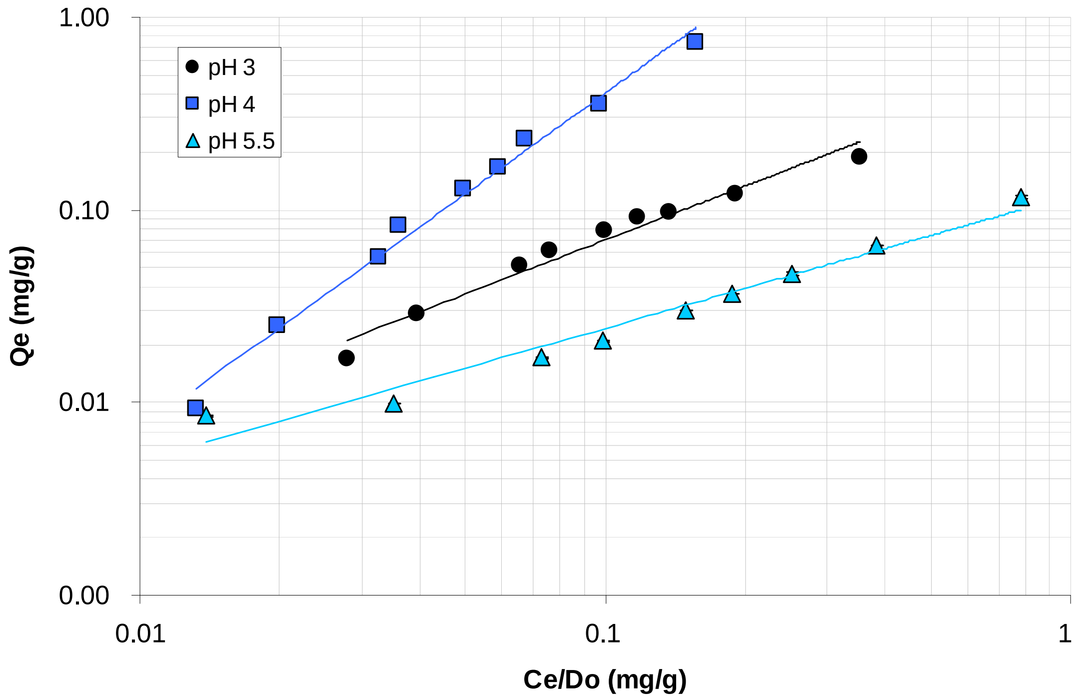


Figure 21. The modified Freundlich isotherm showing the amount of TOC in coagulated water at equilibrium per g of Norit SA Super against the amount of TOC adsorbed per gram of PAC.

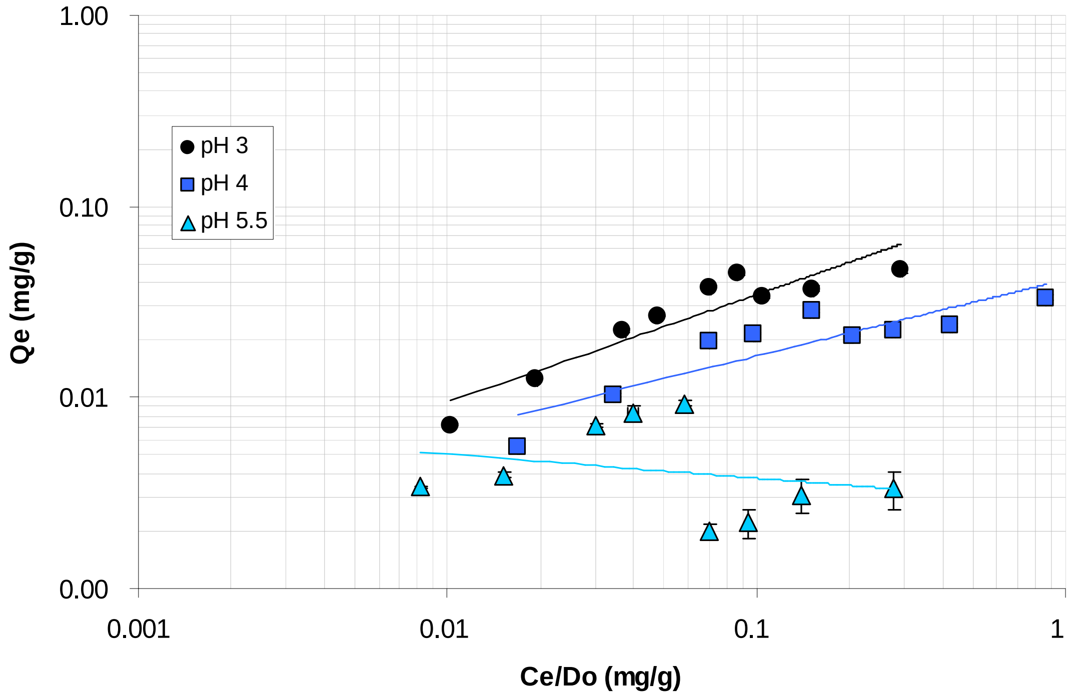


Figure 22. The modified Freundlich isotherm showing the amount of TOC in coagulated water at equilibrium per g of Pulsorb C against the amount of TOC adsorbed per gram of PAC.

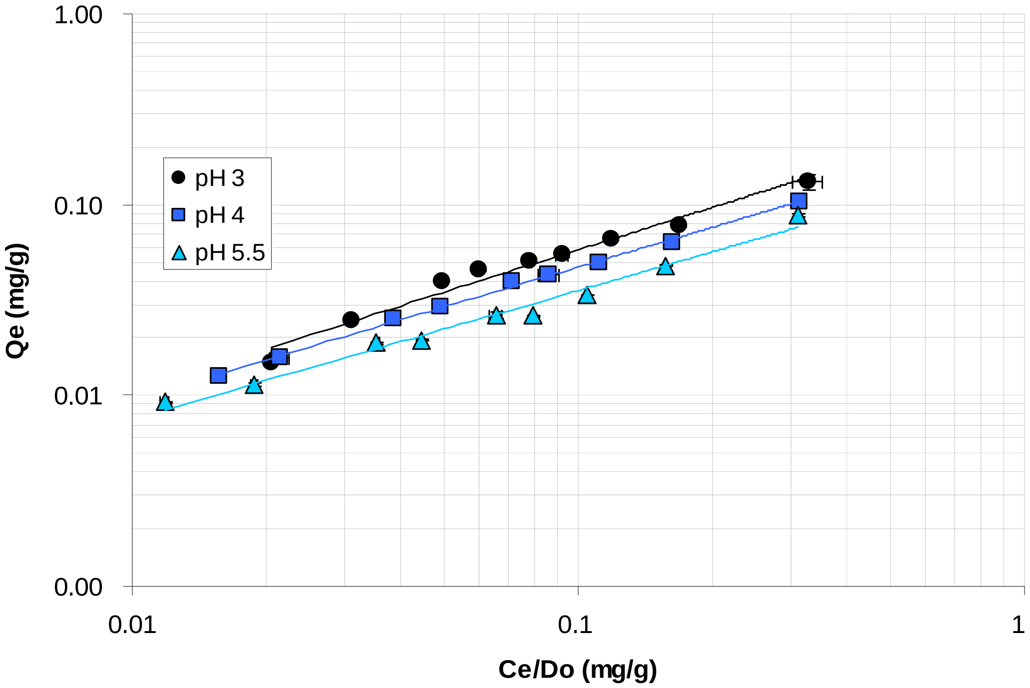


Figure 23. The modified Freundlich isotherm showing the amount of TOC in coagulated water at equilibrium per g of Pulsorb 207 CP-90 against the amount of TOC adsorbed per gram of PAC.

4.4. PAC and coagulant interactions

Further experiments were carried out using PAC combined with coagulation using conditions that were likely to be experienced at full scale to determine the impact that the dosing sequence has on NOM removal and related factors such as turbidity and THM formation (Figures 24-27). The rapid mix stage in all experiments was 90 seconds and the effect of dosing PAC at the same time as coagulant as well as dosing it before and after the coagulant was investigated. In these tests the PAC was dosed either 60 or 30 seconds before or after the coagulant. The results showed that when the PAC and coagulant were dosed at the same time, a longer mixing time was most effective. When PAC and coagulant had a contact time of 90 seconds the TOC (figure 24), UV_{254} absorbance (figure 25), turbidity (figure 26) and THM formation (figure 27) were lowest. Conversely a contact time of 30 seconds for both PAC and coagulant produced the highest residual TOC, UV_{254} absorbance, turbidity and THM formation.

The amount of TOC in the raw water was 14.9 mgl^{-1}, which was lowered to 6.6 mgl^{-1} using coagulation alone (Figures 24 a-c). Dosing just PAC produced TOC values of 9.9mgl^{-1}, 10.4 mgl^{-1} and 11.1 mgl^{-1} for Norit, Pulsorb 207 CP-90 and Pulsorb C respectively. The lowest TOC value, and hence best removal, was seen when PAC and coagulant were dosed at the same time for 90 seconds resulting in TOC values of 2.1, 2.5 and 3.6 mgl^{-1} for Norit, Pulsorb 207 CP-90 and Pulsorb C respectively (Figure 24c). Dosing the PAC before the coagulant showed TOC values of 6.2, 6.3, and 7.2 mgl^{-1} (Figure 24b) compared to dosing the PAC after the coagulant that gave TOC values of 4.0, 4.3 and 5.3 mgl^{-1} for Norit, Pulsorb 207 CP-90 and Pulsorb C respectively (Figure 24a). The poorest removal was observed when PAC and coagulant were added at the same time and mixed for 30 seconds which gave TOC values of 6.9, 7.0, and 8.1 mgl^{-1}.

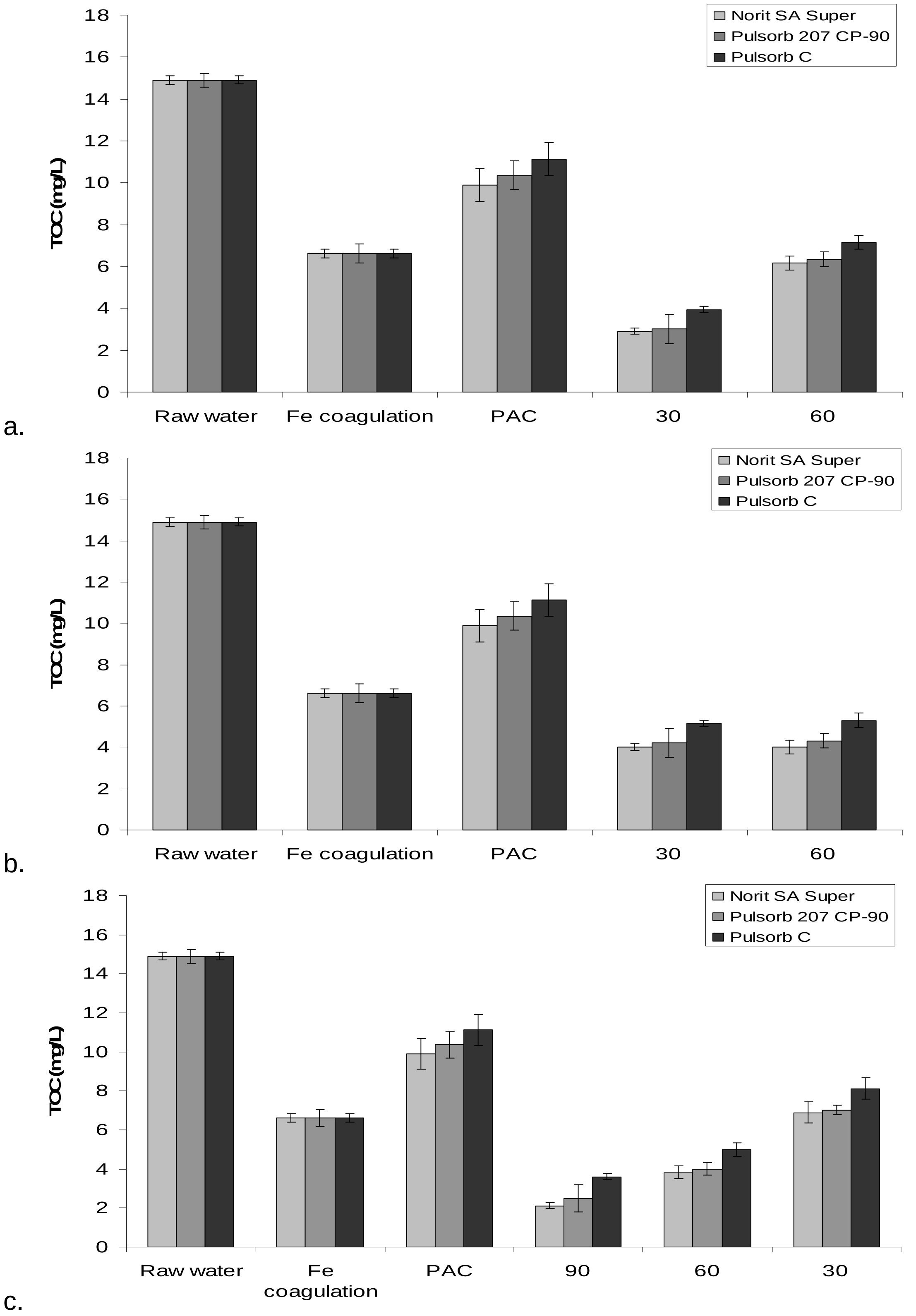


Figure 24. The effect that different dosing sequence has on mean (±SD) TOC when treated with 20mgl^{-1} of Norit SA super dosed with 11.5mgl^{-1} of ferric at pH4. The PAC was dosed after (a), before (b) and at the same time as the coagulant (c).

Figures 25a-c show that there was a small difference in the UV_{254} for the three PAC for removal of NOM from raw water. Norit SA super was the most effective at lowering UV absorbance from $57.1m^{-1}$ to $44.2m^{-1}$. The absorbances for Pulsorb 207 CP-90 and Pulsorb C were $44.4m^{-1}$ and $45.4m^{-1}$. Figures 25a-c show that the UV_{254} absorbances followed the same trend as for the TOC removal (Figure 24a-c). When coagulant and PAC were dosed at the same time, a longer rapid mix period produced a lower UV_{254} with the UV_{254} absorbance for 90 seconds mixing being 4.2, 4.3 and 4.9 m^{-1} compared to absorbances of 7.9, 7.9 and 8.9 m^{-1} for 30 seconds rapid mix (figure 28c). If PAC and coagulant are dosed separately then dosing PAC before coagulant achieves better NOM removal of 32.8% compared to NOM removal of 29.1% if PAC is dosed after the coagulant.

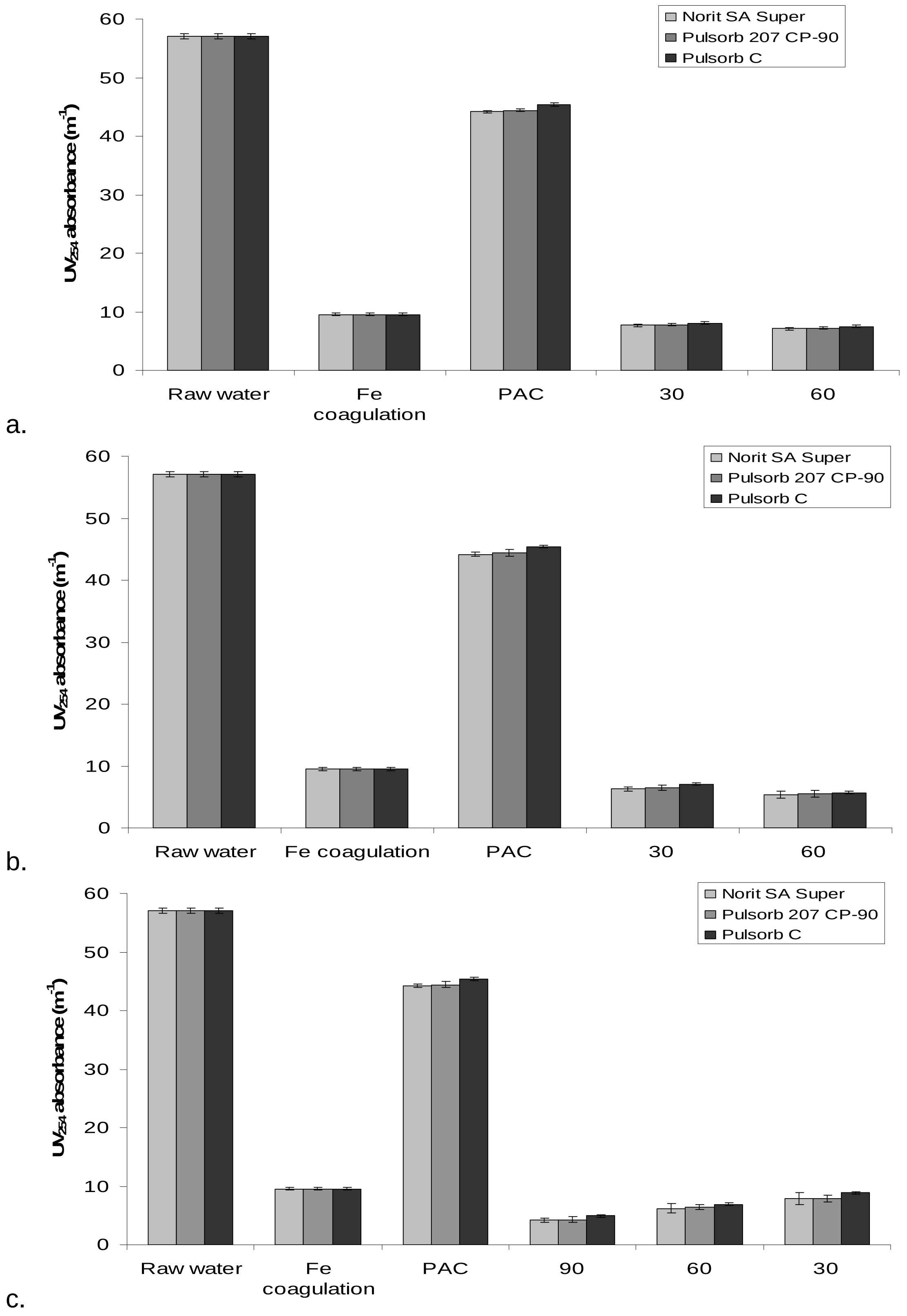


Figure 25. The effect that different dosing times has on mean (±SD) UV_{254} absorbance, when treated with 20mgl^{-1} of Norit SA super, 11.5mgl^{-1} of ferric at pH 4. The PAC was dosed after (a), before (b) and at the same time as the coagulant (c).

Figures 26 a-c shows the turbidity of treated water following treatment with PAC and coagulation over a 90 second rapid mix stage. Dosing PAC before or at the same time as the coagulant produced a lower turbidity (Figures (26 b and c). Dosing PAC after the coagulant increased the turbidity of the treated water (Figure 26a). It was also seen that the longer the period of time between dosing the PAC after the coagulant the higher the turbidity (Figures 26 a). The lowest turbidity was achieved by mixing coagulant and PAC for 90 seconds. The turbidity was 2.2, 2.2 and 2.3 NTU for Norit, Pulsorb 207 CP-90 and Pulsorb C respectively. The highest turbidity was 5.6 NTU for Norit, 5.3 NTU for Pulsorb 207 CP-90, and 5.5 NTU for Pulsorb C which was observed when the rapid mixing stage of coagulation was for 60 seconds and PAC was dosed 30 seconds after the addition of coagulation.

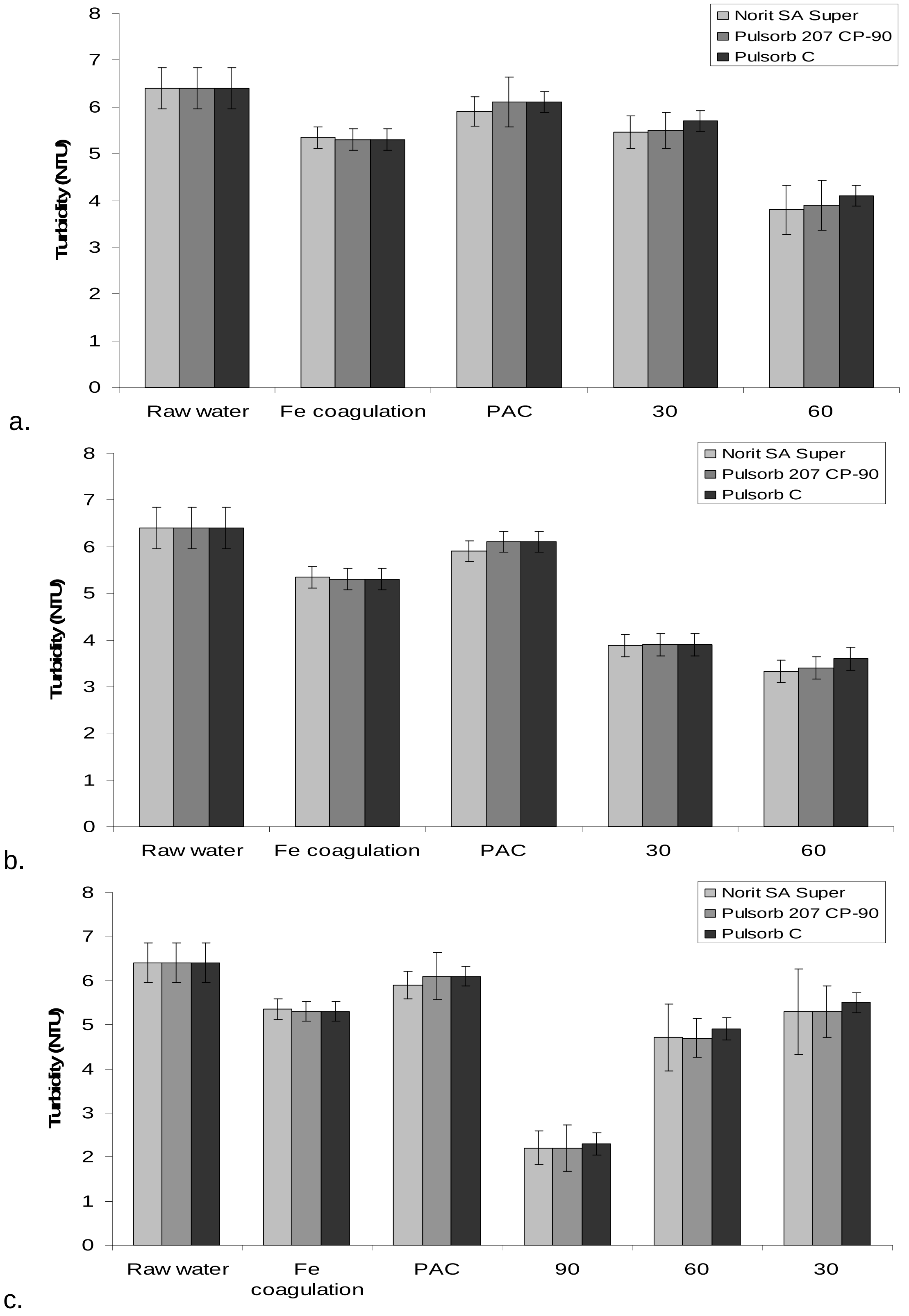


Figure 26. The effect that different dosing times has on mean (±SD) turbidity when treated with 20 mgl^{-1} of Norit SA super and 11.5mgl^{-1} of ferric at pH 4. The PAC was dosed after (a), before (b) and at the same time as the coagulant (c).

Figures 27a-c show the THM formation potential (THMFP) of water samples treated with Norit, Pulsorb 207 CP-90 and Pulsorb C at pH 4 and 11.5 mgl^{-1} of Fe. The effect of dosing sequence can be seen on the THMFP of the treated water. Irrespective of dosing sequence with regards to coagulant it can be seen that Norit SA Super significantly reduced the THMFP of the raw water to a much greater extent than Pulsorb 207 CP-90 and Pulsorb C ($F_{41,}$ = 4653.7, p = 0.0036). The THMFP followed a similar pattern to the TOC removal (Figures 24a-c) and UV_{254} absorbance (Figures 25-a-c) in that dosing PAC and coagulant together and allowing a longer contact time removed the most NOM and therefore produced the least THMs.

The THMFP of the raw water was 194.6 μgl^{-1} and the lowest THMFP of 27.2 μgl^{-1} was observed for Norit SA Super with 90 seconds coagulation and 90 seconds PAC adsorption resulting in a reduction of THMFP by 86%. The UK legislation for THMs is $100\mu gl^{-1}$ and is represented by the red line transecting the y axis in the figures. All dosing sequences using Norit SA Super meet UK legislation compliance whereas many dosing regimes using Pulsorb 207 CP-90 and in particular Pulsorb C fall extremely close to or even exceed this threshold level. However, it must be remembered that the THMFP represents the DBPs formed after being saturated with chlorine for 7 days. These are conditions that are not likely to be experienced in any practical situation, so can only be used as a guideline to show which PAC will be more effective at THM reduction.

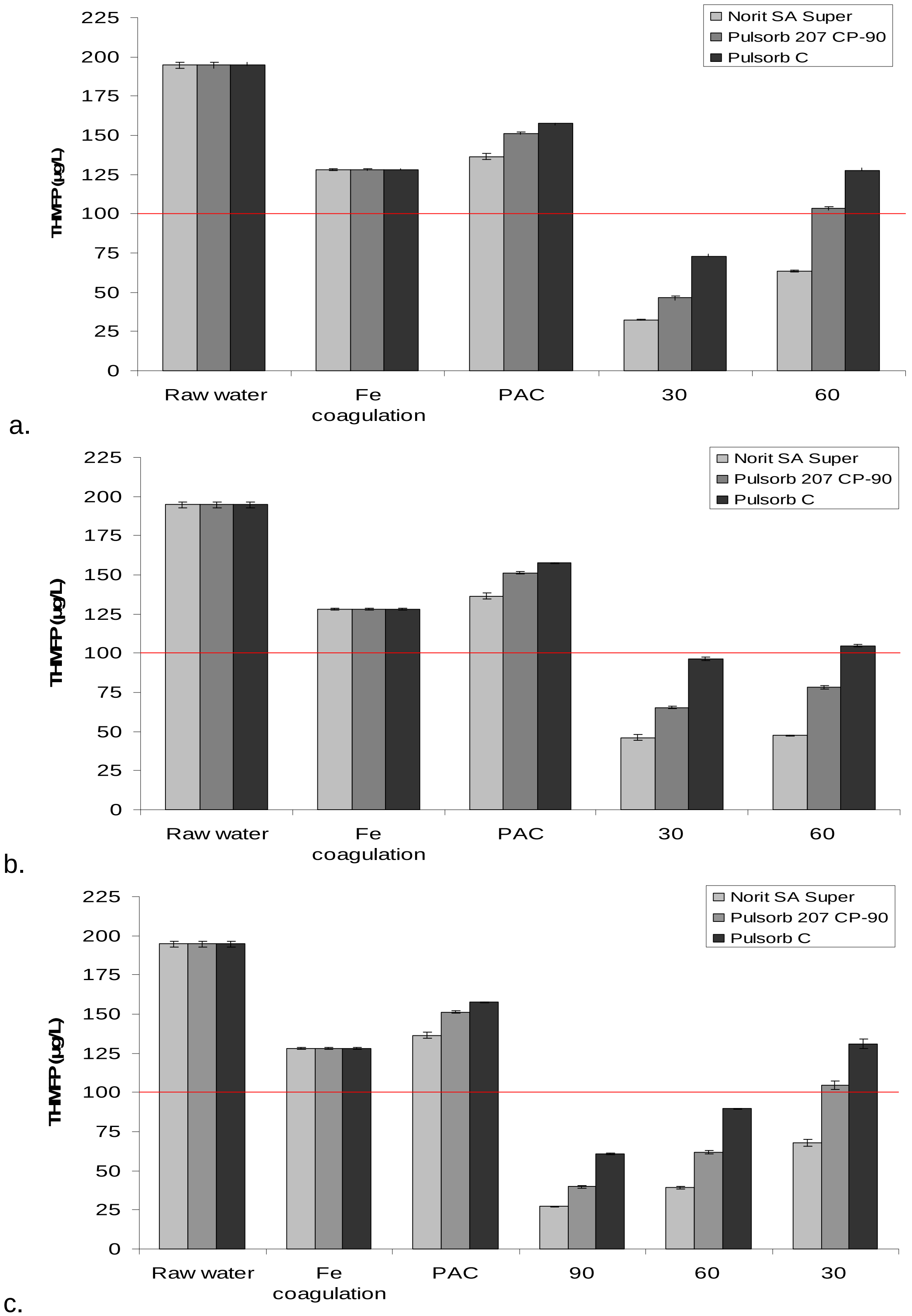


Figure 27. The effect that different dosing times have on THM levels when treated with 20mgl^{-1} of Norit SA super, Pulsorb 207 CP-90 and Pulsorb C, with 11.5mgl^{-1} of ferric at pH4. The PAC was dosed after (a), before (b) and at the same time as the coagulant (c). The red line shows current UK legislative limits.

4.5. Characterisation of NOM removed

The removal of different NOM fractions showed that the levels of HAF and FAF decreased significantly from raw water to the coagulated water. The amount of HAF and FAF was further reduced when PAC was added to augment the coagulation process. The TOC of the hydrophilic non-acid fraction (HPINA) remained unchanged for coagulation combined with the two Pulsorb PACs, but decreased slightly with the addition of Norit SA Super. Similarly the concentration of the hydrophilic acid fraction (HPIA) decreased only slightly between raw water, coagulant and the two Pulsorb PACs, whereas it decreased by much more (0.7mgl^{-1}) with the addition of Norit SA Super. This was further evidence that the Norit SA Super was the PAC with the best removal capacity.

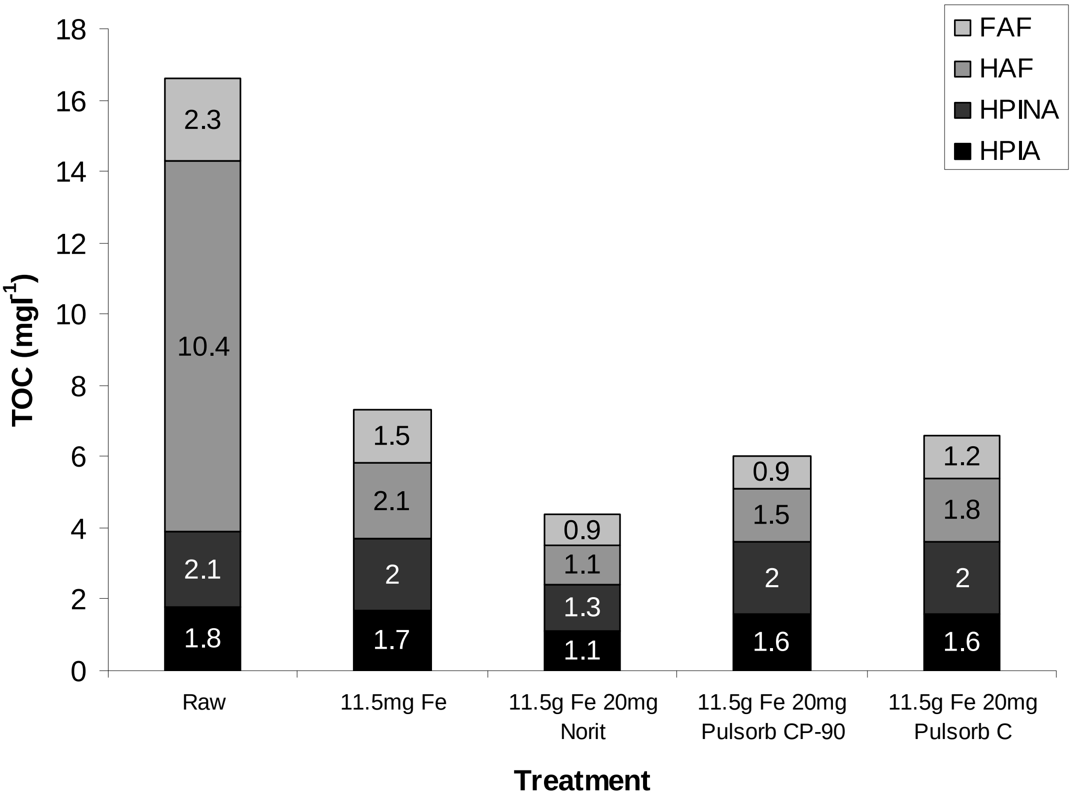


Figure 28. The fractionation of raw water and water that has been treated by coagulation and coagulation with the addition of PAC.

4.6. HPSEC analysis

The HPSEC spectra show that a lot of the high molecular weight aromatic organic compounds were removed using coagulation (Figure 29-30). In the coagulated water the spectra shows that low-molecular weight UV_{254} absorbing compounds remain. Figure 29 shows that treatment of raw water with both coagulant and PAC was capable of removing more than either coagulant or PAC alone. From the work of Fearing *et al*. (2004) most of the molecules removed have a MW of 1-5kDa and >5kDa molecules with a retention time (T_R) of 8.0 - 8.5 and 8.6 - 9.0 respectively. Figure 29 also shows that the addition of PAC to augment coagulation helps to remove molecules of molecular weight <1kDa (T_R = 10.2 - 11.0) which coagulation does not normally remove.

There was a small difference between the three PACs in terms of the quantity of NOM that was removed based on the HPSEC traces (Figure 30). The Norit SA super showed a greater level of removal of molecular weights eluting between 7-9 minutes.

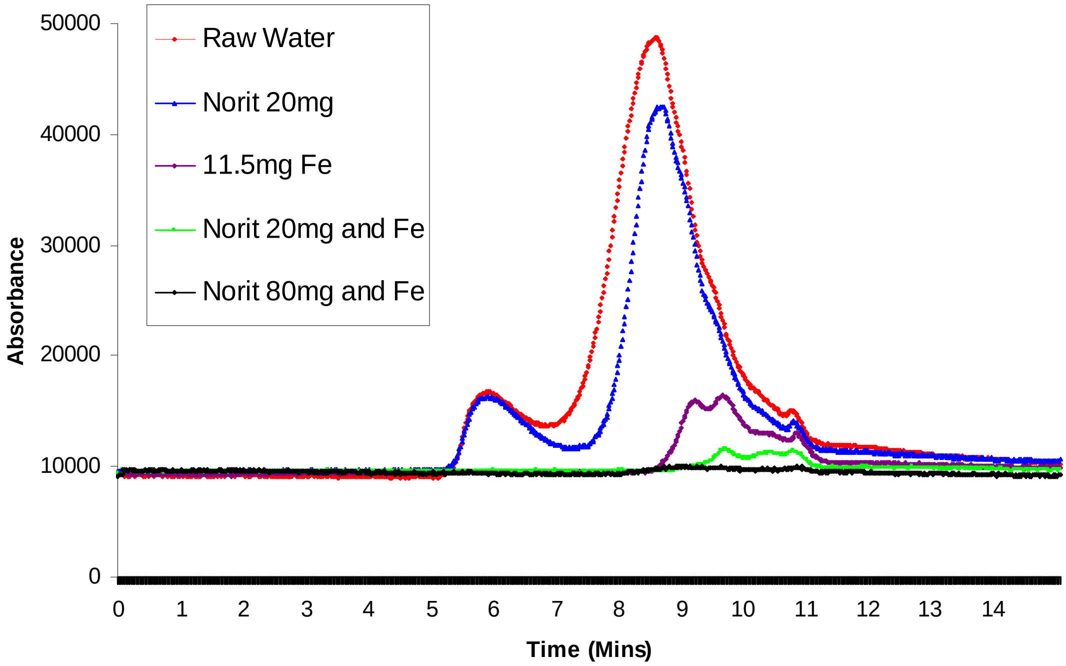


Figure 29. The HPSEC spectra showing the level of removal of NOM from raw water using coagulation and coagulation with Norit SA Super PAC.

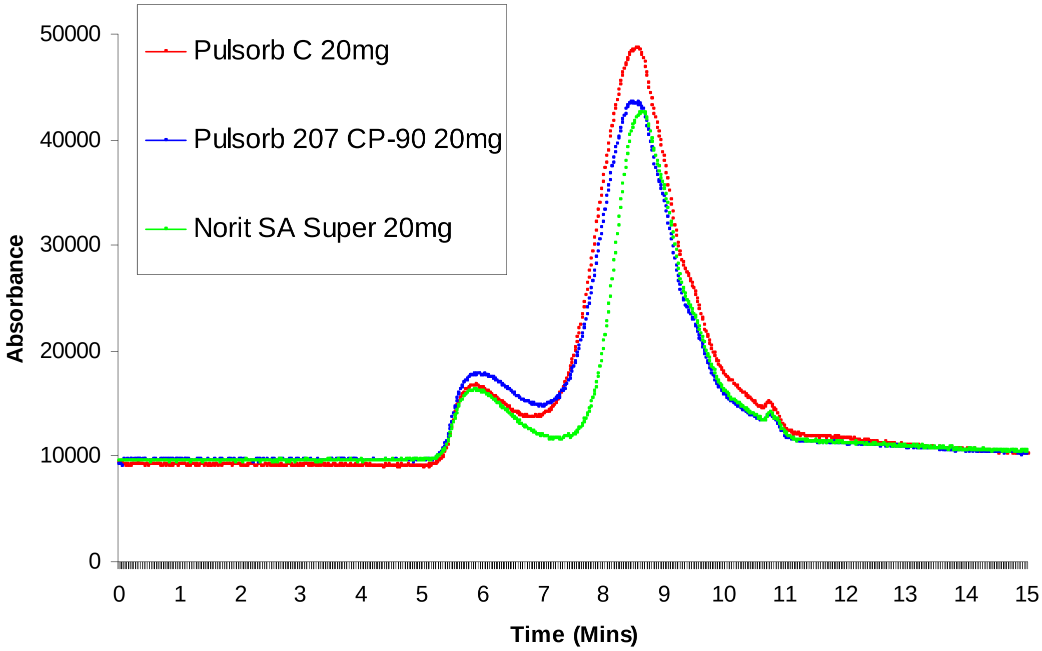


Figure 30. The HPSEC spectra showing the removal of NOM using three different types of PAC dosed at 20mgl^{-1}.

4.7. Charge of NOM and PAC

All of the PAC had similar charge profiles with increasing pH in de-ionised (DI) water and raw source water (Figures 31 and 32), implying that the charge that was measured was due to the changing charge on the NOM rather than the surface charge of the PAC. As the pH increased the net charge of the PAC changed from the positive to negative in both DI water and NOM. In DI water the isoelectric point (IEP) was between pH 5.5 and 6.5 for all of the PAC (Figure 32). The surface charge of activated carbon has been measured in many studies (see for example; Bjelopavlic *et al*., 1998; Biniak *et al*., 2009; Başar *et al*., 2003; Reed and Matsumoto, 1991) although not all of these studies used a zetasizer to measure charge. For example, Babić *et al*., (1999) used potentiometric titrations to measure establish the isoelectric point of an activated carbon cloth. The charge on the PAC needs to be considered in context of the coagulation pH utilised for coagulation at Ewden WTWs which is typically around pH 4. When the PAC is used on-site, the adsorption was therefore in a region where the PAC was positive, increasing the likelihood of electrostatic attraction between the PAC and negatively charged NOM. The key difference between the different PAC was that Pulsorb 207 CP90 had less positive charge at pH between 3-4 when compared with the Norit SA Super and Pulsorb C (+2.5-5.0 mV compared with +10.0-13.0 mV). The surface charge of the PAC can change with the change in pH. The two most common mechanisms for surface adsorption are surface complex formation and charge-transfer reactions (Biniak *et al*., 2001). The protonation and/or de-protonation of the surface of PAC with pH can be measured with respect to charge and therefore can suggest an increase in adsorption efficacy.

When in source raw water, all of the PAC had similar shaped curves to that of the raw water, indicating that the charge of the NOM (adsorbed or non-adsorbed material) controlled the charge of the system (Figure 32).

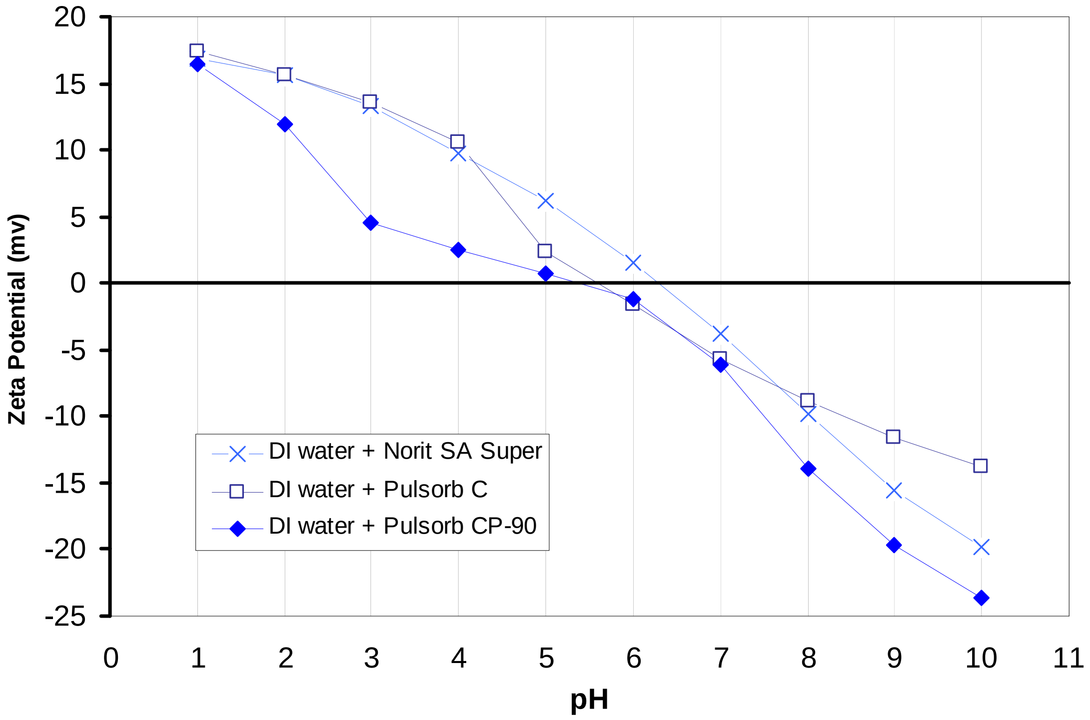


Figure 31. The charge of PAC at different pH in distilled water (DW) measured using a zetasizer.

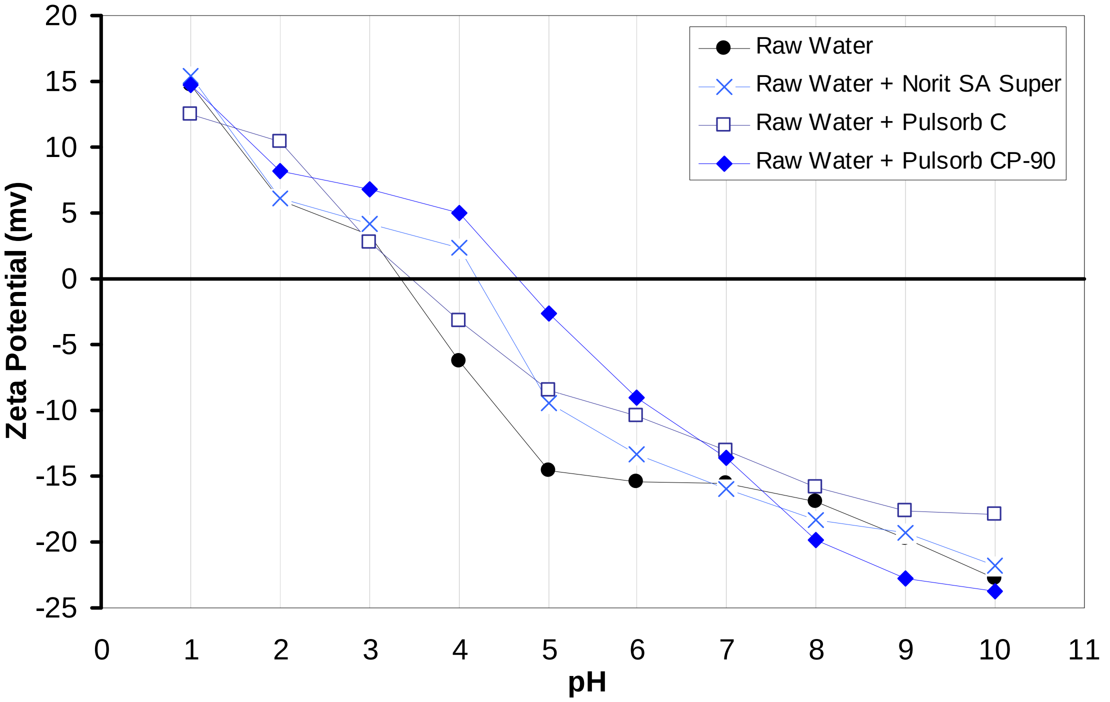


Figure 32. The charge of PAC in raw water with pH in raw water measured using a zetasizer.

4.8. PAC and coagulant floc interaction

Image analysis was carried out to understand how PAC incorporates into flocs based on different dosing strategies. An image of a floc that contains PAC has been compared against a floc without PAC dosing in Figure 33. The PAC particles can be clearly seen within the floc matrix. This enabled image analysis to be carried out to compare how different PAC dosing strategies results in variable PAC incorporation in the floc. If PAC is not captured in the floc it will be a cause of turbidity in a settled sample because of the low settling rate of the PAC due to its small particle size.

For all of the coagulation and PAC dosing conditions, there was a linear relationship between floc area and the number of PAC particles contained in the floc matrix producing R^2 values of between 0.88 and 0.93 (Figures 34a-c).

From this data it was possible to extract a normalised value for the average area of floc per PAC contained in the floc (a lower value indicating that more PAC particles are contained in the floc). This showed that the strategy of dosing PAC and coagulant together for 90 seconds resulted in normalised PAC values of between 1616-2161 PAC particles per μm^2 of floc. Dosing the PAC after the coagulant resulted in higher values between 2182-3339 particles per μm^2. Dosing the PAC before the coagulant resulted in similarly high values between 2183-2870 μm^2.

This was confirmation that better PAC incorporation into the floc was responsible for the lower residual turbidity when the PAC and coagulant were added together for the long coagulation period. There was little difference in the particles incorporated into the floc for the different varieties of PAC, indicating that the different particle size of the PAC did not have a big effect on incorporation into the floc, or the image analysis was not sensitive enough to discriminate significant differences.

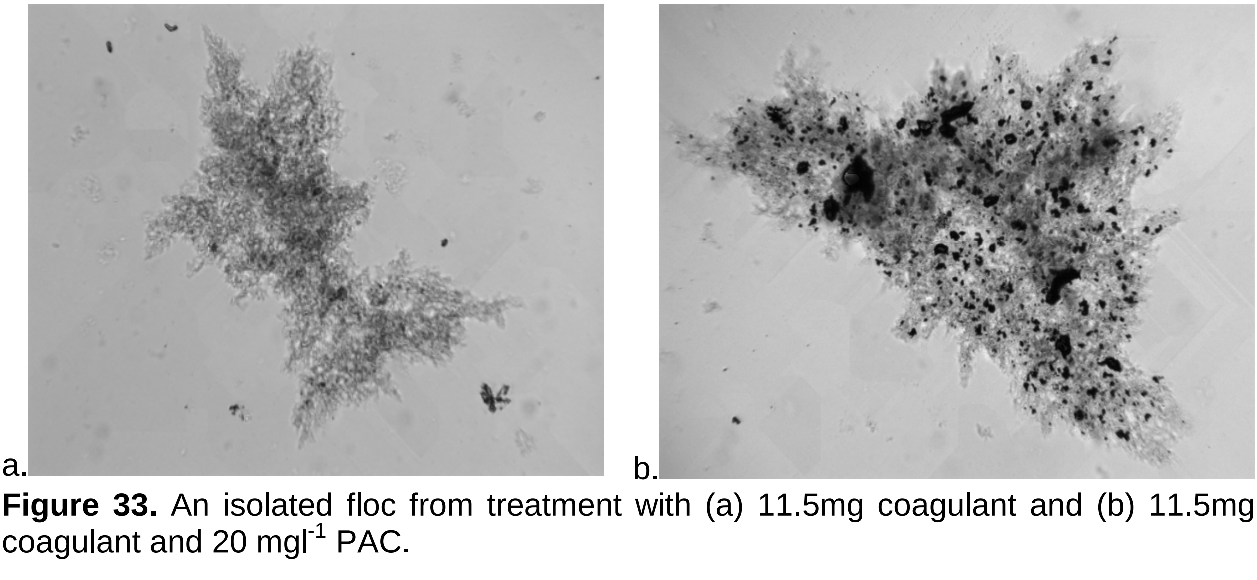
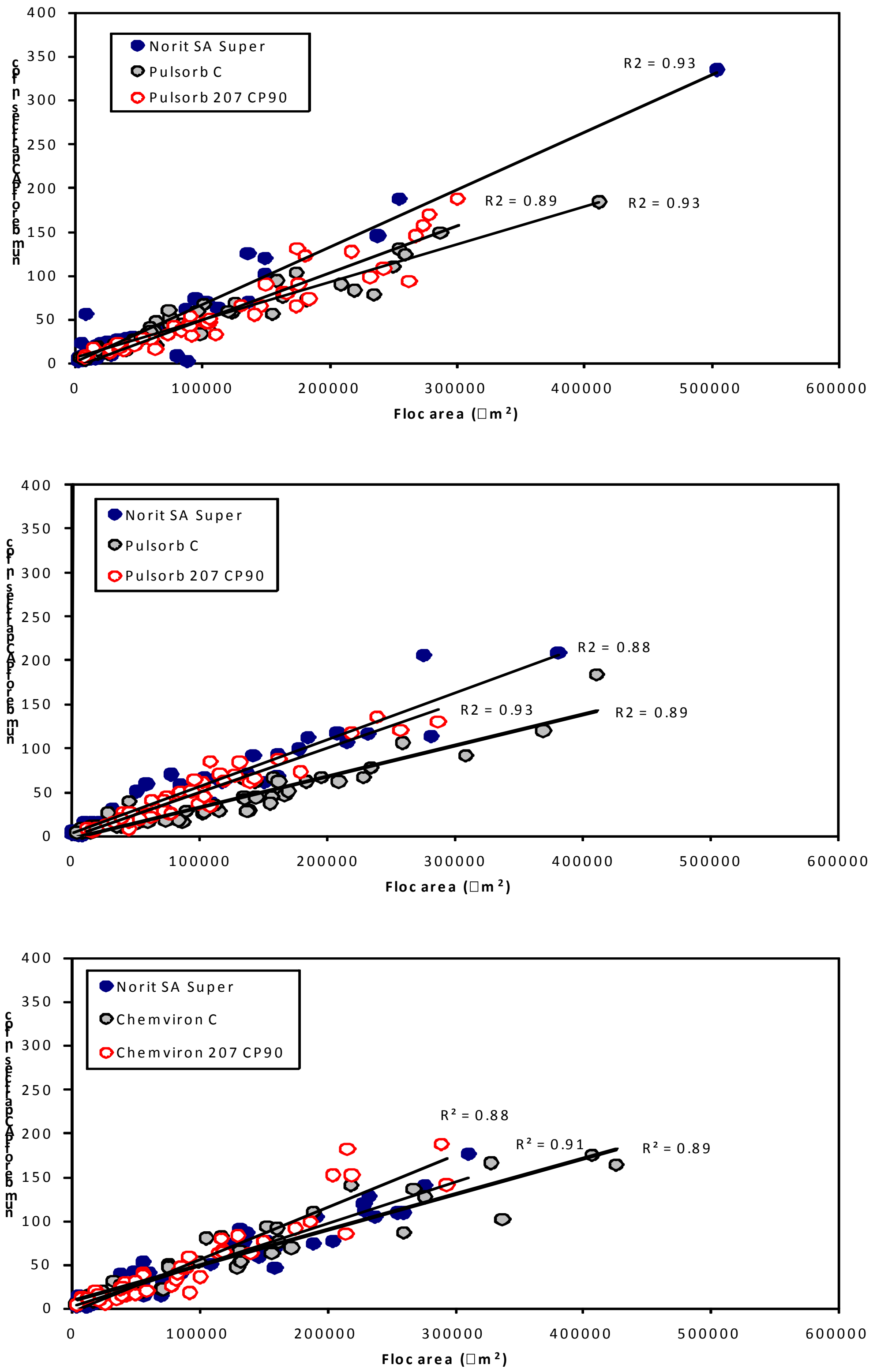


Figure 33. An isolated floc from treatment with (a) 11.5mg coagulant and (b) 11.5mg coagulant and 20 mgl^{-1} PAC.



a.

b.

c.

Figure 34. The relationship between floc size and number of PAC particles within the floc when PAC is dosed at the same time as the coagulant (a), after the coagulant (b) and before the coagulant (c).

4.9. On-site trials

Full-scale trials were carried out at Ewden WTWs over a four week period (Figure 35). During the duration of the trial, the raw water NOM increased as shown by an increase in the TOC of the raw water from 18.4 mgl^{-1} in week 1 to 24.1 mgl^{-1} in week 4. After treatment the TOC gradually reduced from week 1 to week 4 with an average TOC of 2.3 mgl^{-1} and 1.7 mgl^{-1} respectively. This represented an increase in removal from 87 to 93%. Baseline readings were conducted to establish how much NOM was removed using coagulation alone. The mean ±SD percentage of NOM removal using coagulation was 91.8% ± 0.3%. Dosing coagulant and PAC into tank 3 increased the mean percentage NOM removal to 93.6% ± 0.8%. When coagulant was dosed in tank 3 and PAC dosed in tank 2 the mean percentage NOM removal increased to 95.3% ± 0.5%. The greatest level of NOM removal could be seen by dosing coagulant into tank 3 and PAC into tank 1. This dosing regime produced a mean percentage NOM removal of 97.0% ± 0.2%. Dosing PAC into tank 1 allowed for a greater rapid mix time for the PAC to adsorb NOM. The PAC is incorporated into the floc, and provides a greater level of NOM removal by augmenting the coagulation and flocculation process.

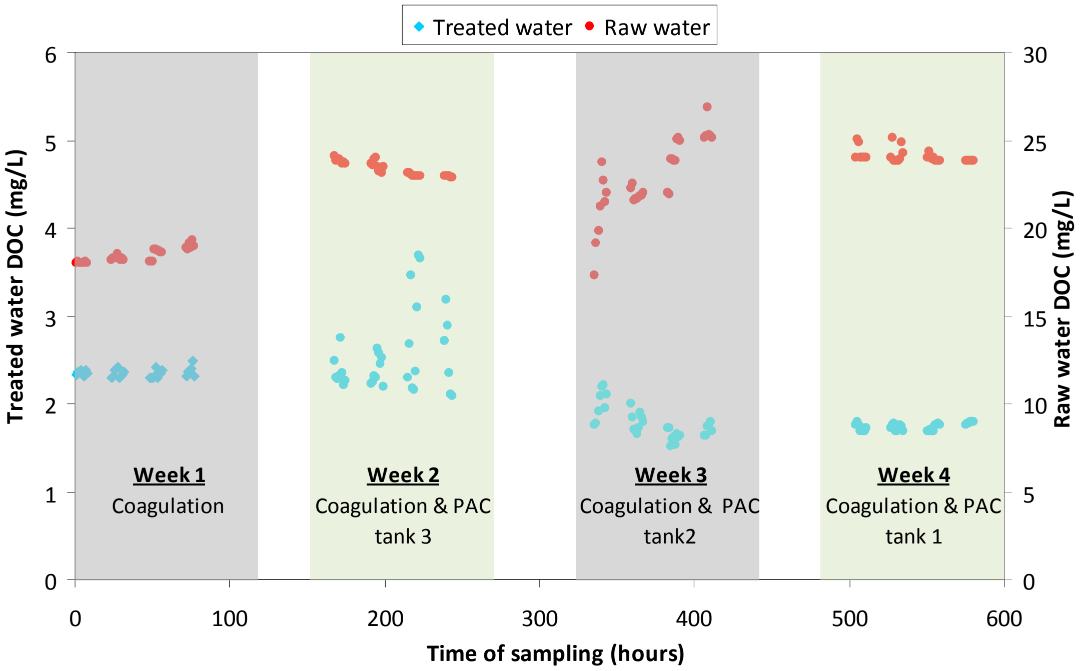


Figure 35. The removal of NOM using coagulant and PAC at Ewden WTW based on TOC removal that has been treated with either coagulant or coagulant and PAC.

The residual turbidity after DAF was also changed by the dosing position of the PAC (Figure 36). When no PAC was dosed (week 1) the turbidity from the DAF averaged 1.2 ± 0.2 NTU, this increased to 1.8 ± 0.7 NTU when PAC was dosed into tank 3 for the shortest rapid mix period (week 2). Turbidity decreased to 1.3 ± 0.2 NTU for dosing in tank 2. The lowest residual turbidity (0.3 ± 0.2 NTU) was seen for the best dosing conditions for NOM removal, i.e. dosing PAC into tank 1 for the longest rapid mix period. The reduced rapid mix periods did not allow a long enough coagulation time to enable all of the PAC to be incorporated in the floc, resulting in more PAC in suspension and a higher residual turbidity.

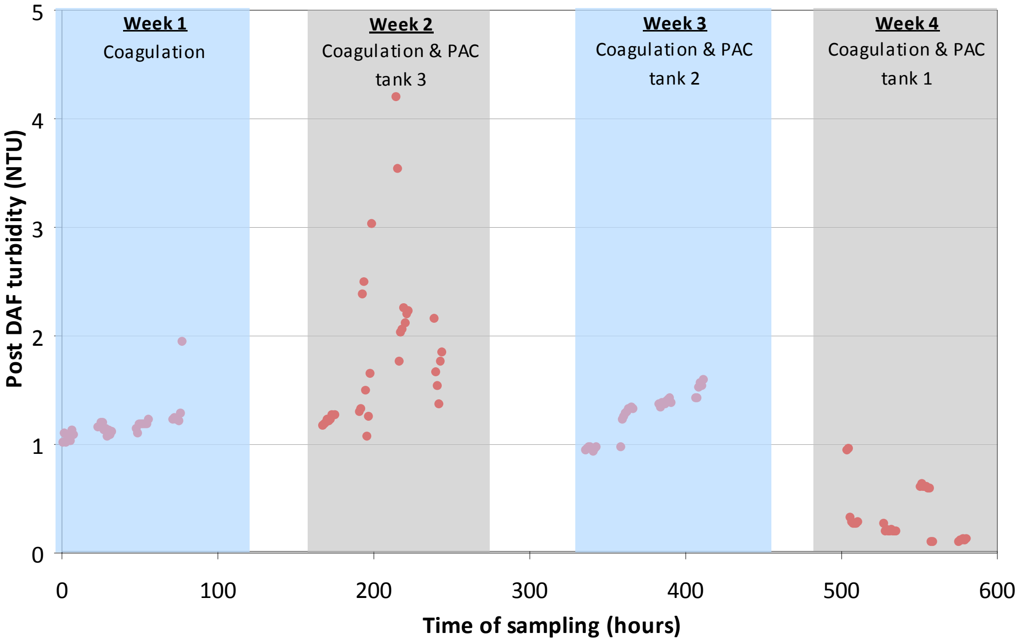


Figure 36. The post-filtered turbidity of water at Ewden WTW that has been treated with either coagulant or coagulant and PAC.

4.10. Pilot Hall Trials

Pilot scale trials were carried out to determine the removal of NOM obtained using coagulation and coagulation with either Pulsorb C or Norit SA Super at the pilot hall at Cranfield University (Figures 37-39). It can be seen from both figures that dosing PAC as well as coagulant removes more NOM than dosing coagulant alone and that Norit SA Super was more effective at removing NOM than Pulsorb C. It can also be seen that when PAC was dosed into the flocculator tank the greatest level of NOM was removed. The mean TOC (mgl^{-1}) for coagulant, coagulant and Pulsorb C and coagulant and Norit SA Super was 5.1, 3.1 and 1.4 respectively. The mean removal for Norit SA Super dosed into a flocculator tank was 0.6mgl^{-1}.

The level of NOM removal based on UV_{254} absorbance for coagulation and coagulation using Pulsorb C and Norit SA Super followed the same trend as for TOC removal (Figure 38). The most effective dosing regime was achieved by dosing Norit SA Super into the flocculator tank giving a mean UV_{254} absorbance of $1.7m^{-1}$. When PAC and coagulant were dosed into the same rapid mix tank Norit SA Super was more effective at removing UV_{254} absorbing NOM resulting in levels of $2.5m^{-1}$ compared to $4.9m^{-1}$ for Pulsorb C. Dosing PAC in conjunction with coagulant was still more effective at removing NOM than coagulant alone which gave a UV_{254} absorbance of $7.1m^{-1}$.

The drawback of dosing Norit SA Super into the flocculator tank was that this condition produced the highest residual turbidity after sedimentation giving a mean turbidity of 11.1 NTU (Figure 39). Dosing just the coagulant, dosing Pulsorb C with the coagulant and dosing Norit SA Super with the coagulant produced turbidities of 4.4, 4.3, and 3.8 NTU respectively.

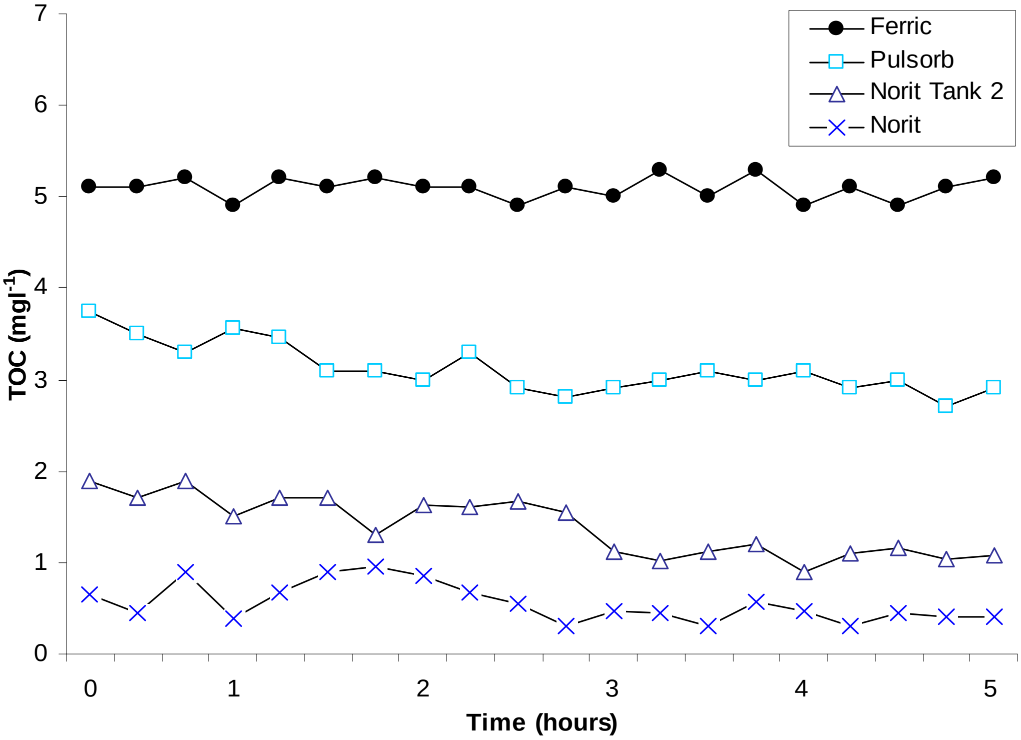


Figure 37. The removal of NOM from raw water based on TOC using coagulant and coagulant with PAC conducted at the pilot hall, Cranfield University.

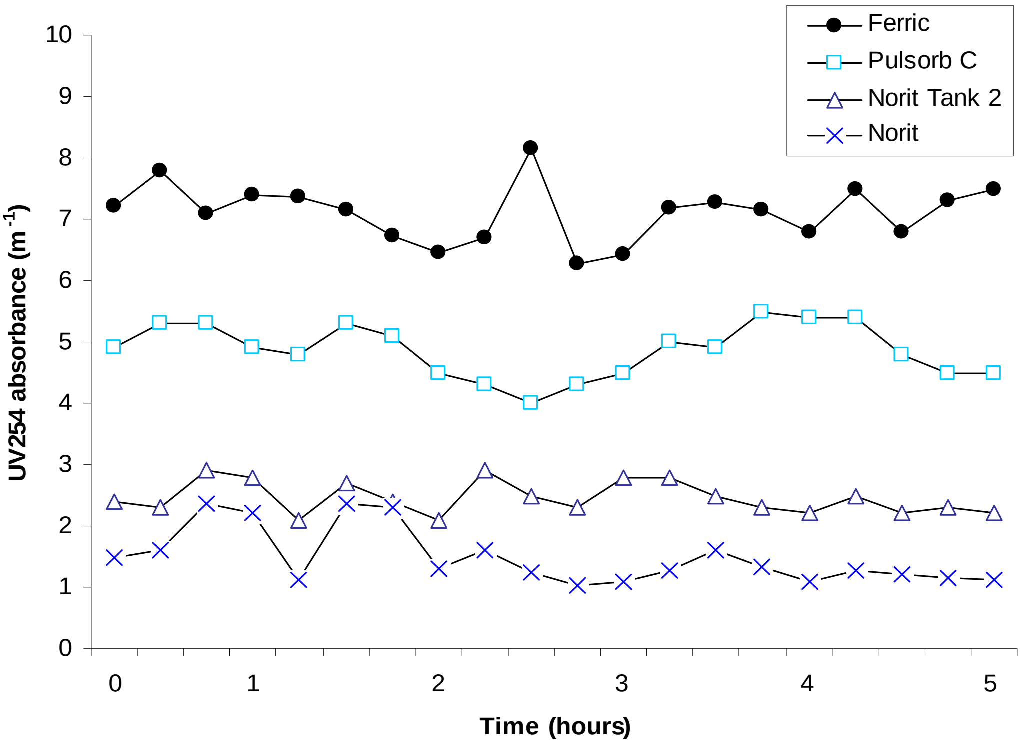


Figure 38. The removal of NOM from raw water based on UV_{254}, using coagulant and coagulant with PAC conducted at the pilot hall, Cranfield University.

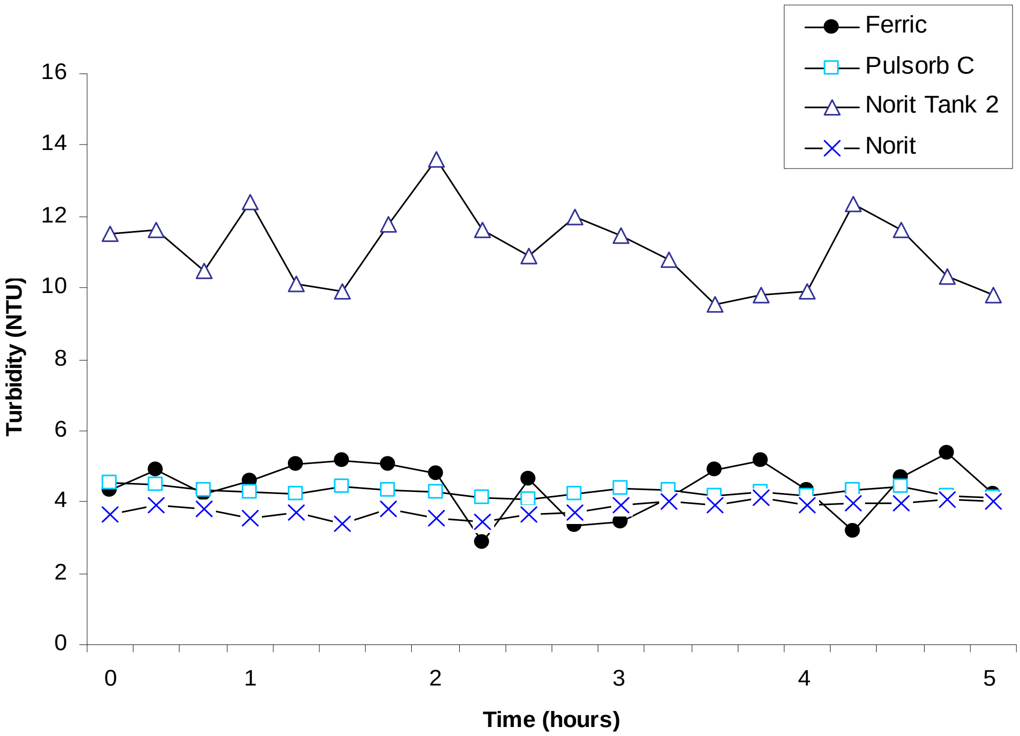


Figure 39. The turbidity of water treated using coagulant and coagulant with PAC conducted at the pilot hall, Cranfield University.

5. Discussion

There are a number of different factors that affect the adsorption of chemicals onto the surface of PAC. The surface characteristics of the PAC are very important. This includes characteristics such as the surface area, pore size and distribution as well as the surface functionality and charge (Reed and Matsumoto, 1991; Smith, 1994; Newcombe and Drikas, 1997; Bjelopavlic *et al*., 1998; Duan *et al*., 2002; Daifullah *et al*., 2003; Patnukao and Pavasant, 2006; Aksu *et al*., 2007; Yin *et al*., 2007).

The three PACs used in this study showed a number of differences with regards to particle size distribution, pore size and surface area (figure 11, high activity PAC (HAPAC) from Norit and Chemviron and one being regarded as being of standard activity PAC (SAPAC) from Pulsorb. The data presented in this study showed that the HAPACs were better at removing NOM than the SAPAC. The equilibrium determination (figures 12, 13), the adsorption tests, (figures 14-17) and the isotherm data (figures 18-23, tables 12, 13) all show that the HAPACs removed more NOM than the SAPAC. The more efficient of the HAPACs was Norit SA Super, which slightly outperformed the Chemviron HAPAC. If removing the most DOC and hence NOM from a system is what is required, then the data presented so far would suggest that this could be best achieved by dosing Norit SA Super as a WTWs.

This study examined the level of removal of NOM using a combination of coagulation, PAC and coagulation with the addition of PAC. A similar study was carried out by Uyak *et al*., (2007) which examined the removal of NOM using PAC dosed at 80mgl^{-1}, coagulant at 100mgl^{-1} and a combination of PAC and coagulant. The main difference between that study and the work conducted in this study was that the pH of both PAC adsorption and the ferric coagulation was not altered, whereas this study looked at a range of different pHs with respect to PAC adsorption.

The results presented by Uyak *et al*., (2007) show that coagulation alone only achieved removal of 45% DOC, whereas PAC adsorption achieved a DOC reduction of 76% . The experimentation that they used was rapid mixing at 150 rpm for 2 min, flocculation at 30 rpm for 10 min, and at 20 rpm for 20 min. PAC adsorption had an equilibrium time of 4 hours, and when dosed in conjunction with the coagulant was added 1 minute into the rapid mix stage. When dosed at the same time PAC adsorption and ferric coagulation removed 84% of NOM. The results presented in this study showed that Norit SA Super at 80mgl^{-1} reduced DOC by 32.7% after 6 hours, coagulation reduced DOC by 88% (table 11), and when Norit SA Super was dosed in coagulated water gave up to 97% DOC removal of NOM (figure 16). While the percentages between the two studies show a degree of variation, the same conclusion can be reached that a combination of PAC dosing and coagulation was more efficient at removing NOM than either regime alone. One possible reason for the changes in percentage removal between Uyak *et al*., (2007) and this study could be due to the character of the water. The increase in percentage of NOM removed observed in this study was due to the fact that there was more NOM to remove and a higher proportion of NOM that was easy to coagulate.

Ewden water had a much higher NOM content than the water used by Uyak *et al*., (2007), which was 15mgl^{-1} DOC versus 5.01mgl^{-1} and 60.1m^{-1} UV$_{254}$ absorbance versus 18.8m^{-1} . This means that there were more aromatic compounds such as that were more likely to be removed by coagulation. Uyak *et al*. (2007) report that coagulation is more likely to remove high molecular weight charged particles such as HA and FA, whereas PAC is more likely to remove low molecular weight mainly uncharged molecules. In their conclusions Uyak *et al*., (2007) suggest that a combination of PAC adsorption and ferric coagulation would be the best dosing regime for the removal of NOM and hence reduction in DBPs.

The data presented in this study is in agreement with the conclusions of Uyak *et al*. (2007). The optimum dosing sequence from the data presented in the bench scale trials (figures 14-27) and the full scale trials (figures 35-39) was that the optimum dosing sequence is to dose PAC and coagulant together and to allow the maximum possible time for mixing. A longer mixing time for the PAC allows a greater reaction time for the NOM to adsorb to the surface of the PAC in order to achieve maximum adsorption. For the PAC used in this study, the maximum adsorption time was observed after six hours (figures 12 and 13). While a six hour mixing time for coagulation is not feasible in a full-scale WTWs (figure 14), it was still observed that increasing the reaction time for both PAC and coagulation from 30 seconds to 90 seconds increased NOM removal from between 45-52% up to 76-83% (figures 24-27).

In laboratory jar test experiments, dosing the PAC before or at the same time as the coagulant provided better removal than dosing PAC after the coagulant (figures 24-27), however if the difference in the period of time between dosing PAC and coagulant was greater than 30 seconds then there was a risk of increased residual turbidity after settlement (figure 26). Dosing PAC after the coagulant resulted in a particularly high increase in turbidity with the most likely explanation being that insufficient PAC was incorporated into the flocs during the coagulation process. Dosing PAC before and at the same time as the coagulant produced a lower turbidity primarily because the PAC could be integrated into the floc during the precipitation reactions during coagulation (figures 33, 34a-c).

Dosing PAC after the coagulant resulted in a greatly increased turbidity in both bench scale and pilot scale trials (figures 14-27 and 35-39 respectively). However, in pilot-scale trials dosing 80mgl^{-1} of Norit SA Super into coagulated water (after the dissolved air flotation stage) showed that a DOC removal of 97%, or UV$_{254}$ removal of 95.9% of NOM could be achieved, albeit with a contact time of 6 hours (figure 16). Dosing PAC after the DAF stage in a water treatment works may yield a greater level of NOM removal but has the significant drawback of requiring a robust treatment stage in order to remove the PAC from solution following treatment. The downstream filtration process could be an option for the removal of the PAC, but even the most robust of filters would be prone to filter blockage from the high particle load and possible filter breakthrough from the small size of the PAC. In addition, at Ewden WTWs, the pH of the water following DAF was raised from pH 4 to 6.7 by the addition of lime which could result in reduced adsorption of NOM and even release of adsorbed NOM back into solution

All of the data presented in this study showed that a more acidic pH produced a greater level of NOM removal. This optimum pH for the removal of NOM was pH 3 which gave the lowest TOC and UV_{254} absorbance.

In principle, the optimum strategy for dosing PAC in combination with coagulation would be to adjust the pH of the raw water to 3 and to add the PAC and allow a considerable contact time of several hours. This could be applied before the coagulation stage that would be carried out under the optimum conditions at a pH of 4 using ferric sulphate. However, this dosing strategy has a number of issues that mean that this strategy is unlikely to be implemented in any WTWs. The low pH would likely cause considerable corrosion to any tanks that the water and PAC are mixed in. This treatment strategy would also require an unfeasibly large tank in order to achieve the several hours of PAC adsorption. There would also be a significant cost implication of altering the pH by so much in a relative short period of time as large quantities of lime and hydrochloric acid would be required. Therefore, the dosing strategy that would be best that can fit into existing treatment plant infrastructure is to dose PAC and coagulant together for the longest rapid mix period under the acidic conditions of the coagulation process (pH 4). The results from both the bench scale and pilot scale trials all show that for operational conditions, dosing PAC and coagulant together and allowing the maximum amount of mixing time would provide the most efficient level of NOM removal and lowest downstream turbidity. Due to constraints of the water treatment works it was not possible to alter the dosing position of the coagulant. However, it is hypothesised, based on bench scale results, that moving the coagulant position to the same place as the PAC dosing would increase the level of NOM removal. This would also require consideration of where the lime dosing should be positioned.

Using PAC as a method to augment coagulation is a viable dosing strategy for the removal of NOM and hence the reduction of DBPs. From a water with a high UV_{254} absorbance ($<100m^{-1}$), coagulation was shown to remove 88% of the DOC of NOM which with the addition of PAC to coagulated water, this could be increased to 97% DOC reduction for this specific type of water. Similarly THM concentrations were also significantly reduced with PAC dosing: the THMFP in untreated water was $194.6\mu gl^{-1}$, which could be reduced by 34.1% with coagulation alone but was reduced by 75.7% with PAC and coagulation suggesting that the addition of PAC augments the coagulation process. The mechanism by which combined PAC and Fe coagulation removes NOM is at this time still unclear. The adsorption time that is needed to remove considerable levels of NOM is greater than the 90 seconds rapid mix given in both pilot and full scale trials. A more reasonable explanation is that the PAC adds to the structural stability and aids in the formation of flocs as seen in figure 33a-b.

Whilst there are a number of alternative dosing strategies that could be employed to remove NOM and lower DBP formation, such as ion exchange (such as MIEX), the results of this study, and the advantages and disadvantages of alternative treatment options (table 4) show that PAC should be considered a viable option for enhanced NOM removal provided the correct PAC is chosen and the best dosing procedure followed. MIEX combined with coagulation may achieve a level of removal comparable to PAC and coagulation (Fu and Symmons, 1990; Owen *et al*., 1993; Newcombe *et al*., 1997; Summers and Roberts, 1998; Bolto *et al*., 2002; Fearing *et al*., 2004) but the cost (particularly the initial capital expenditure) associated with MIEX is far greater than that of PAC dosing. As indicated in this study, the level of NOM increase in the source water is seasonal meaning that the addition of PAC is only towards the latter end of the year. Dosing PAC periodically is easier than starting and stopping an expensive MIEX treatment process that would remain unused for large parts of the year.

6. Conclusions.

There are a number of conclusions that can be drawn from the evidence presented in this work. The conclusions can be divided into different sections based on the type of work that was conducted. The main sections have been designated: 1) Activated carbon performance; 2) NOM removal; 3) Disinfection by-products; and 4) On-site implications.

6.1. Activated carbon performance

The following conclusions can be drawn about the performance of the 3 activated carbons used in this study.

- High activity carbons remove more NOM from water than standard activity carbons based on UV_{254} and DOC reduction.
- Out of the two high activity carbons used, Norit SA Super was capable of removing more NOM than Pulsorb 207 CP-90.
- Decreasing pH caused a greater removal of NOM with pH3 producing the lowest levels of NOM after treatment.
- The most efficient PAC dose, based on the amount of NOM removed in comparison to amount of PAC dosed, was $20mgL^{-1}$.

6.2. NOM removal

When dosing PAC and coagulant to remove NOM the following conclusions were drawn:

- When dosing PAC and coagulant together a longer rapid mix stage produced a greater removal of NOM.
- Dosing PAC after the addition of coagulant resulted in an increased turbidity as the PAC was not incorporated into the flocs.
- Floc formation appears to be improved at bench scale, pilot scale and full scale trials, with the addition of PAC before or at the same time as coagulation.

6.3. Disinfection by-products

Insufficient NOM removal leads to DBP formation and the following conclusions were drawn regarding DBP formation:

- Norit SA Super was the most effective PAC that can be used in conjunction with coagulation to lower DBPs.
- Allowing a longer contact time for coagulation and PAC adsorption produced the lowest THM levels.

6.4. On site implications

This study has a number of implications for WTWs treating moorland water containing high concentrations of NOM that could be used to improve efficiency of NOM removal:

- Dosing Norit SA Super with coagulant may be an effective way of achieving sufficient levels of NOM removal in WTWs when seasonal increase in NOM mean that coagulation alone cannot meet the legislative THM levels.
- Norit SA Super and coagulant could, according to documented literature (table 3), achieve removal equivalent to that of MIEX pre-treatment combined with coagulation.
- The best dosing regime for NOM removal that also effectively removed PAC from the water (and therefore the lowest turbidity) was to dose the PAC and coagulant together and allow the longest possible rapid mix period.
- Dosing PAC at a point downstream of the rapid mix stage, i.e. after coagulation and DAF was an alternative option that would result in even further NOM removal and lower DBP formation. However in reality removing the residual PAC from the system would be problematic and would require a robust filtration stage which is likely to reduce filter run times due to the high particle loading.

7. References

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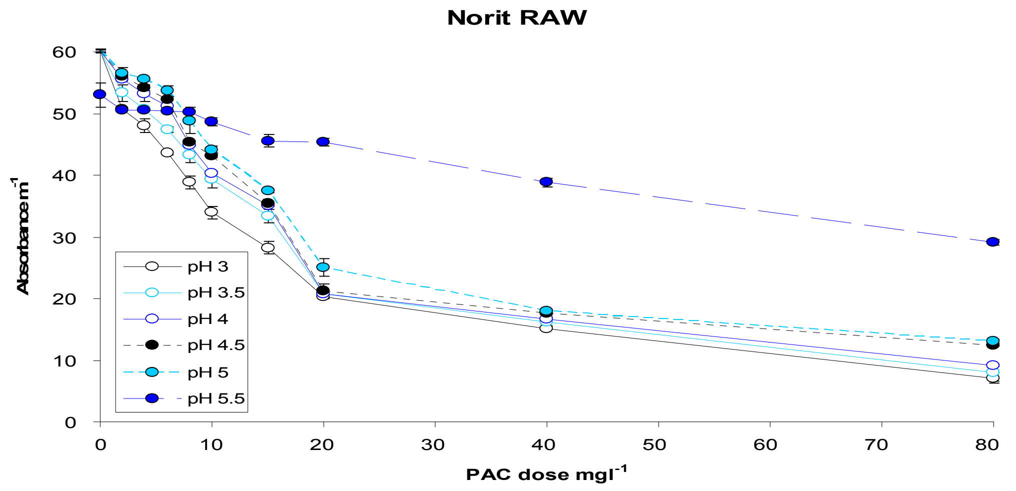
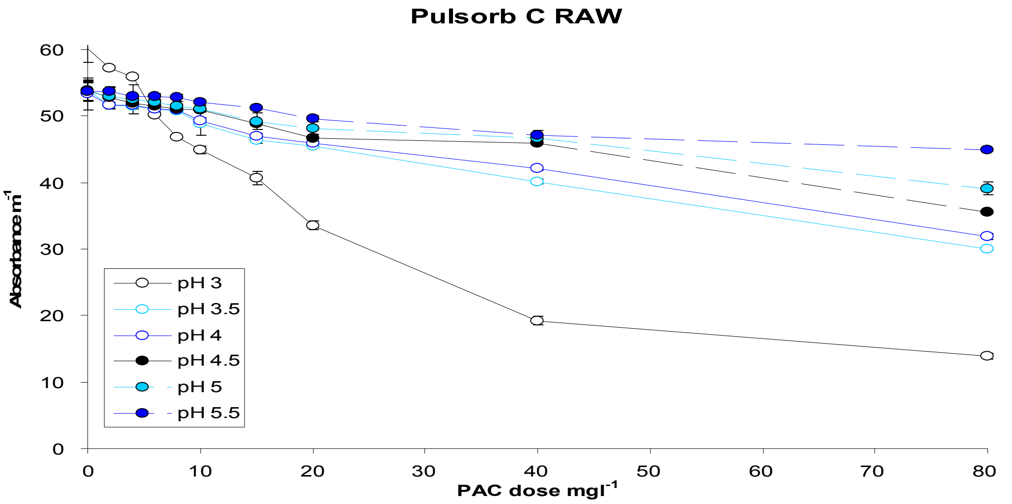
8. Appendix



a.



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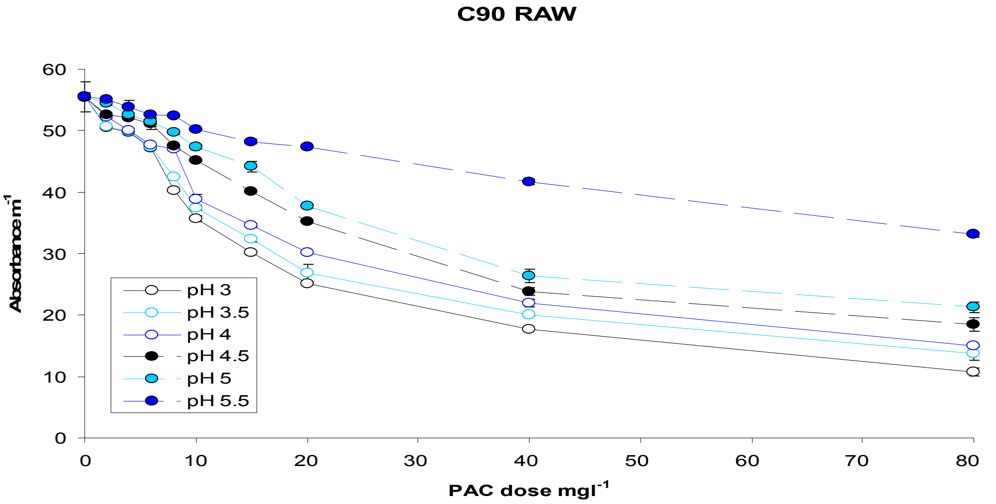
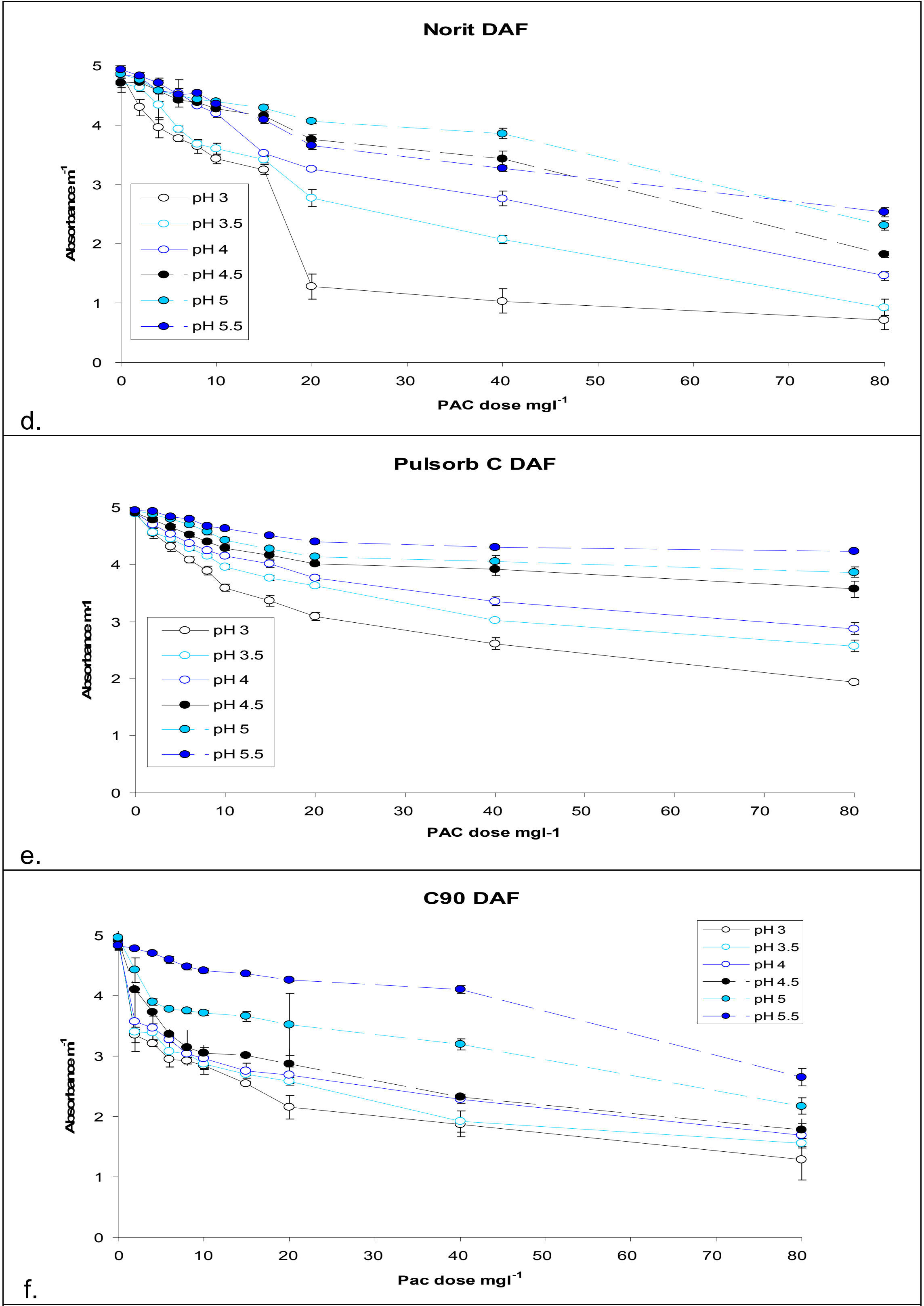
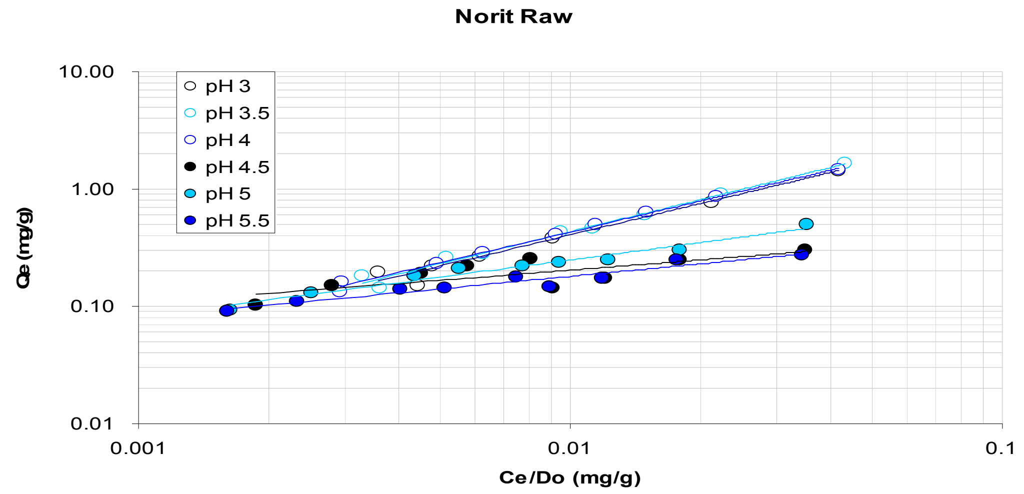


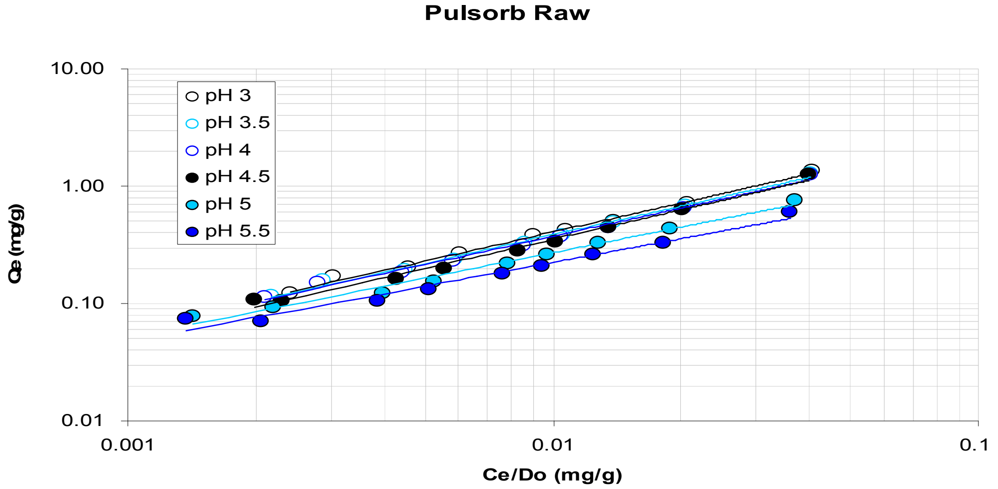
c.



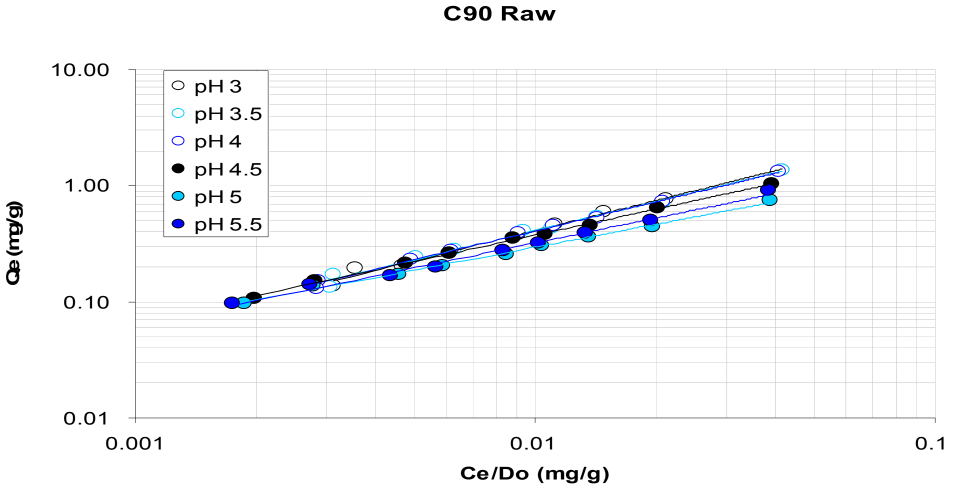
Appendix 1. The UV_{254} absorbance of raw and coagulated water treated with three different PACs at 6 pHs at 10 different concentrations of PAC.


Norit Raw
10.00
1.00
0.10
0.01
Qe (mg/g)
0.001
0.01
0.1
Ce/Do (mg/g)
○ pH 3
○ pH 3.5
○ pH 4
● pH 4.5
● pH 5
● pH 5.5

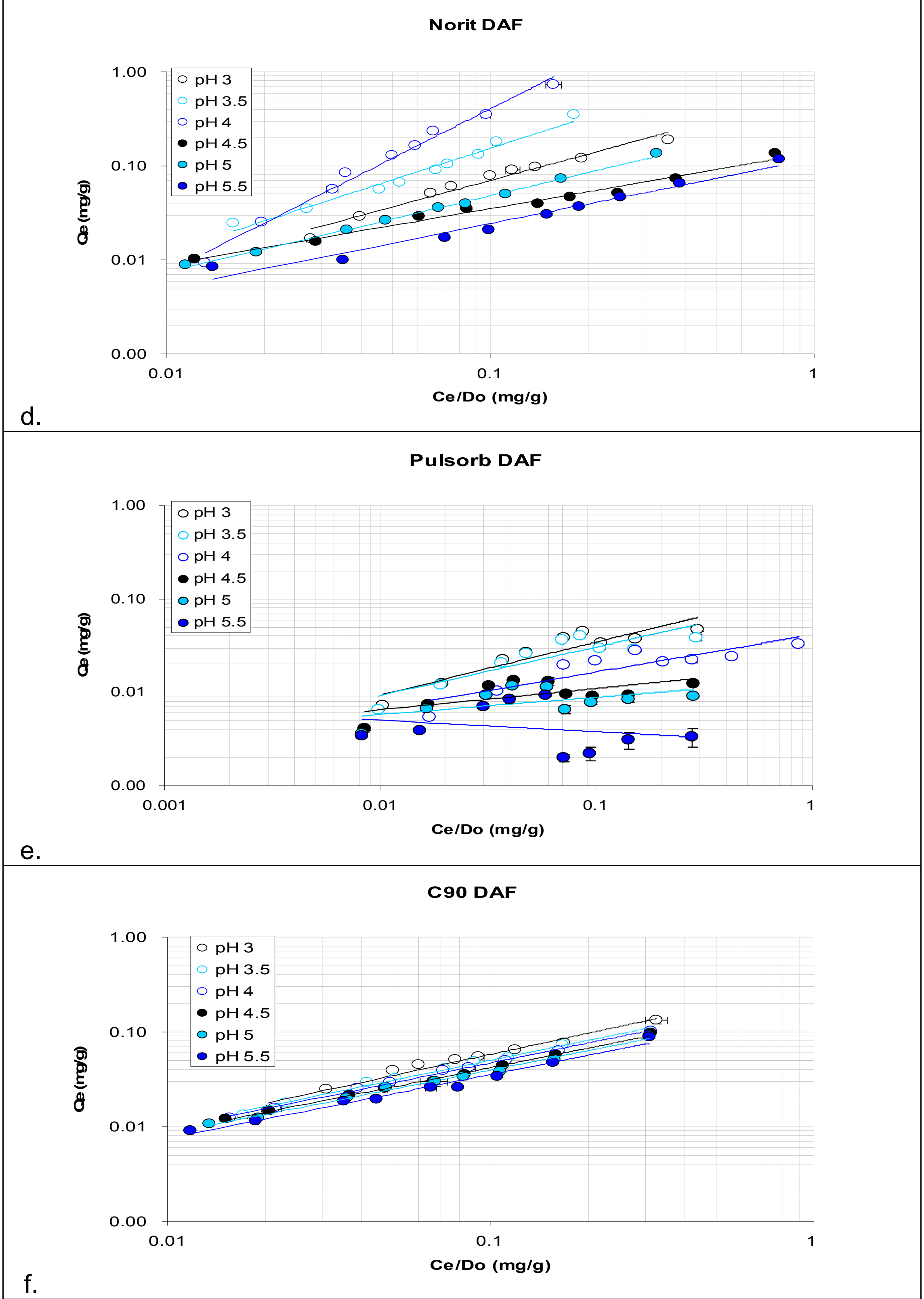
a.


Pulsorb Raw
10.00
1.00
0.10
0.01
Qe (mg/g)
0.001
0.01
0.1
Ce/Do (mg/g)
○ pH 3
○ pH 3.5
○ pH 4
● pH 4.5
● pH 5
● pH 5.5

b.


C90 Raw
10.00
1.00
0.10
0.01
Qe (mg/g)
0.001
0.01
0.1
Ce/Do (mg/g)
○ pH 3
○ pH 3.5
○ pH 4
● pH 4.5
● pH 5
● pH 5.5

c.



Appendix 2. The modified freundlich isotherms of raw and coagulated water treated for three different PACs at 6 different pHs.