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Drinking water purification from natural organic matter by different order addition of alum coagulant and powdered activated carbon

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This thesis is presented for the Degree of

Master of Philosophy (Civil Engineering)

of

Curtin University

March 2020

DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

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ABSTRACT

Combined coagulation with powdered activated carbon (PAC) was considered to be the most effective integrated water treatment process to reduce the dissolved organic matter (DOM) compounds in treated water. Also, the combined water treatment process application fulfils requirements of safe and clean drinking water. The main aim of this study was to evaluate alum coagulation, powdered activated carbon (PAC) adsorption, and the effect of order addition of alum coagulant and PAC to remove natural organic matter in terms of reduction of dissolved organic carbon (DOC), ultra-violet absorbance at 254 wavelengths (UV_{254}) and specific ultraviolet absorbance (SUVA) from an open reservoir of water in the southwest of Western Australia. Moreover, the water treatment process study focused on optimisation of aluminium, PAC dosages and pH. Particularly, the following combined treatment techniques: (i) simultaneous combination of alum with PAC adsorption (Al+PAC), (ii) alum coagulation with subsequent PAC adsorption addition (Al─PAC) and (iii) PAC adsorption with subsequent alum coagulation addition (PAC─Al) processes were studied to enhance natural organic matter (NOM) removal in surface water. Based on experimental data, the simultaneous alum coagulation, Al+PAC, PAC adsorption, Al+PAC, and alum coagulation addition before PAC adsorption, Al—PAC processes had high and similar NOM removal efficiency comparing with PAC adsorption addition before alum coagulant, PAC─Al process. The combined simultaneously (Al+PAC), and subsequent alum coagulation- PAC adsorption (Al—PAC) processes study revealed that the best water purification results were observed by applying 25 mg/L aluminium and 200 mg/L PAC dosages at pH 6.5.

ACKNOWLEDGEMENT

I would like to thank Associate Prof. Anna Heitz for all her aid in all ways by guiding and encouraging me in hard times during this research journey. I am thankful that she has provided me with this opportunity to begin and complete the MPhil research project. I would like to appreciate her vast knowledge and her time, which helped me to complete my research program successfully and her tremendous support in all possible ways. I would also like to thank Dr Dipok Sarker for his vast laboratory experience, which helped me in all laboratory work and many ways. My research would not have been possible without his help in conducting laboratory experiments. My special acknowledgement goes to the Australian Government for the contribution and support of this research through an Australian Government Research Training Program Scholarship. Also, I wish to express my gratitude to my husband for his aid to express research problems and solutions in familiar mathematical notation through MatLab software and my dearest daughter and son for allowing me without complaint to focus on my study. I am endlessly grateful for their patience, back up, and love. Finally, I would like to thank everyone sincerely for their assistance to begin and complete my MPhil research program successfully within and outside the Curtin University.

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LIST OF ABBREVIATIONS

ADWG	**Australian Drinking Water Guidelines**
DBP	**Disinfection By-Product**
DOC	**Dissolved Organic Carbon**
DOM	**Dissolved Organic Matter**
EC	**Enhanced Coagulation**
HAAs	**Haloacetic acids**
HANs	**Haloacetonitriles**
HMW	**High Molecular Weight**
LMW	**Low Molecular Weight**
MW	**Molecular Weight**
NOM	**Natural Organic Matter**
PAC	**Powdered Activated Carbon**
SUVA	**Specific Ultraviolet Absorbance at Wavelength 254 nm**
THMs	**Trihalomethanes**
UV_{254}	**Ultraviolet Absorbance at Wavelength 254 nm**

CHAPTER ONE

1. INTRODUCTION

1.1 Introduction

The order of addition of alum and PAC has been considered one of the most effective integrated water treatment techniques to optimise dissolved organic matter contaminants removal and production of safe and clean drinking water. The aim and the novelty of this study was to investigate the effects of all possible combinations of order addition of alum coagulant and PAC adsorbent to maximise DOC, UV_{254} and SUVA reductions in the treated surface water sample collected from surface water of Western Australia. Therefore, in this study three integrated methods of water treatment based on alum coagulation and powdered activated carbon adsorption were investigated for the removal of natural organic matter from an open surface water reservoir in the southwest of Western Australia. Also, water treatment conditions, such as aluminium and PAC dosages, as well as pH, were optimised by using a single coagulation and PAC adsorption only water treatment processes before the combined water treatment processes studies. The target analytes for water treatment processes optimisation are as followed: dissolved organic carbon, ultra-violet absorbance at 254 wavelength, and specific ultraviolet absorbance. The analytes indicate the effectiveness of natural organic matter (NOM) removal for each testing process. The single and the combined water treatment processes were studied as follows: i) single alum coagulation, ii) PAC adsorption; iii) simultaneous combination of alum coagulation with PAC adsorption, Al+PAC process; iv) alum coagulation prior to PAC adsorption, Al─PAC process; PAC adsorption prior to alum coagulation (PAC─Al). Based on the data from laboratory jar tests, the impact of the order of addition study of alum and PAC revealed that the best water purification treatment was the simultaneously combined Al+PAC water treatment process.

1.2 Aim and Objectives.

The aim of this study was to conduct a series of intensive laboratory experiments to assess the effect of the order of the addition of alum coagulant and PAC to remove NOM from surface water. For a better understanding of the effect of alum and PAC order of addition by combination of coagulation and adsorption processes, the DOC, UV_{254} and SUVA removal values were measured and compared to the single alum coagulation and single PAC adsorption treatment processes. The research objectives were achieved by optimising pH, aluminium and

PAC doses for maximum reduction of the water quality parameters (DOC, UV_{254}, and SUVA). Also, the cost-effectiveness were evaluated for the optimised water treatment systems.

1.3 Significance of the Study

Dissolved NOM fractions are naturally occurring macro- and micro molecules and they are ubiquitous in natural water systems. Increased concentrations of high molecular and low molecular weight NOM compounds, like humic and non-humic substances in surface water is the reason disinfection by-products (DBPs) formation in treated water which have negative impact on the quality of drinking water (Uyak et al. 2007; Takdastan and Eslami 2013). DBPs such as trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs) are formed during disinfection process with chlorine (Panyapinyopol et al. 2005). The reaction of NOM with chlorine is expressed as follows: organic matter + free chlorine → THMs + HAAs + HANs + cyanogen halides + other DBPs (Panyapinyopol et al. 2005). The Australian drinking water guidelines (ADWG) for the maximum level of THMs in treated water is 250 µg/L. There is a need to meet water treatment requirements. HAAs next important DBPs which are formed by the reaction of NOM with disinfectants, like chlorine, chloramine, chlorine dioxide and ozone (Kimura et al. 2017). According to the researchers Pressman et al. (2010) and Parvez et al. (2011) around 25% of total halogenated DBPs are formed during water chlorination. THMs and HAAs are regulated DBPs in drinking water, while HANs are an unregulated class of nitrogenous disinfection by-products (N-DBPs). N-DBPs are produced by NOM reaction with chlorine, chloramine, or chlorine dioxide (Muellner et al. 2007). The HANs are more toxic than carbon - based DBPs, such as HAAs. The class of N-DBPs include nitrosamines, cyanogen halides, haloacetonitriles, haloacetamides and halonitromethanes. Limited research data exists for the other DBPs classes (Bond et al. 2011). Thus, surface water must undergo various treatment processes to remove NOM and precursors of harmful DBPs, derived from hydrophobic (high molecular weight) and hydrophilic (low molecular weight) fractions. The strong hydrophobic fractions are aquatic humics, such as humic and fulvic acids (Edzwald 1993). It is reported in the latest research work, that the natural colour in water is caused by aquatic humics fractions. Hydrophilic fractions associated with hydroxyl acids, sugars, sulfonics, and other low molecular weight organic compounds (Edzwald 1993). Generally, coagulation water treatment process is effective at removing hydrophobic fraction rather than hydrophilic (Edzwald 1993). Takdastan and Eslami (2013) reported that the coagulation process, in conjunction with PAC adsorption, can reduce coagulant consumption

and DBP formation after drinking water chlorination. Najm et al. (1991) outlined that a significant decrease in water treatment cost can be achieved by decreasing coagulant and PAC dosages. For example, the reduction of PAC dose from 50 mg/L to 10 mg/L, the water treatment cost will significantly drop. For instance, if a fixed plant (a plant attached or situated on the land whether or not it is removable) operating at full capacity by treating 10 million gallons water per day (mgd) and saving 10 mg/L of PAC, the saving would be $138,700 per year (Najm et al. 1991). Therefore, there are practical ways to decrease PAC dosage and to increase PAC adsorption capacity by choosing the right type of PAC. Also, there are the ways to increase PAC adsorption capacity are pH optimisation, changing ionic strength, optimisation of contact time with organic contaminants, mixing procedure, and reducing residual chemicals after the complete coagulation stage (Najm et al. 1991. The PAC use will decrease the chemical consumption and metal salt concentration in treated water (Bolto 1995). The order addition of alum and PAC could be promising in terms of dosage of coagulant, level of residual aluminium in treated water, the volume of sludge, and water treatment cost reduction by 25-30 %, respectively. (Bolto and Gregory 2007, Nozaic et al. 2001). Thus, NOM of the high molecular weight (HMW), medium molecular weight (MMW), and low molecular weight (LMW) fractions reduction can be enhanced at low aluminium and PAC dosages by studying the order addition of alum coagulant and PAC.

1.4 Organization of Thesis

Ten chapters are included in the proposed thesis. The first chapter comprises an introduction to the thesis study. Chapter one consists of the introduction, aims and objectives, significance, and the organisation of the thesis. Also, it provides a short description of NOM in terms of DOC, UV_{254}, and SUVA. There is pH, alum, and PAC dosages optimisation mentioned as complementary goals for the following water treatment processes: single alum coagulation, PAC adsorption, and combined coagulation with PAC processes, such as Al+PAC, Al—PAC, and PAC—Al. The aim, objectives, and significance of the study have presented in this chapter.

Chapter two is a literature review related to the research in the field of NOM removal from drinking water by using combined coagulation with PAC water treatment processes. The discussed topics include single coagulation and PAC adsorption processes as well as the combined coagulation and adsorption processes, hydrophobic humic and hydrophilic non-

humic compounds, and water quality parameters (pH, DOC, UV_{254}, and SUVA). Australian guidelines for DBPs limits have also reviewed in this chapter.

Chapter three describes the materials and methods used in this research project.

Chapter four includes a single alum coagulation process study, jar test experimental results, and conclusions.

Chapter five describes the PAC adsorption process jar test data and conclusions. In chapter six presents the finding of the simultaneous combined alum and PAC processes. For example, pH and PAC dosage effect on the surface water treatment. Chapter seven examines the combined alum coagulation prior to PAC adsorption process.

Chapter eight discusses experimental data of the combined PAC adsorption before the alum coagulation process. Each of these chapters from Chapter four to Chapter eight comprises a brief introduction, the results, and conclusion sections.

Chapter nine examines the cost estimation of optimised water treatment processes.

Chapter ten discusses the conclusions of the studies and provides recommendations for future research.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Introduction

Water from an open reservoir used as drinking water should be of acceptable purity and safe for consumers (Carriere et al. 2009). An important drinking water quality parameter is the concentration of dissolved organic carbon which can indirectly cause health problems and can be responsible for unpleasant tastes and odours. DOC is defined as high and low molecular weight dissolved natural organic compounds, including fulvic and humic acids, carbohydrates, and amino acids (Uyak et al. 2007) with nominal organic matter fraction sizes < 0.45 micron (Buffle and Leppard 1995). According to Amy et al. (1992) the HMW compounds, such as humic acids characterized as high molecular size (e.g., 5000 to 10000 Daltons) organic matter compounds which can be removed from the water source by coagulation water treatment process. The organic carbon material of medium molecular weight and size (e.g., 1000 to 5000 Daltons) would be amenable to remove by adsorption water treatment process. While low molecular weight and size (>1000 Daltons) fulvic acids are almost hydrophilic compounds and not responsive to removal by coagulation or adsorption. Natural organic matter characterised as DOC discharge from living and decomposing biota (Mopper et al. 1996), which primarily consists of hydrophilic, acidic, and humic substances (Koch et al. 2005). It has been reported that about 45% of DOC in surface water consist of hydrophobic humic fractions (Thurman 1985). NOM occurring in water can be divided into two groups: non-humic fractions, such as amino acids, hydrocarbons, carbohydrates, fats, waxes, resins, low molecular acids, and humic fractions (i.e. humic and fulvic acids). Also, NOM content can have different characteristics depending on the origin of the source water. Furthermore, NOM compounds classified as hydrophobic and hydrophilic organic fractions. The aromatic fraction of NOM can be a significant reacting component for DBPs formation and its composition varies with different sources (Fabris et al. 2004). Due to the complexity of NOM compounds, some studies have also divided them into various molecular weight organic fractions (Zhao et al. 2006). NOM compounds removal is essential due to their propensity to form potentially carcinogenic DBPs (Navalon et al. 2008). The hydrophobic and aromatic fractions have higher tendencies to form disinfection by-products, such as THMs and haloacetic acids (HANs) than hydrophilic compounds. Therefore, the hydrophobic compound's removal from surface water is particularly necessary (Panyapinyopol et al. 2005).

Small particulates that comprise colloids, including colloidal NOM pollutants, do not settle naturally by gravity. Therefore, for their removal from water require enhanced coagulation or adsorption, leading to the development of new approaches for the removal NOM from surface water. High molecular weight hydrophobic compounds are largely removed by alum coagulation, and this fraction controls the alum dosage demand because of its high charge density which is due to negatively charged carboxylic acid organic functional groups (Szlachta and Adamski 2009). The low molecular weight hydrophilic compounds are less able to be removed by coagulation due to their lower charge density (Fabris et al. 2004). The combined alum coagulation with PAC adsorption process has been used as an improved water treatment process for DOC, UV_{254}, and SUVA reduction than alum coagulation by itself (Najm et al. 1998). The impact of pH and PAC dose on the efficiency of the simultaneously combined coagulation-adsorption process was investigated at a fixed aluminium dose of 25 mg/L. The aluminium dose of 25 mg/L was chosen based on a single alum coagulation jar test experimental results Figs (4.4 and 4.7). Previous studies have shown NOM removal from drinking water using a combination of alum and PAC (Carriere et al. 2009). However, there are no studies that have investigated the impact of the order addition of alum and PAC for maximum DOC and UV_{254} reduction in the treated surface water samples.

2.2 Surface water treatment processes

The application of water treatment processes, such as a single alum coagulation and PAC adsorption by itself are not sufficient for the high level of NOM, taste, and odour removal from surface water. The reasons can be an increased level of NOM, the nature of the NOM occurring in water, as well as high requirements for DBPs precursors' removal. Single alum coagulation process removes HMW fractions of NOM (Szlachta and Adamski 2009). Single PAC adsorption process is often used for LMW species of NOM removal (Uyak et al. 2007). Furthermore, an increase in the removal of HMW and LMW fractions of NOM were achieved by applying the combined enhanced coagulation with PAC adsorption process. The effectiveness of the single coagulation, PAC adsorption and combined coagulation with PAC adsorption processes were determined by measuring DOC, UV_{254}, and SUVA parameters. SUVA reduction tends to decrease significantly by adding PAC as a coagulant aid (Szlachta and Adamski 2009). The trend of coagulation mechanism can depend the ligand ratio (OH^-/organic ligand concentration) and the affinity of the ligand of NOM (Edzwald and Van

Benschoten 1990). The ligand ratio OH-/organic ligand concentration can be affected in the coagulation process by order of the chemical additions (Edzwald and Van Benschoten 1990). Simultaneous addition of alum coagulant and base for pH adjustment will possibly increase aluminium hydroxide precipitates and an adsorption mechanism (Edzwald and Van Benschoten 1990).

In contrast, sequential addition of alum coagulant before base addition should favour complexation of aluminium species with organic ligands (Edzwald and Van Benschoten 1990). Therefore, it was suggested that order addition of alum coagulant and PAC could increase NOM removal by using combined coagulation with PAC adsorption process. The order of chemical additions in coagulation treatment appears to be influential in some cases (Edzwald and Van Benschoten 1990, Vik et al. 1985). Although the aspect of different order addition of alum coagulant and PAC on the reduction of NOM has not been studied previously and no research investigation was published to our knowledge.

2.2.1 Alum coagulation

Enhanced coagulation water treatment process can be beneficial for removing hydrophobic organic compounds over hydrophilic fractions of NOM, and HMW compounds over LMW materials (Edzwald 1993). Alum $Al_2(SO_4).18H_2O$ has been most widely used coagulant for drinking water treatment (Matilainen et al. 2011). NOM removal using alum coagulant can occur through hydrolysis, complexation precipitation or adsorption reactions (Edzwald 1993). The coagulation water treatment process was successfully used for the removal of higher molecular weight organic materials. According to previous research (Glaser and Edzwald 1979), anionic functional group of humic acids were naturalised by cationic function groups of alum to form cross-linked molecules by electrostatic forces. The reduction of NOM by alum coagulation was succeeded through precipitation of soluble organic species by soluble aluminium sulphate species (Semmens and Field 1980). Moreover, the degree of NOM removal depends on both water characteristics and operating chemical and physical conditions. For example, pH, chemical dosage and mixing speed (Shen and Chaung 1998). The character of the NOM in water is an essential factor for determining its treatability (Chow et al. 2004). More significant NOM reduction was achieved for a surface water sample with a high concentration of HMW humic substances (Chow et al. 2004, Shen and Chaung 1998). Lower NOM removal was observed for a water sample with a high level of LMW non-humic organic

compounds (biopolymers, nucleic acid residues, carbohydrates, and fats) (Chow et al. 2004, Shen and Chaung 1998). Many reports based on research investigation suggested that the enhanced alum coagulation process improves NOM removal (Cheng et al. 1995, Edzwald and Van Benschoten 1990, Uyak et al. 2007, Volk et al. 2000, Wang et al. 2002). Thurman (1985) noted that a little research was studied on LMW hydrophilic fraction removals, which are most likely to form a high percentage of DOC in surface water. Croue et al, (1985) reported that alum coagulation better removes HMW hydrophobic fraction of NOM than LMW hydrophilic fraction. Edzwald (1993) proposed two guidelines for DOC reduction. First, if the raw water sample is composed of the high level aquatic humic substances than the water has a high SUVA value, and 50% or greater DOC removal should be expected from such water sample. Next, if the water sample is composed of the low level aquatic humic compounds then the water sample has a relatively low level of SUVA. Therefore, DOC reduction from such water sample will be achieved less than 50%. Also, Edzwald (1993) claimed that if the water sample has a SUVA value less than 3 then the DOC reduction will occur around 30% or less. The experimental data observed in previous research (Collins et al. 1986) showed that THM reactivity increases with every increasing level of the higher molecular weight organic compounds. The research leads to a suggestion that the most reactive DBP precursors are removed during alum coagulation treatment. Also, according to Collins et al. (1986), HMW hydrophobic fractions of NOM more reactive in generating THM precursors in the Grasse River Water. Also, the optimised and enhanced alum coagulation, flocculation, and precipitation water treatment techniques were evaluated by DOC, UV_{254}, and SUVA removal from surface water (Alexander et al. 2012). pH optimisation study to maximize NOM removal from the water sample has the most significant impact than type and dosage of a coagulant (Pruss 2015).

Matilainen et al. (2010) reported that high molecular mass (HMM) species are hydrophobic fractions of NOM. Water resources with HMM species require a low coagulant dose for NOM removal because the removal mechanism expected to be charge neutralisation (Matilainen et al. 2010). Also, the HMM hydrophobic fractions are considered to be aromatic compounds that can be readily removed by coagulation than LMW hydrophilic fractions. The HMW hydrophobic compounds are organic materials with negative charge because of the presence of carboxylic and phenolic groups as a mixture of the complex NOM materials. Enhanced coagulation water treatment process has been previously reported as water treatment which tends to decrease the HMW hydrophobic compounds.

2.2.2 PAC adsorption

Historically, PAC has been used to monitor the odour producing organic compounds and to reduce DBPs in drinking water (Najm et al. 1991). The NOM contaminants removal from surface water primarily depends on the source water quality which defines the concentration of PAC required to achieve the desired NOM reduction, as well as type, and a dose of PAC (Kristiana et al. 2011, Najm et al. 1991). The characteristics of PAC, such as pore structure and high surface activity are responsible for high NOM removal efficiency (Joseph et al. 2012). The compatibility of the molecules to absorb on an adsorbent (PAC) is essential compared to its affinity for water (Weber and Vliet 1981). PAC adsorption water treatment process has an advantage over the other methods because of its simplicity to operate and no investment is required to redesign or rebuild the water treatment plants. Laboratory-scale PAC adsorption tests were conducted for NOM removal and the molecular weight distribution analysis by using the same apparatus as for coagulation process (Ho et al. 2012). In this investigation it was observed that the PAC with a larger volume of pores was more effective in DOC and UV_{254} removals. Also, the kinetics of adsorption of NOM by the PAC were slow since the reduction of NOM was higher at equilibrium time of about three days (Ho et al. 2012). However, PAC removes medium- and low molecular weight NOM, involving dissolved organic carbon species in water with low SUVA value (Ho et al. 2012).

The PAC adsorption test results acquired from tests performed by Shen et al. (1988) to remove nonpurgeable dissolved organic carbon (NPDOC) from drinking water source revealed that PAC removes 60% of NPDOC, while enhanced coagulation removed 40% only. PAC adsorption process was selected as the preferred and affordable technology to improve NOM reduction from the water reservoir in the southwest of Western Australia because of the high level of DOC concentration (ranging from 20 to 40 mg/L) in the water (Kristiana et al. 2011). Furthermore, PAC has been used in combination with coagulation treatment to increase the overall removal of NOM (Kristiana et al. 2011, Najm et al. 1991, Uyak et al. 2007). Incorporation of a small amount of 50 mg PAC/L allowed to decrease by 50% THM formation potential, as well as the coagulant dose (Álvarez-Uriarte et al. 2010). In the research report by Alvarez-Uriarte et al. (2010) single PAC adsorption water treatment experimental data revealed that a large amount of lower and average molecular weight fractions of NOM were removed. Also, in the same research was reported a slight reduction of LMW fractions of NOM, while HMW organic materials reduction increased by using simultaneous addition of PAC with polyaluminium chloride (Álvarez-Uriarte et al. 2010).

The particle size distribution of PAC is important because the smaller PAC particles adsorb NOM more rapidly than large PAC particles. Adsorption at a low pH probably will increase the adsorption capacity of PAC particles because a large amount of NOM contaminants are weak acids. At a high pH, some NOM compounds can efficiently become ionised to turn into a more hydrophilic fractions (Najm et al. 1991).

2.2.3 Simultaneously combined alum coagulation with PAC adsorption process

The combination of coagulation and PAC adsorption processes have been found to enhance NOM removal in terms of DOC, UV_{254}, and SUVA in both laboratory study and at water treatment plant (Alexander et al. 2012). In a laboratory-scale study, Alvarez-Uriarte et al. (2010) demonstrated that the removal of THM precursors increased from 40% to 70% by applying a simultaneous enhanced coagulation (EC) with PAC, EC+PAC process. Simultaneous combination of alum coagulation with PAC adsorption is a straightforward option to remove THM formation from drinking water because no additional mixing tank required. Some THMs have been identified as genotoxic, mutagenic, and carcinogenic disinfection by-product compounds (Xiao et al. 2009). Uyak et al. (2007), demonstrated that supplementing enhanced coagulation with PAC adsorption also increased the reduction of DOC to 76%. In the research study by Uyak et al. (2007) it was reported that PAC removes uncharged and LMW fractions of NOM.

2.2.4 Alum coagulation prior to PAC adsorption process

The combined iron based coagulant addition before PAC, $FeCl_3$—PAC process was studied by Zhang et al. (2013). According to Zhang et al. (2013), the combined water treatment $FeCl_3$—PAC was more effective compared with the PAC addition before iron chloride, PAC--$FeCl_3$ process. The coagulation subsequent adsorption process was proposed as the optimum combined process for NOM reduction. The removal of DOC by 70 ± 10% was observed by enhanced coagulation followed by PAC adsorption system (Watson et al. 2015). By applying the combined coagulation-adsorption process, the overall total chlorinated THM and HAA reduction were achieved by 80% and 85% (Kristiana et al. 2011). However, the increase of bromide to DOC (Br: DOC) ratio was also noticed in the research (Kristiana et al. 2011). According to Uyak et al. (2007) DOC removal increased from 45% to 76% by applying EC—

PAC water treatment process. Also, Takdastan and Eslami (2013) reported that coagulation process application prior to PAC resulted in noticeable polyaluminium chloride and TOC reduction.

2.2.5 PAC adsorption before alum coagulation

The combined PAC adsorption before alum coagulation process study showed a lower efficiency of DOC reduction in treated wastewater (Zhang et al. 2013). The combination of PAC—EC process successfully removed 78% of TOC in treated water. Also, the THM concentration level formed as a by-product during chlorination was reduced by 80% using PAC—EC process (Najm et al. 1998). Thus, the reduced TOC level by applying the combined PAC—EC process allowed to decrease the amount of chlorine that was needed to disinfect water.

2.3 Effect of coagulant dose and pH

The efficiency of the coagulation water treatment process depends on operational factors, such as coagulant dose and water pH (Pruss 2015). Pruss (2015) reported that pH has more considerable influence on NOM removal than a coagulant dose. Many researches showed that the pH and coagulant dose have a significant effect on the reduction of DOC from water (Dempsey et al. 1985, Semmens and Field 1980). Type and concentration of NOM in water can also control coagulant choice and coagulant dose (Edzwald 1993). Using alum coagulation water treatment, 50% of DOC reduction was achieved from the Mississipi River at optimum pH (Semmens and Field 1980). Vik et al. (1985) reported that 75% of DOC fractions were removed from a Norwegian lake using the same chemical conditions (pH and alum dose). There is a correlation between pH, coagulant dose, and coagulation mechanism was reported by Edzwald (1995). The cationic charge of aluminium solids increases with decreasing pH level of the water sample. Moreover, NOM adsorption on aluminium hydroxide solid surfaces increases (Davis and Gloor 1981).

Sorption of NOM onto the precipitated metal is a result of physical and chemical forces between $Al(OH)_3$ solid surface and negatively charged NOM species. The pHzpc (the pH of zero points of charge) of the $Al(OH)_3$ solid surface was considered to be 8.0 (Stumm and Morgan 2012). According to previous researches, the optimum pH by using alum coagulant

various from 5.0 to 6.0 (Pruss 2015, Szlachta and Adamski 2009, Volk et al. 2000). Volk et al. (2000) reported that the optimum pH for alum coagulation varies from 5.0 to 6.0. Edzwald (1990) investigation of natural organic matter reduction involving alum coagulation demonstrated that maximum reduction of NOM takes place at a pH level between 5.0 and 6.0.

Also, Matilainen et al. (2010) showed that the high molecular mass polymers formed at a pH higher than pH=6.3 are hydrolysis products (which is the pH of solubility of alum), while at a pH lower than 6.3 the hydrolysis products are medium polymers or monomers. Edzwald (1993) stated that the solubility of Al increases at pH below 6.2 and decreases at pH higher than 6.2. Alum coagulation can remove DOC through one of two mechanisms: 1) adsorption of DOC fractions onto aluminium hydroxide floc or 2) insoluble complexes formation through charge neutralisation (Cheng et al. 1995). Typically, the charge neutralization mechanism is predominant at higher pH and a higher aluminium dosage, while the latter mechanism is dominant at lower pH and lower aluminium dosage (Cheng et al. 1995). Also, according to the Cheng et al. (1995) investigation, optimum pH for maximum NOM removal is in the range of 5.0 to 6.0 when alum is used as coagulant. pH control plays a dominate role in NOM fractions removal from the surface water sample by coagulation treatment (Chow et al. 2009). However, DOC removal by alum coagulation depends on both pH and character of NOM pH (Chow et al. 2009). Chow et al. (2009) demonstrated that the optimum pH range was between 5.0 and 6.0 for DOC removal by alum coagulation. While Matilainen et al. (2010) reported that the optimum pH range for alum coagulation between 5.0 and 6.5. In previous research investigation (Edzwald and Van Benschoten 1990) pH=5.5 was defined as optimum pH for humic substances removal by using alum coagulation. Also, the coagulation test results showed that the elevated level of humic substances reduction were achieved at pH higher than pH=5.5 (Edzwald and Van Benschoten 1990). Based on the literature review, the expected optimum pH was between pH range of 5.0 and 7.0, while the expected optimum aluminium dosage was between 5 - 100 mgAl/L. Also, the water temperature and mixing conditions have a tremendous influence on water treatment process.

2.4 Correlation among DOC, UV_{254} and SUVA

The linear correlation of DOC to UV_{254} was found for the surface water samples (Szerzyna et al. 2017). The relationship observed between DOC (TOC), and UV_{254} can give a general idea

of the efficiency of the alum coagulation treatment for DBPs removal (Cheng et al. 1995). In previous research, the achieved TOC removal rates were 26 and 78% (Chadik and Amy 1983). Dissolved organic carbon in the surface water is a complex mixture of molecules of benzenoid aromatic and unsaturated aliphatic compounds that absorb ultraviolet light (Brandstetter et al. 1996). The UV_{254} is used as a water quality parameter to measure UV_{254} adsorbing compounds in the water sample. Furthermore, the substantial effort was made to indicate that SUVA is a good predictor of NOM aromaticity and its reactivity with alum coagulant and chlorine. SUVA was estimated as a sample UV_{254} value divided by the DOC and multiplied by 100 (L/mg-m) (Archer and Singer 2006, Edzwald 1993). Archer and Singer (2006) reported that water with high SUVA value will have high level of DOC compounds. The DOC reduction can be achieved through combined coagulation and PAC adsorption water treatment process, respectively. A low SUVA value signifies that water contains mainly hydrophilic and LMW compounds with low charge density ions (Archer and Singer 2006). In contrast, a high SUVA value indicates that NOM in water is composed primarily of hydrophobic and HMW organic compounds with high charge density ions (Knight et al. 2012, Matilainen et al. 2011). The hydrophobic and HMW fractions of NOM became more critical than hydrophilic organic compounds because of the reaction with chlorine to form DBPs. However, hydrophilic and LMW organic compounds also can react with bromine and iodine to form harmful DBPs during water chlorination process (Matilainen et al. 2011). Therefore, both hydrophobic and hydrophilic contaminants of NOM need to be removed from surface water. Edzwald (1993) underlined that measured SUVA value can be used to evaluate whether the NOM fractions are high or low hydrophobic acids and to evaluate DOC concentration in the water sample. According to Archer and Singer (2006) the waters with the high level of NOM are consist mainly of HMW aromatic organic compounds which are UV_{254}-absorbing organic materials with high ability to react with alum coagulant and precipitate as flocs. Besides, a strong relationship was reported between DOC reduction and alum dose (Edzwald 1993, Archer and Singer 2006). Also, according to the authors, a relationship exists between the raw water SUVA value and NOM compounds removal rate - the higher the SUVA, the higher the effectiveness of coagulation. In previous research was reported that the concentration of DOC in the water sample proportional to water SUVA value (Edzwald et al. 1985, Singer et al. 1981). In addition, the researchers noticed that by measuring SUVA value can be attained information whether the water sample was composed of high level or low level of humic organic substances (Edzwald and Van Benschoten 1990). It was shown that the water samples with high SUVA values have a high concentration of humic substances. Data presented by Edzwald and Van Benschoten

(1990) revealed that humic acids have a SUVA value between 4 and 5, while fulvic acids have SUVA value between 5 and 7.5. The water samples with SUVA less than 3 indicate that these water samples consist of DOC, which is low in humic compounds and high in non-humic substances. In the latest case, it presumed that these waters are less aromatic, relatively hydrophilic and primarily have LMW fractions compared with water samples with SUVA values higher than 3 ($4 \leq SUVA \leq 5$). This type of water requires enhanced coagulation with some supplementary water treatment process. For example, the combination of an alum coagulation and PAC adsorption processes. PAC adsorption process can be used simultaneously or sequentially with alum coagulation to improve the further reduction of LMW and hydrophilic fractions of NOM. Thus, the surrogate parameters of NOM, such as DOC, UV_{254}, and SUVA were measured to determine the optimal order of adding alum coagulant and PAC. Jar test experiments were carried out with subsequent DOC and UV_{254} analysis of treated water samples using single and combined coagulation and adsorption processes.

In the current research, the effect of the order of addition of alum coagulant and PAC was investigated, and integrated coagulation with PAC adsorption water treatment processes were studied for a water source from a surface water reservoir in the southwest of Western Australia. To determine the NOM concentration in the surface water sample, DOC was measured as a surrogate for NOM compounds. The UV_{254} absorbance value was measured to determine the UV_{254} absorbing organic compounds (Marhaba et al. 2000), and SUVA value was calculated to indicate the aromaticity of the water (Wong et al. 2007).

CHAPTER THREE

3. MATERIALS AND METHODS

3.1 Water sample

Surface water samples were supplied by the local water utility in the laboratory large containers from an open surface water reservoir in the southwest of Western Australia. The raw water source picture is presented in Figure 3.1, and the surface water sample quality shown in Table 3.1. All water samples were stored in a fridge at temperature +2 ^{0}C.

Figure 3.1. Surface water reservoir in the southwest of Western Australia

Table 3.1. Water quality characteristics of the collected raw water sample

Sample	DOC (mg/L)	UV_{254} (1/cm)	SUVA (m^{-1} mg^{-1} L)	pH
Raw water	10.20-12.00	0.352-0.432	3.20-3.90	6.80

3.2 Chemicals used for laboratory tests

Alum ($Al_2(SO_4)_3.18H_2O$) was used for jar test experiments. Alum stock solution of 10% prepared by dissolving 100 g of laboratory-grade alum (Ajax Finechem) in 1 litter of deionised

water (DI). 1M solution of hydrochloric acid was and 1M solution of sodium hydroxide were prepared by diluting laboratory-grade hydrochloric acid (32%, Chem Supplier) and by dissolving laboratory-grade sodium hydroxide pellets (Sigma Aldrich) in deionised water. To prepare a 1M hydrochloric solution, slowly was added 23.737 ml of 32% hydrofluoric acid to 63 ml DI water. The final volume of solution was adjusted to 250 ml with DI water. To prepare 1M sodium hydroxide, 10 g of solute was dissolved in DI water to a total volume of solution exactly 250 ml. Powdered activation carbon - Norit SX2, powder from peat, steam activated and acid-washed Sigma Aldrich made up as a slurry of 10% (w/v) by thoroughly mixing 50 g of PAC powder with 500 ml of DI water.

3.3 Instrumental methods

Raw and treated water samples were analysed for DOC using a TOC-L Shimadzu analyser shown in Figure 3.2.

Figure 3.2. TOC-L Shimadzu analyser

The nonpurgeable organic carbon (NPOC) analysis method was used to determine DOC concentration in raw and treated water samples. The 1gC/L of potassium hydrogen phthalate

($C_8H_5O_4K$) solution was used as a standard solution to prepare 1.0; 2.0; 4.0; 6.0; 8.0 and 10.0 mg C/L working solutions for TOC instrument calibration.

Ultraviolet absorbance at 254 nm (UV_{254}) of the water samples was analysed using a Helios Gamma UV/Vis Spectrophotometer shown in Figure 3.3 and 1 cm path length cuvette.

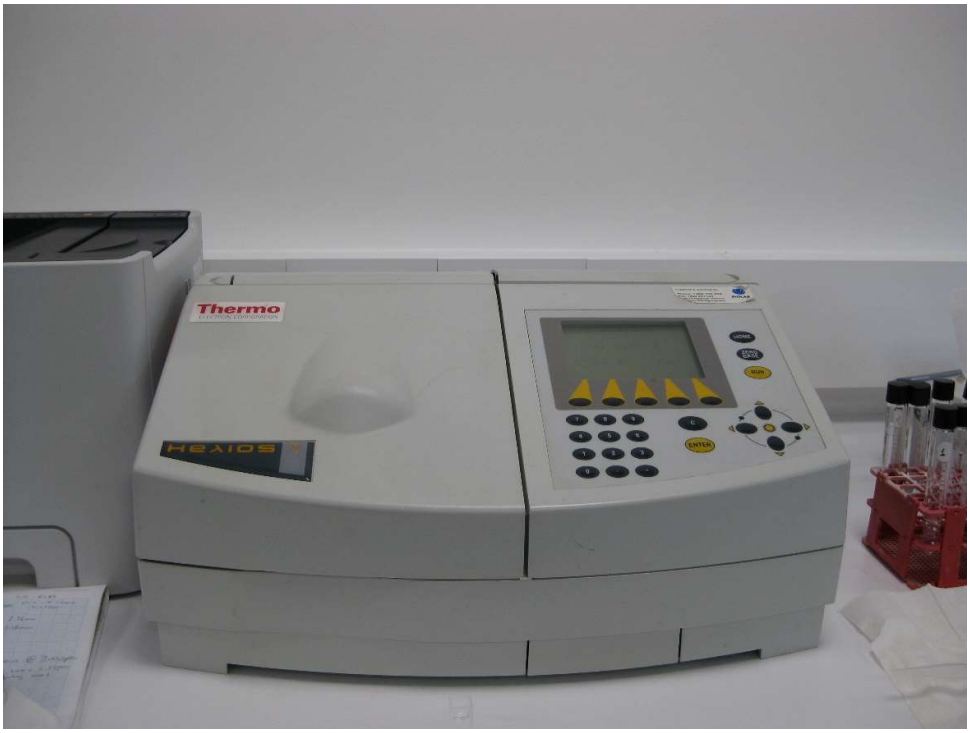


Figure 3.3. Helios Gamma UV/Vis Spectrophotometer

Water samples for DOC and UV_{254} analysis were filtered using 0.45 µm membranes before analysis.

3.4 Jar test procedure

Jar tests of single alum coagulation, single PAC adsorption, and the combined alum coagulation and PAC adsorption water treatment processes were performed using a VELP Scientifica JLT6 Flocculation Tester equipped by straight blade impellers. The jars were the 1-L Griffin Style glass beakers made by Pyrex, as shown in Figure 3.4. The stators were placed into glass beakers with water samples ready to mix with added chemicals. Rapid mixing provided quick and complete dispersion of the coagulant and PAC. PAC dispersion was visible during rapid mixing it with water sample and was not noticed vertical solids gradient distribution. Also, after stopping rapid and slow mixing and waiting for 30 minutes a settling process was clearly

evident. Insoluble solid sedimentation (solids clumped together) was visible on the bottom of the beaker. Furthermore, coagulation and PAC adsorption processes were completed after jar test experiment. Flocculation step was successful and completed, sedimentation occurred and was noticed during jar test experiments (Coagulation and Flocculation Fundamentals). In Figure 3.4 shown flocculation tester and empty glass beakers. The aluminium doses of 10, 25, 50, 75, 100, and 200 mg/L were prepared by adding the measured amounts of 0.31, 0.77, 1.54, 3.10, 4.63, and 6.20 ml of alum stock solutions of 10% into six beakers with a volume of 250 ml of surface water sample in each beaker. pH was adjusted by adding stock solution of 1M NaOH or 1M HCl to the required level. Water samples were subjected to high-speed mixing by straight blade impeller for 1 minute at 200 rpm, followed by slow mixing for 14 minutes at 20 rpm before allowing the flocs to settle for 15-30 minutes — the supernatant of the treated water sample was filtered before analysis for DOC and UV_{254}.

Figure 3.4. JLT6 Flocculation Tester from VELP Scientifica with 1-L Pyrex glass beakers

Five types of jar test experiments were carried out using a VELP Scientifica, JLT6 Flocculation Tester. The 250 ml raw water samples were brought to a temperature of 20 ± 3 °C by using a water bath before adding chemicals. At the first setup, the required amount of alum solution was added into the jar for the single alum coagulation process study. The jar test mixing conditions were as follows: rapid mixing at 200 rpm for 1 min, flocculation at 20 rpm for 14 min and 15-30 min jars settling time.

The next experiment was performed for PAC adsorption study. At this single PAC adsorption process study, the jar test mixing conditions were as followed: rapid mixing at 150 rpm for 1 min, flocculation at 20 rpm for 14 min and 30 min jars settling time.

The third experiment was carried out for simultaneously combined Al+PAC process study in which alum solution was added into beakers simultaneously with PAC. The jar test mixing experimental conditions were rapid mixing at 200 rpm for 1 min, flocculation-adsorption at 20 rpm for 14 min. After rapid and slow mixing the water sample with alum and PAC in it, jars were allowed to settle for 15 to 30 minutes before filtration through a 0.45 µm cellulose acetate membrane filter.

At the fourth setup, alum was added before PAC addition, Al—PAC process. The jar test conditions for the Al—PAC combined process study were rapid mixing at 200 rpm for 1 minute, flocculation at 20 rpm for 14 minutes and jars settling time was 15 minutes. Afterwards, the water samples were dosed with PAC as slurry and fast mixing were carried out at 150 rpm for 1 minute, adsorption at 20 rpm for 14 minutes and jars settling time was 15 minutes.

At the last setup, PAC was added before alum addition, PAC—Al. The jar test conditions for the PAC—Al combined process study were as follows: rapid mixing at 150 rpm for 1 minute, adsorption at 20 rpm for 14 minutes, and jars settling time was 15 minutes. The water sample was dosed with alum and fast mixing was carried out at 200 rpm for 1 minute. Then the water samples were flocculated for 14 minutes at 20 rpm and jars were allowed to settle for 15 minutes before filtration. The PAC doses were varied from 10 to 200 mg/L at fixed alum dose of 308 mg/L (or aluminium dose of 25 ml/L) for the all possible combinations of alum with PAC.

For the initial trial, alum was added into jars for the single alum coagulation process study — the jar test mixing conditions for each set of experiments presented in Table 3.2**.** For subsequent trials, alum and PAC doses and mixing regimes were as specified in the results, tables, and figures.

Table 3.2. Jar test conditions

Treatment	Treatment Phase							
	1	2	3	4	5	6	7	8
	Chemical addition 1	Rapid mix 1	Flocculation: 20 rpm for 14 min	Settling/ ripening	Chemical addition 2	Rapid mix 2	Slow mix 2	Final Settling
Alum only	Alum	200 rpm; 1 min	Adsorption: 20 rpm for 14 min	-	-	-	-	15-30 min
PAC only	PAC	150 rpm; 1 min	Flocculation/ adsorption: 20 rpm for 14 min	-	-	-	-	15-30 min
Simultaneous addition of alum and PAC Slurry (Al+PAC)	Al+PAC	200 rpm; 1 min	Flocculation for 20 rpm for 14 min	-	-	-	-	15-30 min
Alum added prior to PAC (Al—PAC)	Al—PAC	200 rpm; 1 min	Adsorption for 20 min	15 min	PAC	150 rpm for 1 min	Adsorption : 20 rpm for 14 min	15 min
PAC added prior to alum (PAC—Al)	PAC—Al	150 rpm; 1 min		15 min	Alum	200 rpm for 1 min	Floccula-tion: 20 rpm for 14 min	15 min

CHAPTER FOUR

4. SINGLE ALUM COAGULATION STUDY

4.1 Introduction

The alum coagulation water treatment study aimed to estimate optimal water quality parameters in surface water and further assess the effect of order addition of alum coagulant and PAC. This chapter examines DOC, UV_{254}, and SUVA reduction in drinking water sample using single alum coagulation treatment as a function of aluminium dose of 10 to 200 mg/L (or alum dose of 125 to 2500 mg/L) and pH range of 5.0 to 7.5.

The jar tests were performed for NOM reduction from the surface water samples using a single alum coagulation process and varying aluminium dosage in the range of aluminium dose of 10 to 200 mg/L at pH levels of 5.0 to 7.5. Jar tester and glass beakers used for alum coagulation treatment study presented in Figure 4.1.

Figure 4.1. Jar test flocculator and beakers with treated and raw water samples. An empty beaker is given for comparison

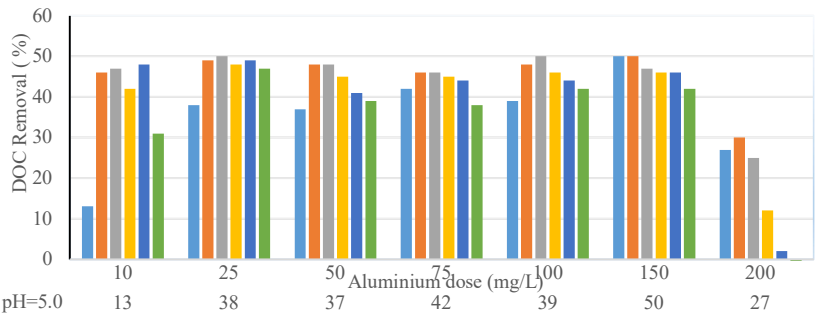
The 250 ml raw water samples were added in each beaker and brought to a temperature of 22 ± 3 °C. For pH adjustment in the range of 5.0-7.5 in the raw water samples of 250 ml were used 1M hydrochloric acid and sodium hydroxide. On the left side of the Figure 4.1 showed a final water sample after alum coagulation treatment and filtration through a membrane filter with 0.45-micron pore size. On the right hand side, an empty beaker is given for comparison. The middle beaker contains a raw water sample with aluminium added into it, Figure 4.1. Depending on pH after adding alum solution as a dose of aluminium to the water sample, the aluminium metal ion is hydrolysed to form aluminium hydroxide flocs and hydrogen ions according to the reaction:

$$Al_2(SO_4)_3.18H_2O + 6H_2O \leftrightarrow 2Al(OH)_3 \downarrow + 6H^+ + 3SO_4^{2-} + 18H_2O$$

Jar test conditions for alum coagulation treatment were presented in Table 3.2. The conditions involved fast mixing for 1 min at 200 rpm, then slow mixing at 20 rpm for 15 min and flocs settling time was between 15 and 30 mins.

4.2 Determining optimum aluminium dose and pH for DOC reduction

As shown in Figure 4.2, DOC removal was the most efficient at aluminium dose of 25 mg/L and pH=6.0.



	10	25	50	75	100	150	200
pH=5.0	13	38	37	42	39	50	27
pH=5.5	46	49	48	46	48	50	30
pH=6.0	47	50	48	46	50	47	25
pH=6.5	42	48	45	45	46	46	12
pH=7.0	48	49	41	44	44	46	2
pH=7.5	31	47	39	38	42	42	-8

Figure. 4.2. Percent removal of DOC by alum coagulation as a function of an aluminium dose of 10 to 200 mg/L and pH of 5.0 to 7.5

The removal of DOC from the surface water sample as a function of pH of 5.0 to 7.5 at a fixed aluminium dose of 25 mg/L is shown in Figure 4.2. Furthermore, aluminium dosage of 25 mg/L suggested to be an optimum dose for DOC reduction at pH around 6.0. The maximum reduced value of DOC was 50% at optimum applied conditions (aluminium dosage of 25, and pH=6.0).

DOC compounds removed from surface water by using alum coagulation are characterised as hydrophobic high molecular weight organic fractions (Carriere et al. 2009, Uyak et al. 2007). DBP precursor's removal by coagulation can depend on the type and concentration of DOC compounds not only of coagulant dosage and pH (Cheng et al. 1995, Takdastan and Eslami 2013). Also, Cheng et al. 1995 and Takdastan claimed that coagulation water treatment process better removes humic HMW organic compounds. Furthermore, Cheng et al. (1995) and Volk et al. (2000) reported that coagulation process by itself is not enough for non-humic and LMW organic matter reduction; the coagulation process can be practical for humic and HMW materials removal only.

According to a research (Amy et al. 1992), the DOC compounds in natural water divided into two fractions, humic and non-humic. The coagulation with adsorption will remove the humic organic species, which are more hydrophobic. While the non-humic species such as proteins, carbohydrates are more hydrophilic. The hydrophilic materials comparing with hydrophobic organic compounds represent the less watercolour and DBPs formation problems.

The optimum conditions for DOC removal by single alum coagulation as a 3D-function of aluminium dose, pH, and DOC removal were showed in Figure 4.3. Maximal removal of DOC observed at aluminium dose of 25 mg/L and pH = 6.0.

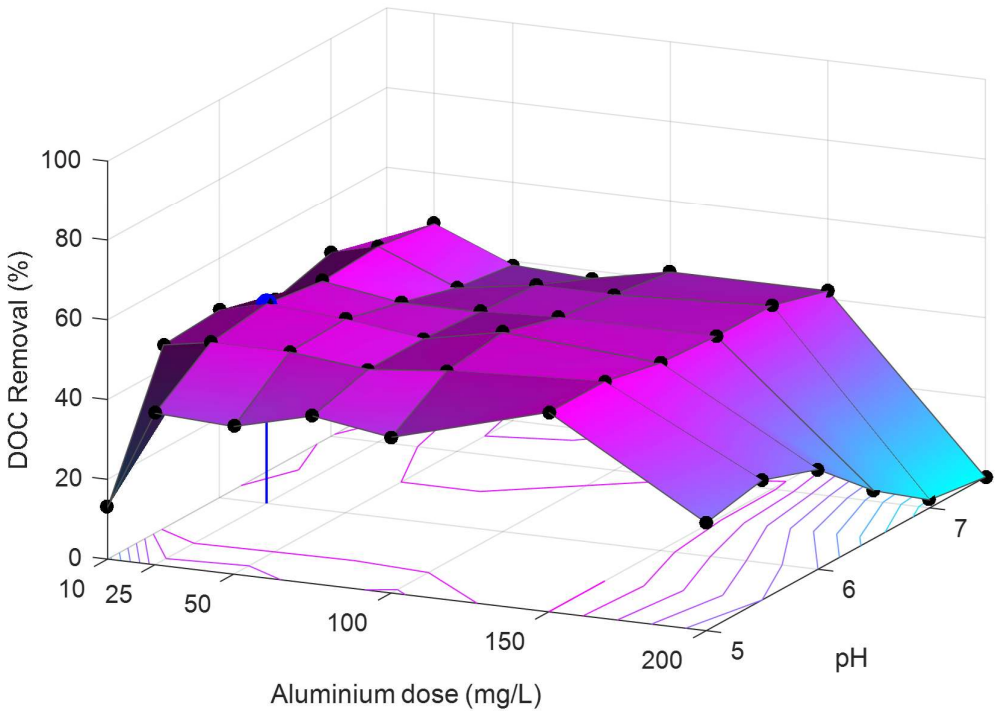


Figure 4.3. Percent removal of DOC by alum as a function of aluminium dose of 10 to 200 mg/L and pH of 5.0 to7.0

Thus, at the observed optimum water treatment conditions (aluminium dose of 25mg/L and pH=6.0) the remaining 50% fraction is most likely of hydrophilic compounds. The untreated surface water sample level DOC of 11.89 mg/L was reduced to level DOC of 5.91 mg/L in the treated water sample.

4.3 Determining optimum aluminium dose and pH for UV_{254} reduction

UV_{254} removals were also efficient at the applied aluminium doses of 25 and 50 mg/L at pH =6.0, as showed in Figure 4.4. Also, the UV_{254} removal gradually decreased from 77% to 71% by increasing aluminium dose of 75 to 150 mg/L at pH=6.0. The small UV_{254} reductions were observed at applied aluminium dosage of 200 mg/L in pH range of 5.0 to 7.5. Therefore, it suggested that the optimum aluminium dosage for NOM reduction in terms of UV_{254} maximum removal is 25 mg/L. pH optimisation data revealed that the UV_{254} reduction values were observed between 74%-81% (at pH=5.5); 71-81% (at pH=6.0); 71-81% (at pH=6.5); and 70-80% (at pH=7.0) at applied aluminium dose of 10 to 150 mg/L, Figure 4.4.

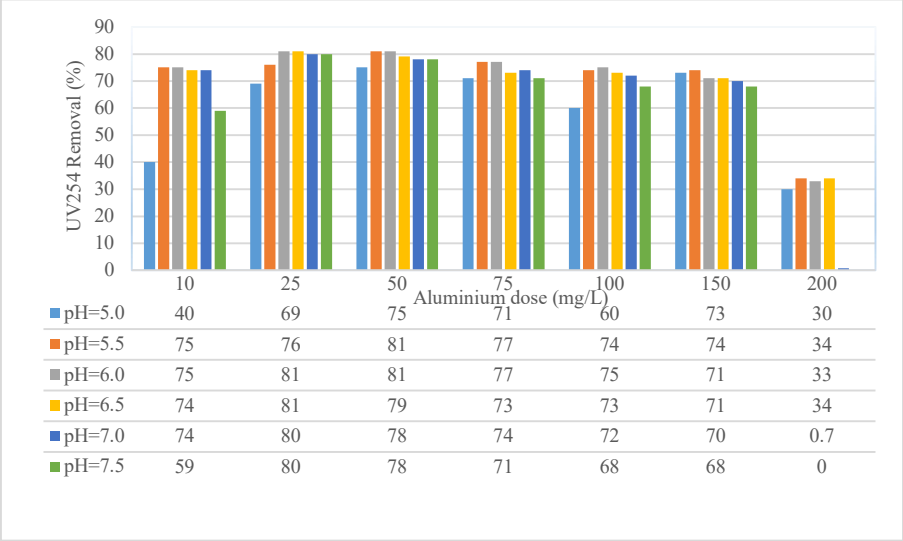


Figure. 4.4. Percent removal of UV_{254} by alum as a function of aluminium dose of 10 to 200 mg/L and pH of 5.0 to 7.5

Based on the experimental results presented in Figure 4.5, the optimum pH level for UV_{254} reduction was between 6.0 and 6.5 at the applied aluminium dosage of 25mg/L. At this pH range, UV_{254} maximum reduction value equaled to 81%, Figures (4.4-4.5).

The percentage removal of DOC value observed at pH=6.0 was higher than DOC reduction achieved at pH=6.5, Figure 4.3, while the UV_{254} removal value achieved at a pH range between 6.0 and 6.5 was almost the same. Therefore, the pH=6.0 was proposed as optimum pH for the UV_{254} reduction by using single alum coagulation water treatment process, Figure 4.4. As showed in Figure 4.5**,** the maximum UV_{254} removal value of 81% was observed at applied aluminium dosage of 25 mg/L and pH=6.0. The results indicated that the maximum UV_{254} removal value was higher than DOC removal by using alum coagulation. Also, the level UV_{254} of 0.427 absorbing compounds in the untreated water sample was reduced to level UV_{254} of 0.080 absorbing compounds in the treated water by alum coagulation.

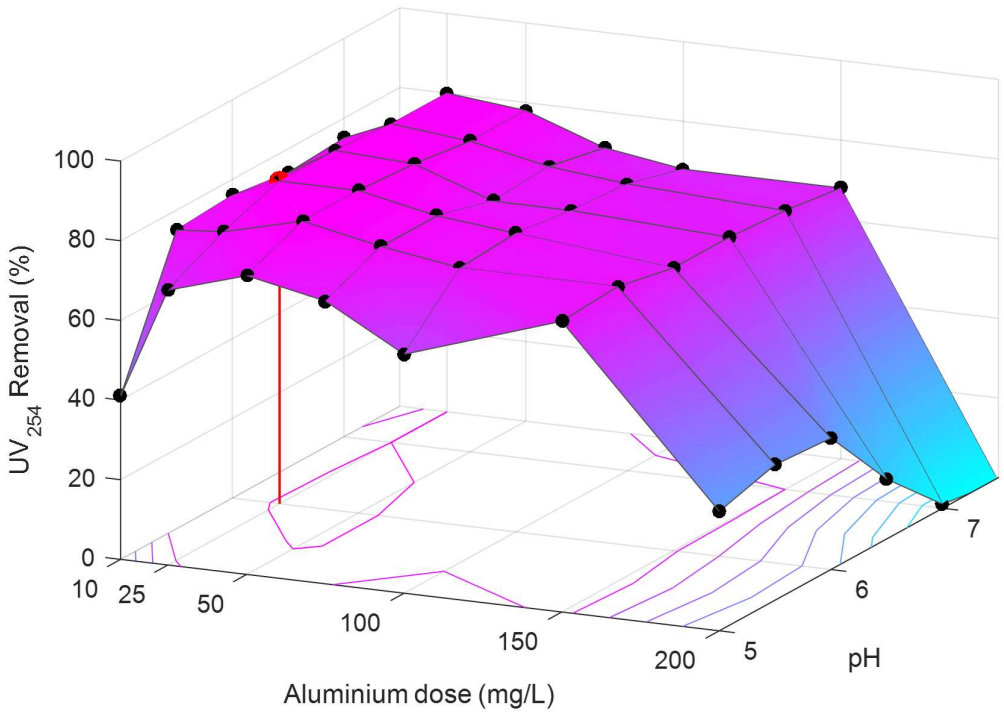


Figure 4.5. Percent removal of UV_{254} absorbance by alum as a function of an aluminium dose of 10 to 200 mg/L and pH of 5.0 to 7.0

Ultraviolet absorbance at 254 wavelengths related to specific ultraviolet absorbance of the water sample; hence UV_{254} reduction can provide structural information about the NOM in the water sample (Weishaar et al. 2003). Thus, these results above suggest that the untreated surface water sample had a high content of HMW aromatic fraction of NOM, which can react with alum coagulant.

4.4 Determining optimum aluminium dose and pH for SUVA reduction

SUVA removals were efficient at around the applied aluminium dosages of 25 and 50 mg/L and at pH levels of 5.5, 6.0 and 6.5, Figure 4.6. Based on experimental data, the optimum aluminium dose of 25 mg/L for DOC and UV_{254} reduction at pH range between 6.0 and 6.5. Also, the highest 64% of SUVA removal was achieved by applying aluminium dose of 25 mg/L at pH=6.5, Figure 4.6.

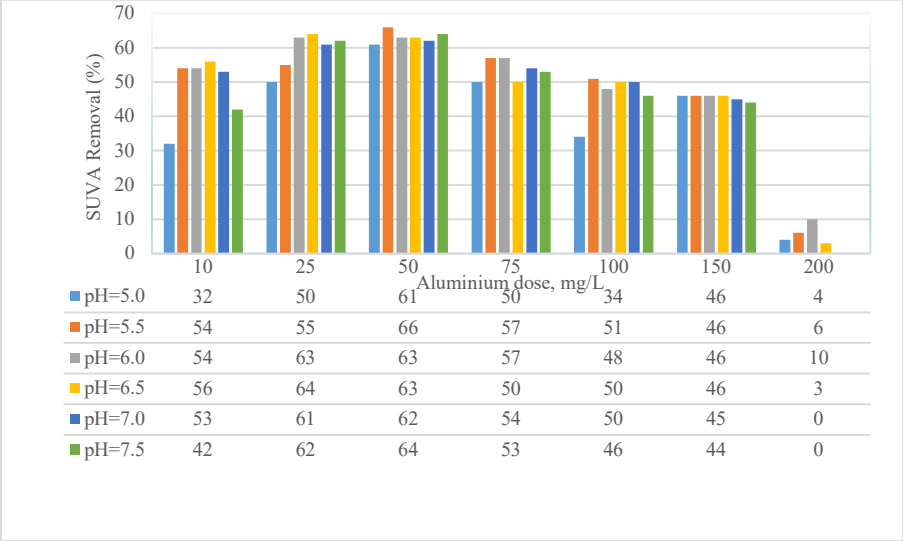


Figure 4.6. Percent removal of SUVA by alum as a function of an aluminium dose of 10 to 200 mg/L and pH of 5.0 to7.5

SUVA is the surrogate for the aromaticity of NOM (Edzwald et al. 1985). Thus, from this coagulant dosage response curve, it was evident that there remained 36% of SUVA value in the treated water sample challenging to remove by a single alum coagulation process, Figure 4.6.

The experimental results indicated that optimum SUVA removal value was observed at pH =6.5 by applying aluminium dose of 25mg/L, as demonstrated in 3D-plot in Figure 4.7.

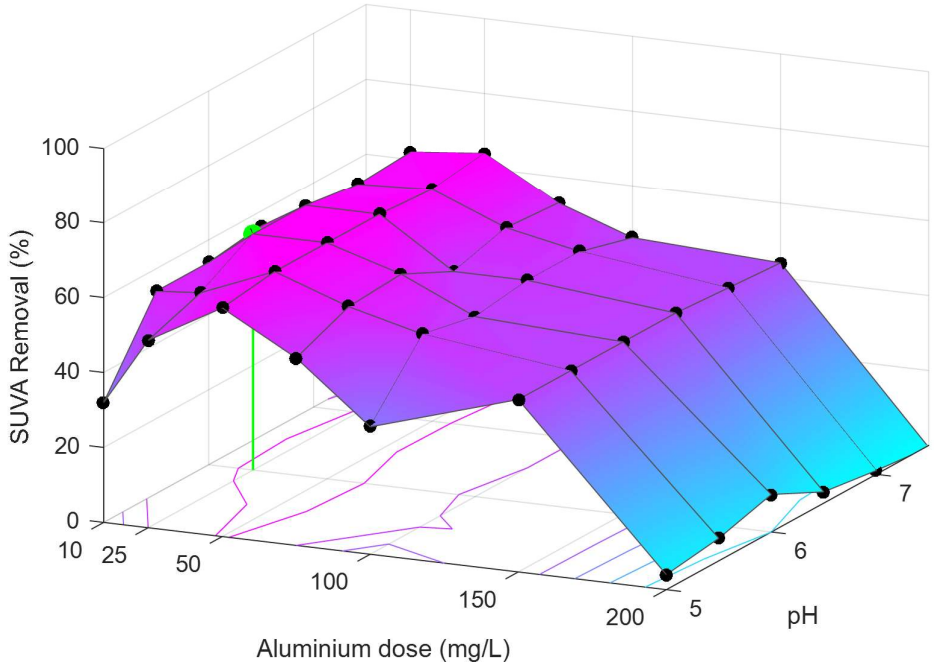
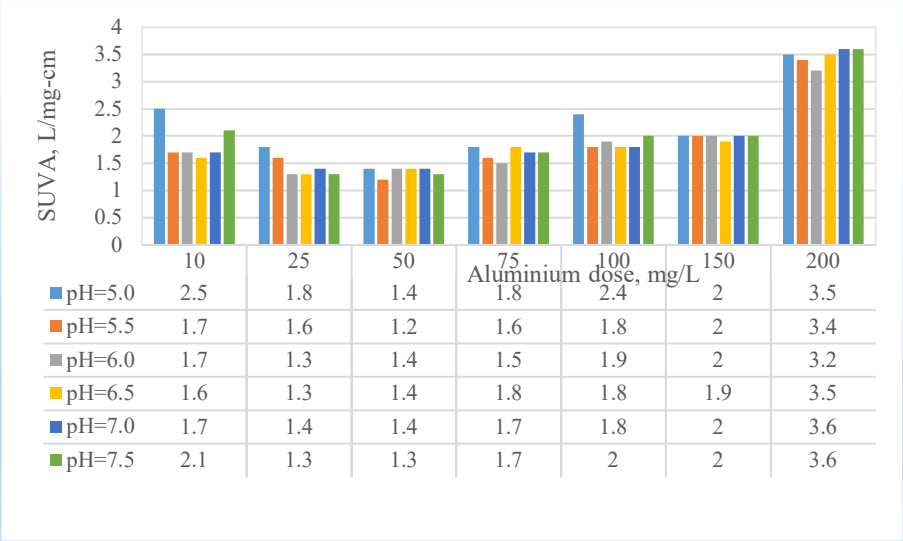


Figure 4.7. Percent removal of SUVA absorbance by alum as a function of an aluminium dose of 10 to 200 mg/L and pH of 5.0 to7.0

The highest SUVA reduction value was observed at pH=5.5, Figures (4.6-4.7). However, the highest DOC and UV_{254} removals were observed at pH=6.0 and aluminium dose of 25 mg/L. At this pH and aluminium dose the level SUVA of 3.61 L/mg-cm in the untreated water sample was reduced to the level SUVA of 1.3 L/mg-cm in the treated water, Appendix Table A1. Based on the data for DOC and UV_{254} reductions, Figures (4.3 and 4.5), pH=6.0 was proposed as the optimum pH for SUVA removal. Literature findings reported that SUVA is an indicator of the aromatic content in water and chlorine reactivity with NOM (Archer and Singer 2006, Weishaar et al. 2003).



	10	25	50	75	100	150	200
pH=5.0	2.5	1.8	1.4	1.8	2.4	2	3.5
pH=5.5	1.7	1.6	1.2	1.6	1.8	2	3.4
pH=6.0	1.7	1.3	1.4	1.5	1.9	2	3.2
pH=6.5	1.6	1.3	1.4	1.8	1.8	1.9	3.5
pH=7.0	1.7	1.4	1.4	1.7	1.8	2	3.6
pH=7.5	2.1	1.3	1.3	1.7	2	2	3.6

Figure 4.8. SUVA values by applying alum as a function of an aluminium dose of 10 to 200 mg/L and pH of 5.0 to7.5

Low SUVA values (1.3 L/mg-cm) were observed for treated water samples at aluminium dose of 25 mg/L and coagulation pH range 6.0 and 6.5. Also, low SUVA values were attained (1.2 L/mg-cm) at aluminium dose of 50 mg/L and coagulation pH=5.5 (Figure 4.8). These values of treated surface water were lower than SUVA value (3.9 L/mg-cm) of the raw water indicating that alum coagulation was effective in removal of high to low molecular weight organic compounds. Hence, a low level SUVA of 1.3 L/mg-cm detected in the treated water sample appears to be an indicator of the low level of hydrophobic humic and high level of hydrophilic non-humic compounds have remained in the treated water sample.

4.5 DOC, UV_{254} and SUVA removal analysis

The removal DOC, UV_{254} and SUVA values by alum coagulation treatment technique varies between 38 to 50% of DOC, 69 to 81% of UV_{254} and 50 to 64% of SUVA as a function of pH of 5.0 to 7.5 at a fixed aluminium dose of 25 mg/L, Figure 4.9. Alum coagulation test results revealed that maximum reduction of DOC, UV_{254}, and SUVA values were equaled to 50% of the DOC, 81% of the UV_{254} and 63% of the SUVA at optimum conditions (aluminium dose of 25 mg/L and pH=6.0). The UV_{254} reduction was the same at pH of 6.0 and 6.5. DOC removal was slightly lower at pH=6.5 comparing with the DOC removal at pH=6.0. Hence, the optimum pH range for DOC and UV_{254} reduction can be widened from 6.0 to 6.5 by applying alum coagulation treatment.

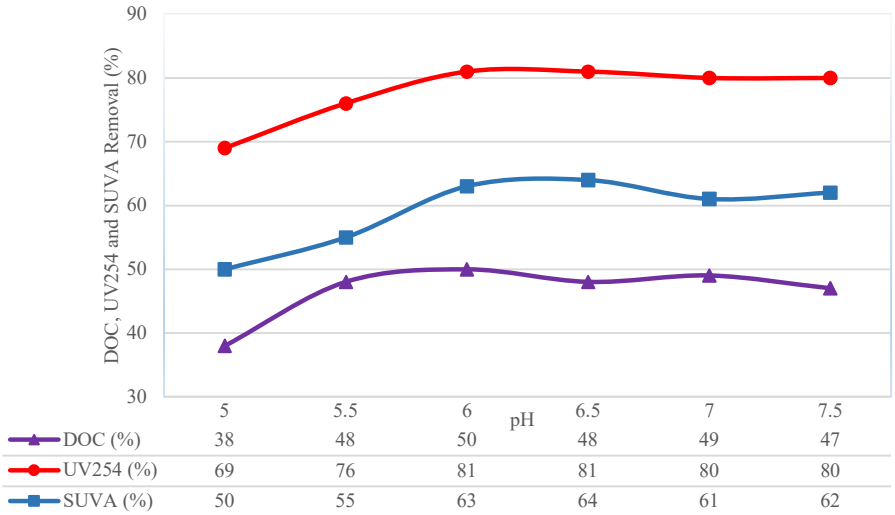


Figure 4.9. Percent reduction of UV_{254}, DOC, and SUVA by alum as a function of pH of 5.0 to7.5 at a fixed an aluminium dose of 25mg/L

As shown in Figure 4.9 among the water quality parameters (UV_{254}, DOC, and SUVA) the highest removal value of 81% was achieved for UV_{254} reduction and the lowest removal value was obtained for the removal 50% of DOC. These experimental data are in agreement with the previous research reports (Carriere et al. 2009, Uyak et al. 2007). It was likely that UV_{254} reduction will be higher by using alum coagulation process because the UV_{254} parameter is an excellent indicator of humic aromatic compounds. The remained levels of water quality parameters in the treated water sample were equal to 5.9 mg/L of DOC, 0.08 of UV_{254} and 1.34 L/mg-cm by using alum coagulation process at optimum aluminium dosage of 25 mg/L and pH = 6.0. The level SUVA of 1.3 L/mg-cm in the treated water sample was below level SUVA of 2 L/mg-cm in the treated water sample at the optimum conditions. Therefore, according to Edzwald (1993), the DOC remained in the treated water sample by alum coagulation mainly composed of non-humic substances. Hence, the alum coagulation water treatment resulted in a high level of SUVA reduction, suggesting that the predominant fraction removed from the surface water sample was the hydrophobic and aromatic humic matter.

4.6 DOC correlation to UV_{254}

The coefficient of determination between DOC and UV_{254} reduction was found to be weak by using the single alum coagulation process, Figure 4.10.

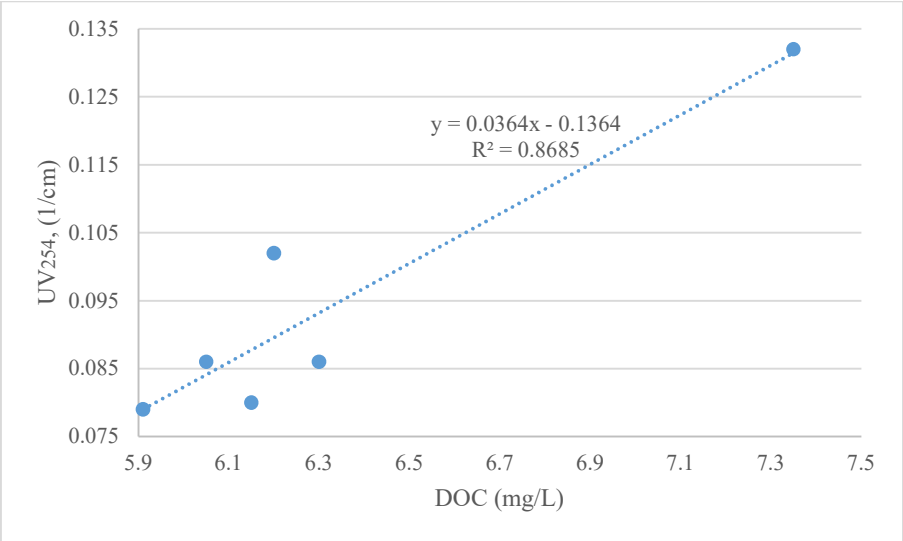


Figure 4.10. DOC correlation to UV_{254} by applying alum coagulation

The defined coefficient of determination (R^2=0.8685) indicated a positive relationship between UV_{254} and DOC. However, based on data, it was suggested that the correlation between DOC and UV_{254} was weak because of aluminium dosage increase had no effect on the water quality parameters reduction. Aluminium dosage addition increase from 25mg/L to 200mg/L did not improve the reduction of NOM. Thus, it was proposed that the alum coagulation process removes better HMW hydrophobic humic and aromatic NOM matter rather than LMW hydrophilic nonhimic and nonaromatic compounds.

4.7 Conclusion

The removal efficiencies of the water quality parameters were found to be as 50% of DOC, 81% of UV_{254} and 63% of SUVA at aluminium dose of 25mg/L and pH=6.0. The jar test experimental data showed that slightly better DOC removals were achieved at pH=6.0, while greater UV_{254} reductions were observed at pH range between 6.0 and 6.5. The DOC, UV_{254},

and SUVA levels in the treated water sample were reduced from 11.89 to 5.91 mg/L of DOC, from 0.427 to 0.0080 1/cm of UV_{254}, and from 3.60 to 1.34 L/mg-cm of SUVA by applying alum coagulation. The UV_{254} absorbance was an indicator of aromatic compounds, and therefore, the UV_{254} reduction from the treated water sample showed to be higher than the removed overall DOC. That probably means that alum coagulation readily removes aromatic materials, and alum coagulation has the poor capability to remove the low molecular weight of NOM in surface water. According to Bose et al., (2007) alum coagulation removes humic and fulvic acids. While hydrophilic and weak hydrophobic acids, hydrophilic and hydrophobic neutrals, hydrophilic and hydrophobic bases can be removed to a less extent by alum coagulation. The removed NOM contaminants by alum coagulation are characterised as charged and hydrophobic HMW organic materials. Army et al. (1992) reported that the removability of NOM by alum coagulation characterised as fulvic acids with a higher charge density or with higher carboxylic acidity. Furthermore, the removed DOC compounds from the surface water sample characterised as hydrophobic high molecular weight organic fractions (Carriere et al. 2009, Uyak et al. 2007). The DOC fractions remaining in the treated water sample were characterised as weak hydrophobic and hydrophilic lower molecular weight organic compounds because of the low level SUVA of 1.3 L/mg-cm was observed in the treated water sample by using alum coagulation process. Hydrophobic fraction tends to contain a higher proportion of materials that have aromatic character and conjugated double bonds.

CHAPTER FIVE

ASSESSMENT OF PAC ADSORPTION PROCESS

5.1 Introduction

The removal of NOM can be monitored and maximised by PAC as an alum coagulant aid. NOM removal from surface water by alum coagulant in combination with PAC was considered as a practical step to research the order of addition of alum and PAC combined water treatment process. Norit as a type of PAC was selected to assess the simultaneous and subsequent combination of PAC with alum coagulant. The first series of jar test experiments were conducted by varying PAC dosage in the range of 20-200 mg/L based on the literature review (Alvarez-Uniarte et al. 2010, Fabris et al. 2004), and pH range of 5.0-7.0 to reduce NOM in the water sample.

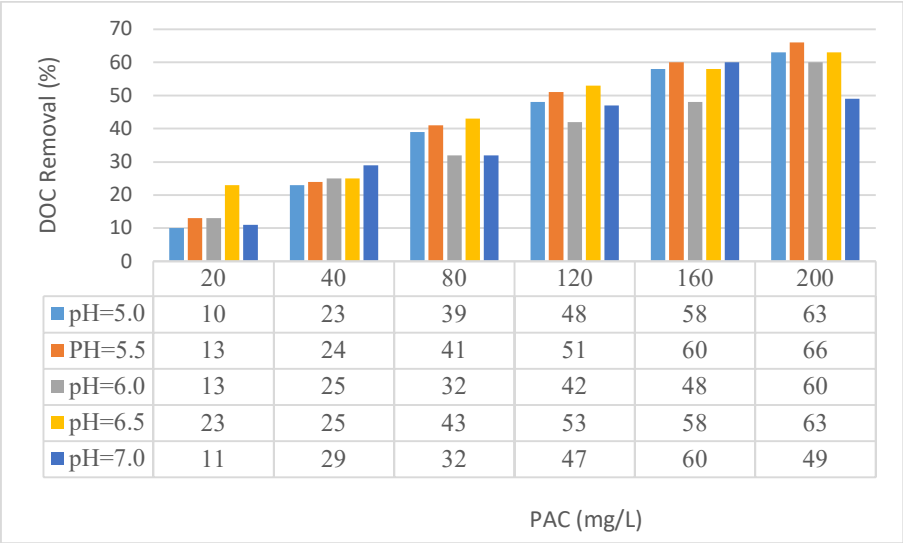
5.2 Jar test procedure for PAC adsorption

Jar test experiments were performed for NOM reduction from the raw water samples by varying PAC dosage in the range of 20-200 mg/L, and pH from 5.0 to 7.0. Jar test preparation for PAC adsorption process assessment performed, as shown in Figure 5.1. The 250 ml raw water samples were added in each beaker and brought to a temperature of 22 ± 3 °C. The water sample temperature was controlled in the range 22 ± 3 to warm up the sample after collecting it from the fridge and make sure that jar test experiments performed at the same temperature. 1M hydrochloric acid and sodium hydroxide used for pH adjustment. The first PAC adsorption experiment setup was performed by varying PAC dosages of 20, 40, 80, 120, 160, and 200 mg/L PAC dose at pH=5.0 in each beaker. The water samples were mixed with PAC using a straight blade impeller for 1 minute at 200 rpm and 14 minutes at 20 rpm (Figure 5.1). After mixing raw water samples with PAC as a slurry by applying high- and low-speed mixing, the water sample mixtures with PAC and adsorbed NOM on it were allowed to settle for 15-30 minutes. The next experimental setups were performed at different pH values 5.5, 6.0, 6.5, and 7.0. In Figure 5.1 presented one of the experimental setups at pH=5.0 by varying PAC dosage from 20, 40, 80, 120, 160, 200 mg/L, which begins with the left side beaker.

Figure 5.1. Jar test treated samples using PAC adsorption process

5.3 Determining optimum PAC dose and pH for DOC reduction

DOC removal was efficient at a high PAC dosage in the pH range between 5.0 and 7.0. The maximum DOC removal values varied between 10-23% at applied PAC dosage 20 mg/L while for 40, 80, 120, 160, and 200 mg/Al/L dosages the DOC reduction varied between 23-29%; 32-43; 42-53%; 48-60%; and 49-66% as a function of pH. It was observed that the DOC reduction values were lower at applied 20 mg/L PAC dosage and higher at 200 mg/L PAC dosage. The DOC reduction values were obtained between intervals 10-63% (at pH=5.0); 13-66% (at pH=5.5); 13-60% (at pH=6.0); 23-63% (at pH=6.5); and 11-60% (at pH=7.0) as a function of PAC dosage of 20 to 200 mg/L. Therefore, it was proposed that the optimum conditions for maximum of 66% DOC reduction are PAC dose of 200 mg/L and pH=5.5.



	20	40	80	120	160	200
pH=5.0	10	23	39	48	58	63
PH=5.5	13	24	41	51	60	66
pH=6.0	13	25	32	42	48	60
pH=6.5	23	25	43	53	58	63
pH=7.0	11	29	32	47	60	49

Figure 5.2. Percent removal of DOC by PAC as a function of PAC dose of 20 to 200 mg/L and pH of 5.0 to7.0

The PAC adsorption process study demonstrated that 160 mg/L of PAC would be required to remove 60% of DOC. The PAC dosage increase up to 200 mg/L during the adsorption jar test experiment, resulted in the higher 66% of DOC removal, Figure 5.2. Based on experimental data, it was proposed that a PAC dosage of 200 mg/L at pH=5.5 as optimum PAC dosage and pH for DOC maximum reduction. The jar test results revealed that the DOC removals are always lower than the UV_{254} reductions by applying the PAC adsorption process as a function of PAC dose and pH, Figure 5.3. The optimum conditions (PAC dose of 200 mg/L and pH=5.5) for DOC maximum reduction value of 66% are plotted in 3D Figure 5.3.

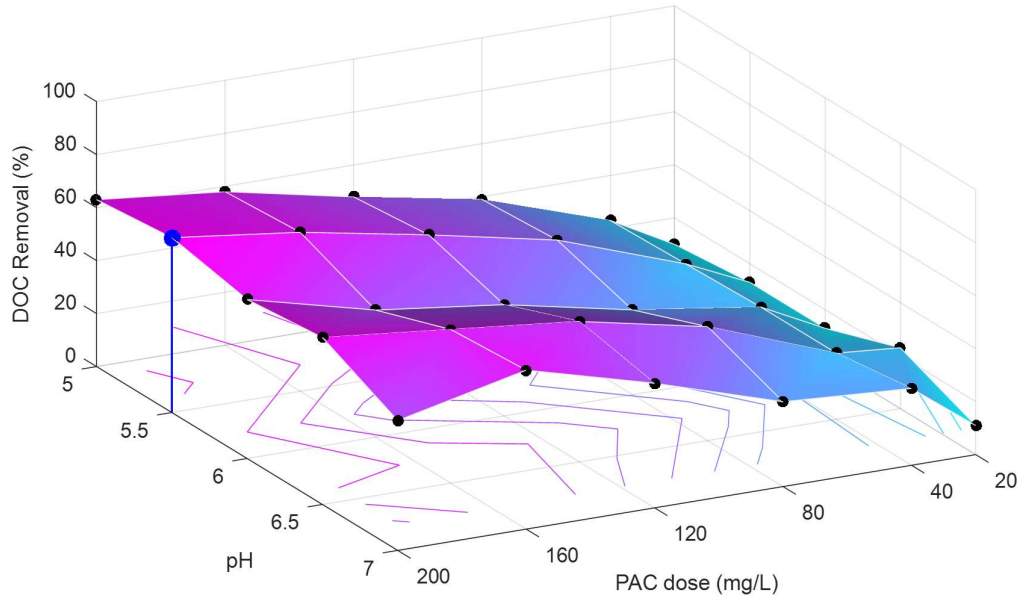


Figure 5.3. Percent removal of DOC by PAC as a function of PAC dose of 20 to 200 mg/L and pH of 5.0 to7.0

DOC maximum reduced value of 66% was higher by applying PAC adsorption comparing with DOC reduced value of 50% by using a single alum coagulation treatment, Figures (4.3-4.4 and 5.2-5.3). If the level DOC of 11.97 mg/L was observed in the untreated water sample, the level DOC of 4.01 mg/L was achieved after water treatment by applying PAC dose of 200 mg/L at pH=5.5. According to Takdastan and Eslami (2013), PAC adsorption technique can remove low molecular weight organics and taste-order causing organic matter, while single alum coagulation has a better capacity to remove high molecular weight humic substances.

5.4 Determining optimum PAC dose and pH for UV_{254} reduction

As demonstrated in Figure 5.4, UV_{254} removal was efficient by applying the same chemical conditions as for DOC reduction: PAC dosage of 200 mg/L and pH=5.5. The UV_{254} removal values varied between 11-20 % for the applied aluminium dosage of 20 mg/L while for aluminium doses of 40, 80, 120, 160 and 200 the UV_{254} reduction values varied between 22-27%; 39-44; 49-57%; 61-65%; and 65-70%. Thus, the highest UV_{254} reduction values were observed by applying PAC dosage of 200 mg/L at pH=5.5. Based on the experimental data, the optimum PAC dosage for NOM reduction in terms of UV_{254} removal could be in the range of 160-200 mg/L. By increasing the PAC dosage from 20 to 200 mg/L the UV_{254} removal values

significantly were improved at applied 160 and 200 mg/L PAC doses. Hence, a PAC dose of 200 mg/L was proposed as optimal PAC dose for maximal reduction of UV_{254}.

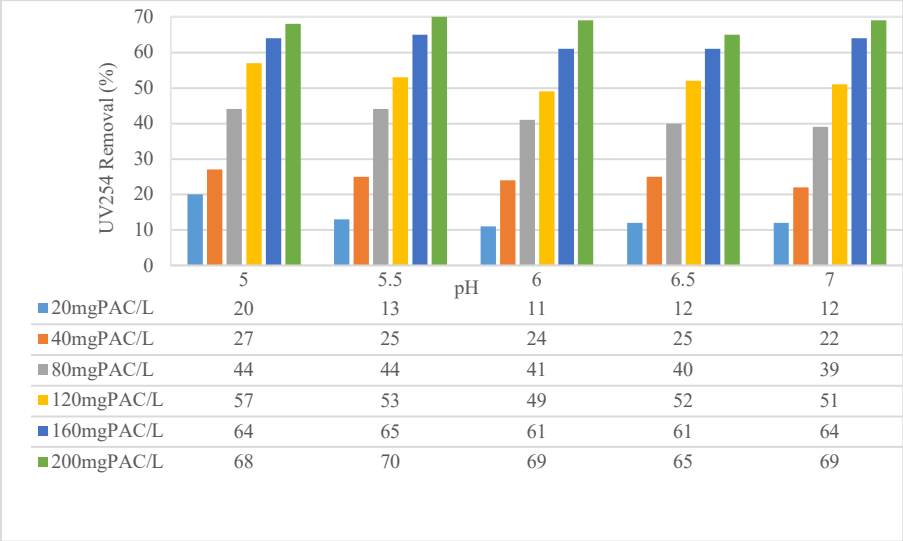


Figure 5.4. Percent removal of UV_{254} by PAC adsorption as a function of PAC dose of 20 to 200 mg/L and pH of 5.0 to7.5

pH optimisation data revealed that the UV_{254} reduction values were observed between intervals 20-68 (at pH=5.0); 13-70% (at pH=5.5); 11-69% (at pH=6.0); 12-65% (at pH=6.5); and 12-69% (at pH=7.0), Figure 5.4. Based on the test results, the maximum reduction 70% of UV_{254} was observed at pH=5.5. From this PAC dose-response histogram, it was evident that there were remained 30% of UV_{254} fractions which were not removed by single PAC adsorption treatment process. Thus, 30% of UV_{254} absorbing compounds are remained in treated water, and they are recalcitrant compounds which are difficult to remove by PAC adsorption. Therefore, the new water treatment approaches were proposed to remove the remained recalcitrant NOM compounds in the treated water. For example, a combination of alum coagulation with PAC adsorption water treatment process and order addition of alum and PAC study.

The experimental data for UV_{254} maximum reduction at optimal conditions (PAC dosage of 200 mg/L and pH=5.5) are presented by red vertical line and red dot, Figure 5.5. The optimum conditions for maximum reduction of UV_{254} using only PAC adsorption water treatment were the same as for DOC removal by applying the PAC adsorption process by itself. Thus, the

optimum conditions for DOC and UV_{254} maximum reductions were achieved by applying PAC dose of 200 mg/L at pH=5.5.

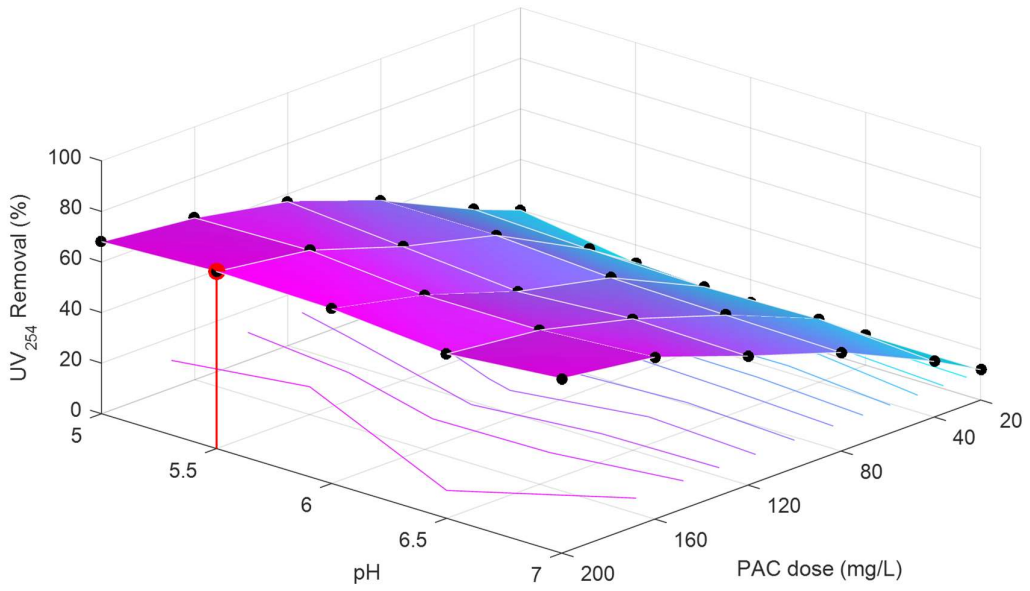


Figure 5.5. Percent removal of UV_{254} absorbance by PAC as a function of PAC dose of 20 to 200 mg/L and pH of 5.0 to7.0

The UV_{254} maximum reduced value by PAC adsorption process was 70%, while 81% of UV_{254} reduction was observed by applying single alum coagulation treatment, Figures (4.4 and 5.4). Therefore, it was suggested that PAC adsorption technique has a lower capacity to remove HMW aromatic humic UV_{254}-absorbing compounds comparing with single alum coagulation process. If the level UV_{254} of 0.402 absorbing compounds were observed in the untreated water sample, the UV_{254} of 0.120 absorbing compounds was achieved in treated water sample by applying PAC dose of 200 mg/L at pH=5.5.

5.5 Determining optimum PAC dose and pH for SUVA reduction

Low SUVA reduction values were observed by applying PAC adsorption compared with single alum coagulation treatment, Figure 5.6. If the high level SUVA of 2.7 L/mg-cm was detected by PAC adsorption treatment (PAC dose of 200 mg/L and pH=6.0), the lower level SUVA of 1.3 L/mg-cm was observed at optimum conditions (aluminium dose of 25 mg/L and pH=6.0)

by applying alum coagulation. Therefore, it suggested that alum coagulation can remove high molecular weight aromatic NOM compounds, which appears to be mostly unaffected by PAC adsorption (Takdastan and Eslami 2013).

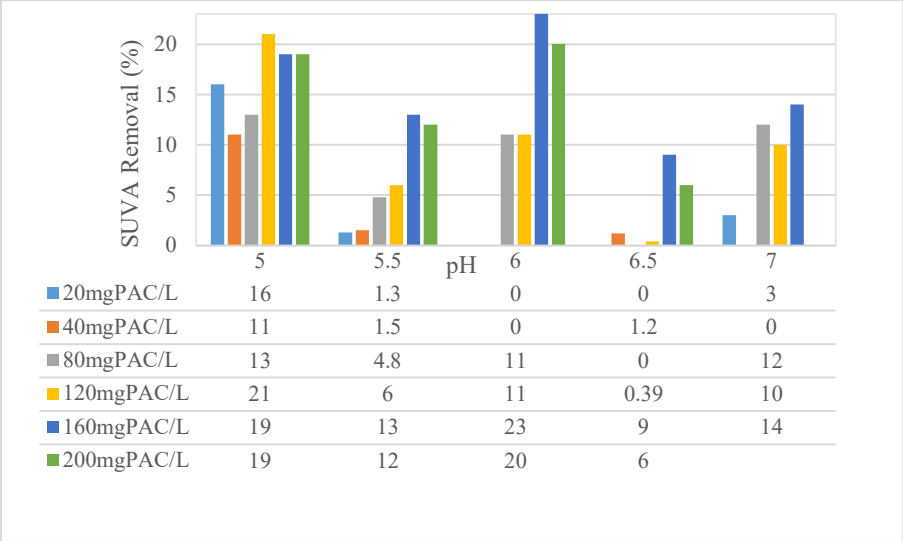


Figure 5.6. Percent removal of SUVA by PAC as a function of PAC dose of 20 to 200 mg/L and pH of 5.0 to 7.0

pH optimisation data revealed that maximum SUVA reduction value was achieved at pH=6.0, Figure 5.6. At that optimum pH, the maximum reduced SUVA value equaled to 20%, which was significantly less than 63% of SUVA removed by using alum coagulation at optimum conditions. Thus, it was evident that SUVA reduction was not efficient by using PAC adsorption treatment. Maximum reduced value 20% of SUVA achieved by applying 200 mg/L PAC dosage at pH=6.0, Figure 5.7. If level SUVA of 3.4 L/mg-cm was observed in the untreated water sample, the SUVA of 2.7 L/mg-cm was achieved in the treated water sample by applying PAC dose of 200 mg/L and pH=6.0. Therefore, it was suggested that PAC adsorption less effective in HMW NOM compounds removal compared with alum coagulation.

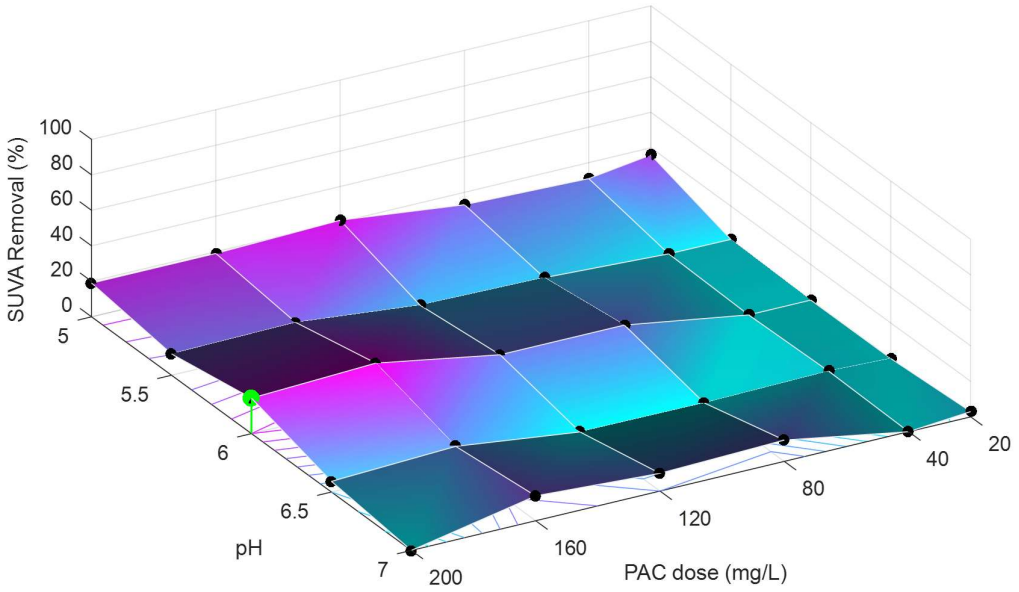


Figure 5.7. Percent removal of SUVA by PAC as a function of PAC dose of 20 to 200 mg/L and pH of 5.0 to7.0

There was a consistent low percentage reduction in SUVA, and therefore more non-UV-absorbing organic compounds were removed than UV absorbing organic compounds (measured as DOC). Thus, it's likely that the untreated water sample mainly consists of HMW aromatic NOM compounds which are recalcitrant for removal by PAC adsorption. The initial SUVA of the raw surface water ranged from 3.2-3.5 (L/mg-cm) and the SUVA value of 3.4 L/mg-cm was achieved at PAC dose of 200 mg/L and pH=5.5, Figure 5.8. At this PAC dose and pH the treated water sample had the highest DOC and UV_{254} reduction and minor reduction of SUVA, Figures (5.4-5.6). The minor reduction of SUVA in treated water throughout of the PAC process demonstrated that hydrophobic humic acids were not removed (Wang et al. 2002). Hence, PAC adsorption process removes effectively non-humic LMW and uncharged DOC compounds (Takdastan and Eslami 2013, Uyak et al. 2007).

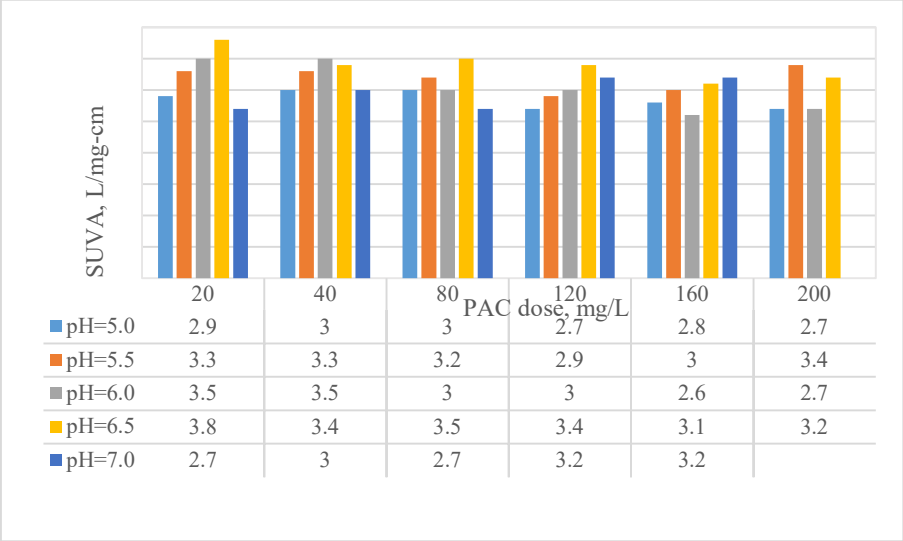


Figure 5.8. SUVA values in treated water by PAC as a function of PAC dose of 20 to 200 mg/L and pH of 5.0 to7.0

5.6 DOC, UV_{254} and SUVA removal analysis

DOC and UV_{254} reduction values increased with PAC dose increase from 20 to 200 mg/L, Figure 5.9.

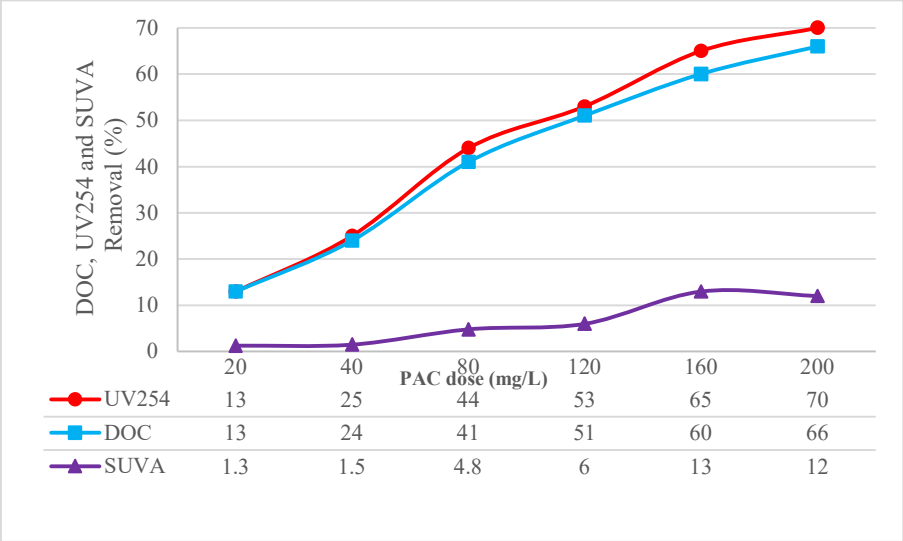


Figure 5.9. Percent reduction of UV_{254}, DOC, and SUVA by PAC as a function of PAC dose of 20 to 200 mg/L at fixed pH=5.5

The removed DOC and UV_{254} values equaled 66% and 70% by applying PAC dose of 200 mg/L at pH=5.5, Figure 5.9. The removed SUVA values from the treated water sample by PAC adsorption were considerably low compared with the removed values of UV_{254} and DOC. Also, the reduced SUVA value by PAC adsorption was lower than the SUVA value removed by alum coagulation at optimum pH=6.0, Figures (4.10 and 5.10). However, slightly higher removal of UV-compounds were observed than non-UV-absorbing compounds, Figure 5.10.

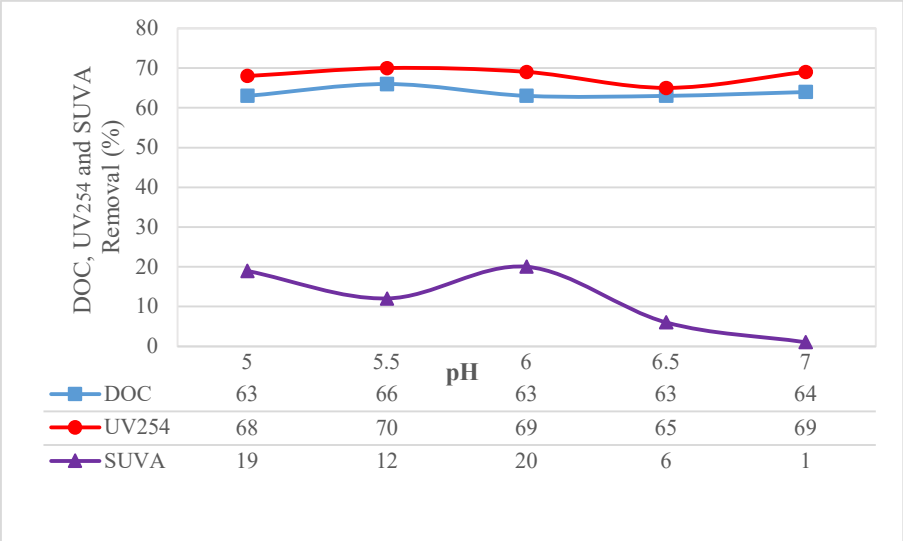


Figure 5.10. Percent reduction of DOC, UV_{254}, and SUVA by PAC as a function of pH of 5.0 to 7.0 at a fixed PAC dose of 200 mg/L

According to Uyak et al. (2007) and Carriere et al. (2009), SUVA value indicates an aromatic content of NOM fractions in the surface water. Because of slightly SUVA value change was observed in the treated water by PAC adsorption, it was suggested that PAC adsorption water treatment process probably removes nonaromatic NOM fractions, which were unaffected by alum coagulation. The experimental results by applying PAC adsorption process revealed that the levels of water quality parameters were for UV_{254} of 0.120 absorbing compounds and DOC of 4.01 mg/L. SUVA level of 2.7 L/mg-cm has changed slightly by applying PAC dose of 200 mg/L at pH=6.0 compared with the SUVA level of 3.4 L/mg-cm of the untreated water sample. Therefore, PAC adsorption process by itself removes different NOM fractions compared with single alum coagulation process.

5.7 DOC correlation to UV_{254}

A good UV_{254} correlation to DOC was defined using PAC adsorption water treatment process, Figure 5.11. The high strength of the relationship between two variables of DOC and UV_{254} were observed by identifying coefficient of determination R^2=0.999. The degree of relation between DOC and UV_{254} shows a positive correlation for one set of experimental data. As one set values of DOC and UV_{254} increases. Moreover, DOC and UV_{254} removals improved with the increased level of PAC dose of 20 to 200 mg/L.

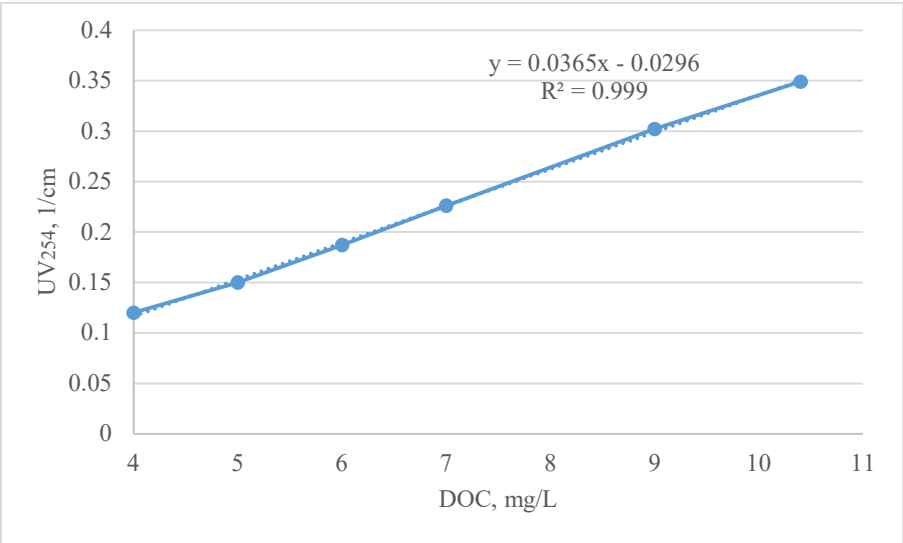


Figure 5.11. DOC correlation to UV_{254} by applying PAC

In the previous research, it was reported that PAC removes LMW nonhumic and LMW uncharged organic species from the water (Takdastan and Eslami 2013).

5.8 Conclusion

By comparing the results obtained by single PAC adsorption and alum coagulation by itself it was assumed that alum coagulation process was more effective for reducing UV_{254} (level UV_{254} of 0.079 1/cm) and SUVA (level SUVA of 1.3 L/mg-cm), with percent of removal 81% of UV_{254}, and 64% of SUVA, respectively. Besides, 70% of UV_{254} removal was achieved at optimum conditions (PAC dose of 200 mg/L at pH=6.0) by applying PAC adsorption process. DOC maximum reduction value of 66% was higher obtained by PAC adsorption treatment

compared with DOC maximum reduction value of 50% observed by alum coagulation. The experimental data indicated that DOC maximum removal value by PAC adsorption process was by 16% higher than DOC reduction by alum coagulation. The level SUVA reduced by PAC adsorption was 2.7 L/mg-cm, while the level SUVA of 1.3 L/mg-m was achieved by applying alum coagulation. The experimental data indicate that alum coagulation and PAC adsorption remove the different levels of NOM fractions. It probably means that PAC removes LMW hydrophilic, nonhumic and uncharged fractions, which cannot be removed by alum coagulation. While alum coagulation removes HMW hydrophobic and humic NOM compounds. The observation is consistent with previous studies showing that PAC process was more effective for the reduction of low molecular weight and uncharged DOC compounds compared with alum coagulation treatment (Uyak et al. 2007). Based on experimental data, single alum coagulation and PAC adsorption treatments could be applied in combination to remove a different NOM fractions. One of the objective of this study was to reduce surface water treatment cost by decreasing chemical consumption. Hence, the optimum conditions for maximum reduction of the water quality parameters (DOC, UV_{254}, and SUVA) were 200 mgPAC/L at pH=5.5 by applying PAC adsorption process. The attempt for further increase of PAC dosage was not made in this research because the further PAC dose increase will not normalise expected water treatment cost. Thus, the PAC adsorption process is reasonable to use as a coagulant aid to study the effectiveness of the order of addition of alum and PAC for DOC, UV_{254}, and SUVA reductions from the surface water.

CHAPTER SIX

6. THE EFFECT OF SIMULTANEOUSLY ADDITION OF ALUM COAGULANT WITH PAC

6.1 Introduction

The effect of simultaneous addition of alum with PAC dose was investigated to maximize the reduction of DOC and UV_{254}. The simultaneous combined Al+PAC water treatment process was studied as a function of PAC dose of 0 to 200 mg/L and pH of 5.5 to 7.5 at a fixed aluminium dosage of 25mg/L. In the chapter four it was reported that a fixed aluminium dose of 25 mg/L was optimum aluminium dose observed for NOM reduction in surface water by using alum coagulation process, Figures (4.2 and 4.4). Based on jar test data, aluminium dose of 25 mg/L was applied for the order of addition study using simultaneously combined Al+PAC technique.

6.2 Jar test procedure for simultaneously combined Al+PAC process

The jar test experiments were performed for the surface water treatment using simultaneously combined Al+PAC process by varying PAC dosage in the range of 0-200 mg/L, and pH of 5.0 to 7.0. Jar test preparation for the simultaneously combined Al+PAC water treatment was performed, as shown in Figure 6.1.

Figure 6.1. Jar testing apparatus by simultaneous addition of alum with PAC

Firstly, in each beaker of six beakers surface water samples of 250 mg/L were poured and the samples brought to a temperature of 22 ± 3 °C. Next, aluminium dose of 25mg/L simultaneously with PAC doses of 0, 40, 80, 120, 160 and 200 mg/L were added into beakers with surface water samples in it. The first glass beaker from the right with no black colour has zero PAC dose in it, Figure 6.1. Also, 1M hydrochloric acid and sodium hydroxide solutions were used for pH adjustment in the range of 5.5-7.5 after alum and PAC addition simultaneously. In the first jar test experiment setup, pH of 5.5 was adjusted in each beaker. Generally, five jar test experimental setups were performed in the range of pH of 5.5 to 7.5. The applied jar test conditions (pH, aluminium and PAC doses) for surface water sample treatment using the simultaneously combined process study were presented in Table 3.2.

6.3 Determining optimum PAC dose and pH for DOC reduction

As presented in Figure 6.2, the maximum reduced DOC value was equaled 85% by adding simultaneously aluminium dose of 25 mg/L with a PAC dose of 200 mg/L at optimum pH of 5.5.

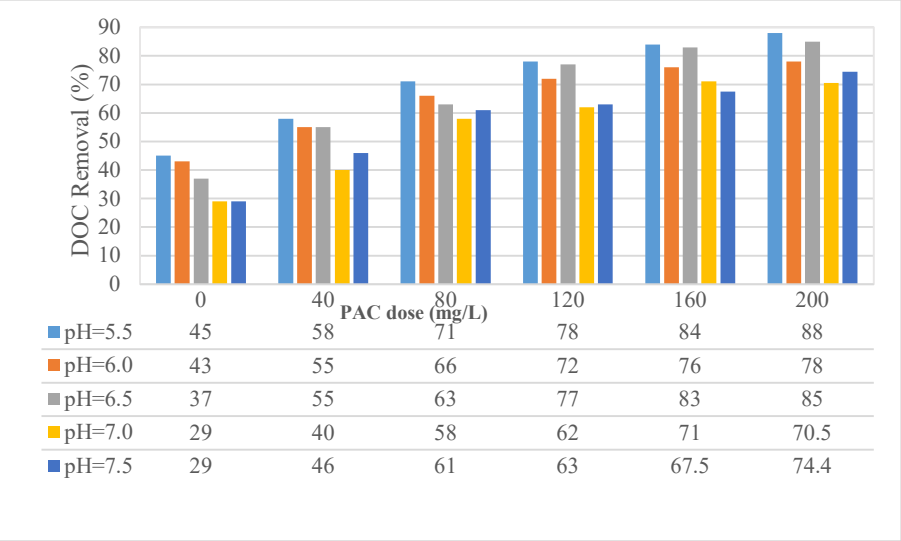


Figure 6.2. Percent removal of DOC by simultaneous addition of an aluminium dose of 25 mg/L with PAC as function of PAC dose of 0 to 200 mg/L and pH of 5.0 to 7.5

The remained DOC concentration in the treated water sample was 1.7 mg/L (DOC concentration detected in the untreated water sample minus DOC in the treated water sample)

at applied optimum conditions, aluminium dose of 25 mg/L and PAC dose of 200 mg/L using simultaneously combined Al+PAC process, Table 6.1. Figure 6.2 shows the high performance of the combined Al+PAC process for DOC reduction in the pH range of 5.5 and 6.5. Thus, the maximum DOC removal values of 88 and 85% were achieved by applying the combined 25mgAl/L+200mgPAC/L water treatment system at pH levels of 5.5 and 6.5.

As demonstrated in Figure 6.3, optimum conditions for maximum DOC reductions are: alumiinium dose of 25 mg/L, PAC dose of 200 mg/L PAC, and pH of 5.5 by using simultaneously coagulation-adsorption process. Jar test results and DOC analysis revealed that DOC removal is characterised by a gradual increase in DOC removals with increasing PAC dosage from 40 to 200 mg/L, approaching the maximum DOC removals of 84-88% at applied 160-200 mgPAC/L dosages and pH=5.5. The similar increase in DOC reduction with gradually PAC dosage increase is described (Najm et al. 1998, Shen and Chaung 1998, Szlachta and Adamski 2009).

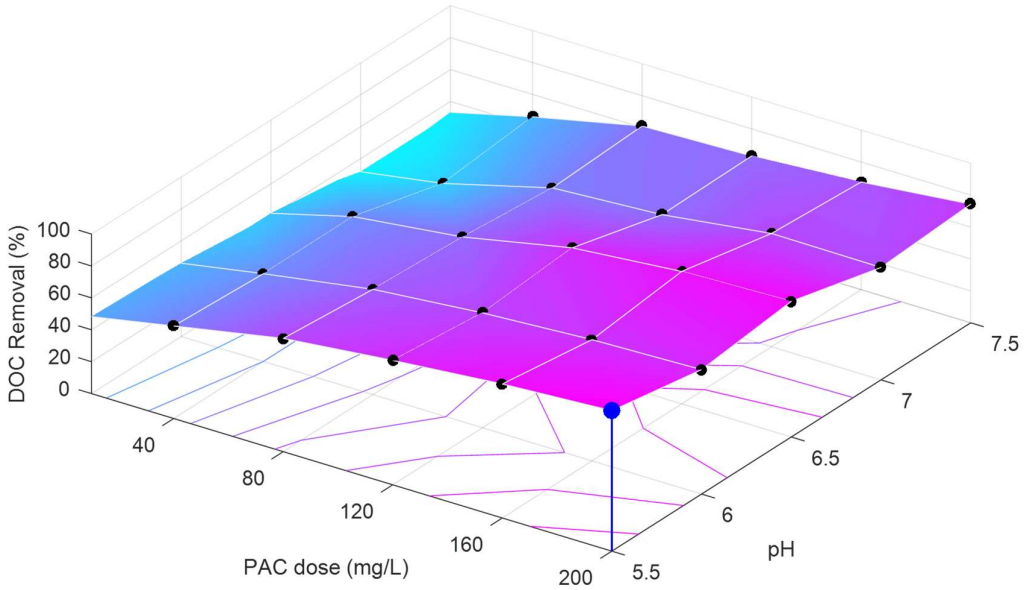


Figure 6.3. Percent removal of DOC by simultaneous addition of an aluminium dose of 25 mg/L as a function of PAC dose of 0 to 200 mg/L and pH of 5.5 to 7.5

Thus, the defined optimum conditions for DOC reduction described as 25mgAl/L, 200mgPAC/L at pH level of 5.5 by using simultaneously combined Al+PAC process. The level

DOC of 1.74 mg/L was detected in the treated water sample, while the level DOC of 12 mg/L was defined in the untreated water sample.

6.4 Determining optimum PAC dose and pH for UV_{254} reduction

The experimental data revealed that low UV_{254} reduction values were observed by applying PAC dosage of 40 mg/L and high reduction of UV_{254} achieved by adding a high PAC dose range of 160-200 mg/L. Figure 6.4 shows that by increasing PAC dosage from 40 to 200 mg/L UV_{254} absorbance removal significantly increased. A maximum 99% of UV_{254} reduction was achieved by applying PAC dose of 200 mg/L. Thus, UV_{254} removal was efficient by applying simultaneously combined 25 mgAl/L+ 200 mgPAC/L system at pH=6.5.

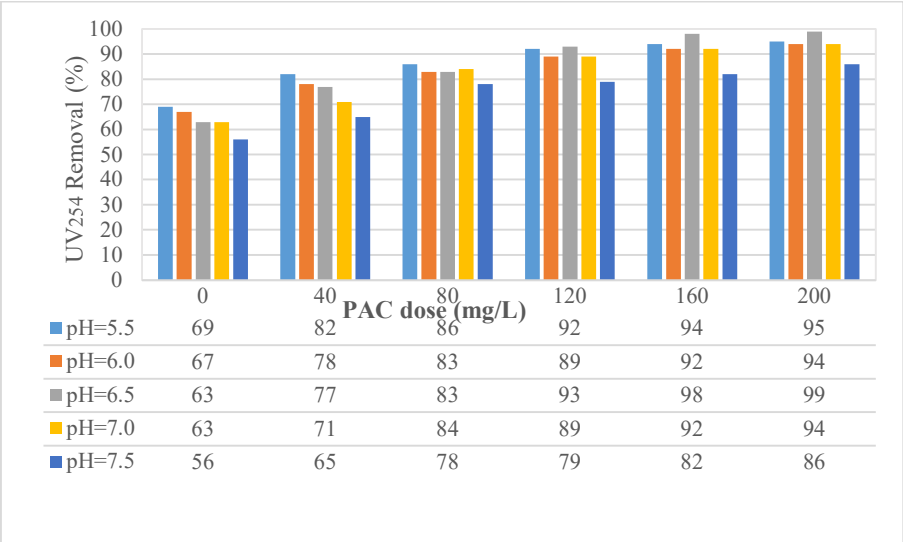


Figure 6.4. Percent removal of UV_{254} absorbance by simultaneous addition of an aluminium dose of 25 mg/L with PAC as a function of PAC dose of 0 to 200 mg/L and pH of 5.5 to7.5

Figure 6.5 shows that 99% of UV_{254} removal value was achieved by applying simultaneously combined 25 mgAl/L+200 mgPAC/L water treatment system at pH=6.5. If level UV_{254} of 0.404 1/cm was observed in the untreated water sample, level UV_{254} of 0.006 1/cm was achieved in the treated water sample by applying the simultaneously combined 25 mgAl/L+200 mgPAC/L system at pH=6.5.

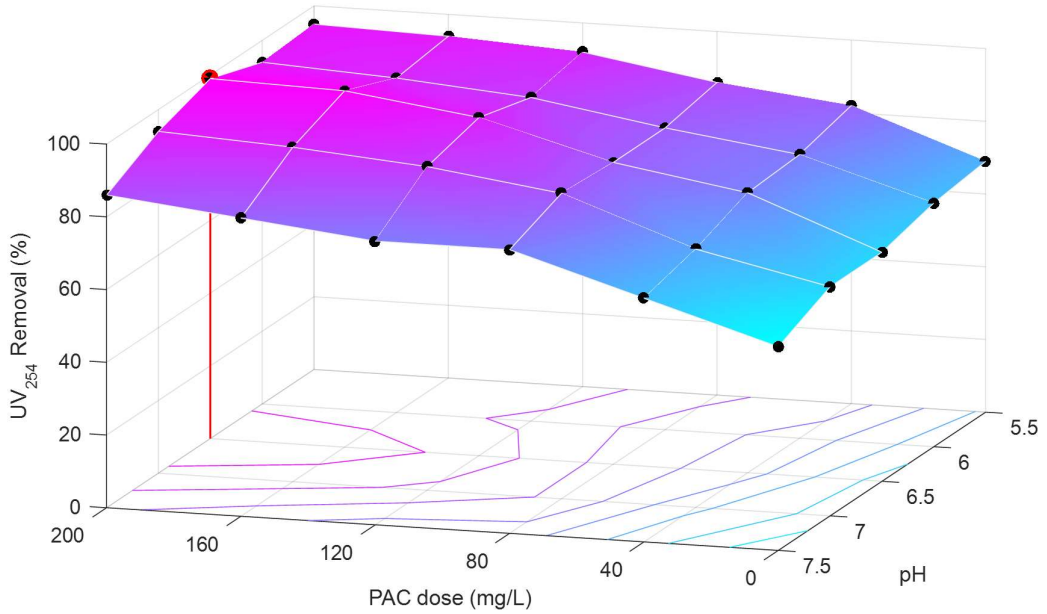


Figure 6.5. Percent removal of UV_{254} by simultaneous addition of an aluminium dose of 25 mg/L as a function of PAC dose of 40 to 200 mg/L and pH of 5.5 to7.5

6.5 Determining optimum PAC dose and pH for SUVA reduction

The optimum PAC dose for maximum reduction of SUVA using simultaneously combined alum coagulation with PAC adsorption defined as PAC dose of 200 mg/L and aluminium dose of 25 mg/L at pH=6.5, Figure 6.6. If high level SUVA of 3.3 L/mg-cm was observed in the untreated water, the lower level SUVA of 0.34 L/mg-cm was achieved in the treated water sample at optimum conditions (aluminium dose of 25 mg/L, PAC dose of 200 mg/L, and pH=6.5).

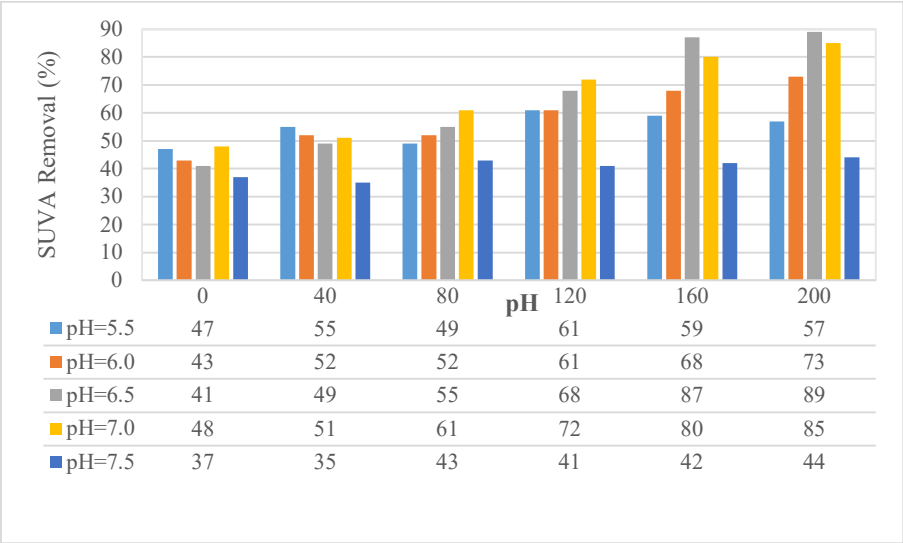


Figure 6.6. Percent removal of SUVA absorbance by simultaneous addition of an aluminium dose of 25 mg/L with PAC as a function of PAC dose of 40 to 200 mg/L and pH of 5.5 to 7.5

The DOC and UV_{254} reductions appear to be dominant at optimum pH=6.5 because at this pH maximum removal value 99% of UV_{254} was achieved, Figures (6.6-6.7). The maximum reduction value 88% of DOC was observed at pH=5.5 compared with slightly lower 85% of DOC reduction value at pH=6.5. DOC, UV_{254}, and SUVA removal values were 85%, 99%, and 89% at the proposed optimum pH=6.5. The lower levels UV_{254} of 0.006 adsorbing compounds, DOC of 1.74 mg/L and SUVA of 0.3 L/mg-cm were detected in the treated water sample by using combined 25 mgAl/L+200 mgPAC/L system at pH of 6.5. Thus, the high level UV_{254} of 0.402 in the untreated water was reduced to lower level UV_{254} of 0.006 UV-absorbing compounds in the treated water. Also, the high level DOC of 11.97 mg/L was decreased to 1.74 mg/L. The level SUVA of 0.3 L/mg-cm in the treated water was lower compared with level SUVA of 3.3 L/mg-cm in the untreated water sample, Appendix Table C1.

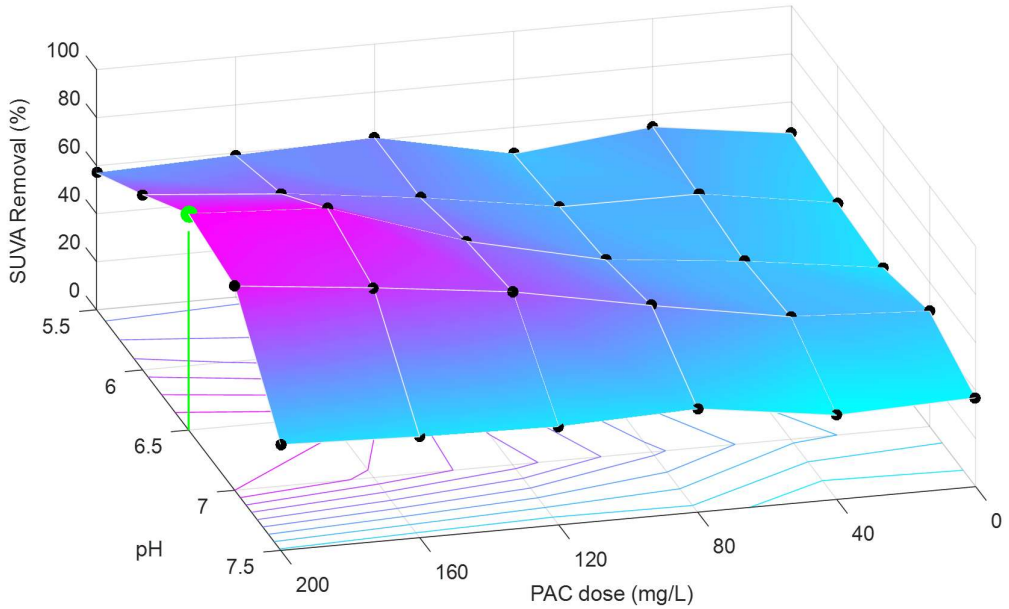


Figure 6.7. Percent removal of SUVA absorbance by simultaneous addition of an aluminium dose of 25 mg/L with PAC as a function of PAC dose of 40 to 200 mg/L and pH of 5.5 to 7.5

The noticeable 89% of SUVA percentage removal value achieved at conditions 25 mgAl/L plus 200 mgPAC/L and pH=6.5 using simultaneously combined coagulation-adsorption treatment. The light green vertical line indicates optimum pH=6.5 and PAC dose of 200 mg/L for maximum reductions of the water quality parameters, including the SUVA parameter, Figure 6.7. Thus, the low level SUVA of 0.3 L/mg-cm was achieved by applying the combined Al+PAC water treatment process compared with the high level SUVA of 3.3 L/mg-cm detected in the untreated water sample.

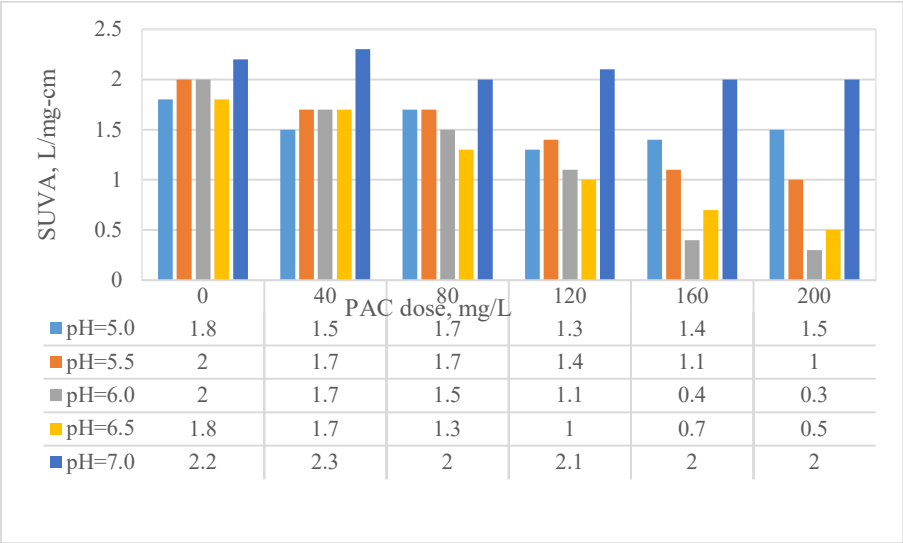


Figure 6.8. SUVA values in treated water by simultaneous addition of an aluminium dose of 25 mg/L with PAC as a function of PAC dose of 40 to 200 mg/L and pH of 5.0 to 7.0

The SUVA value of the raw surface water samples ranged between 3.3-3.5 (L/mg-cm). The low 0.5 SUVA value of the treated water sample at aluminium dose of 25 mg/L, PAC dose of 200 mg/L and pH=6.5. At those PAC dose and pH the treated water sample had the highest 85% of DOC and 99% of UV_{254} reduction and high reduction 89% of SUVA, Figures (6.2, 6.4, and 6.6). The high reduction of SUVA in treated water throughout of the simultaneous addition of 25mgAl/L and 200mgPAC/L process demonstrated that hydrophobic humic acids were successfully removed to very high level. Hence, this study shows that the simultaneously combined Al+PAC process was more effective in NOM reduction than single alum coagulation.

6.6 DOC, UV_{254}, and SUVA reduction analysis

As shown in Figure 6.9, 83-85% DOC, 98-99% UV_{254}, and 87-89% SUVA reduction values were achieved at PAC dose range between 160 and 200 mg/L. The water quality parameters reduction values were slightly different at applied PAC doses of 160 and 200 mg/L. Based on the experimental data, the difference in maximum reduction of NOM at applied PAC doses from 160 to 200 mg/L was in the range of 1 to 3%. However, PAC dose of 160 mg/L will significantly reduce the bulk water treatment cost.

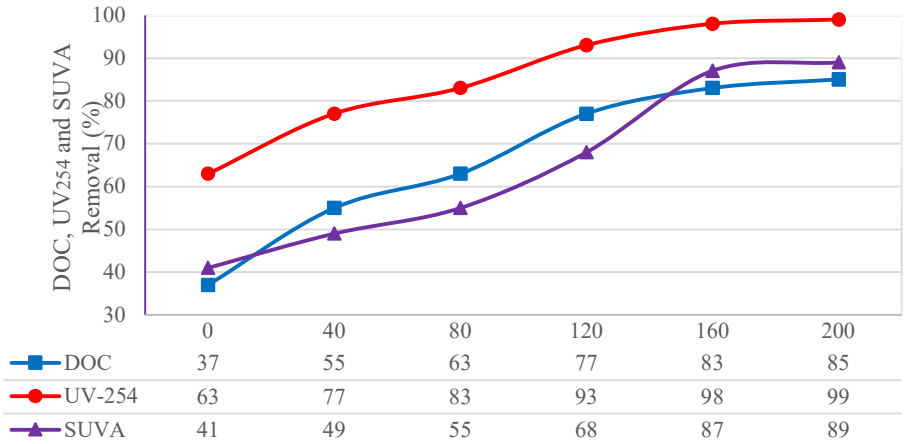


Figure 6.9. Percent removal of DOC, UV_{254}, and SUVA by simultaneous addition of an aluminium dose of 25 mg/L with PAC as a function of PAC dose of 0 to 200 mg/L at pH=6.5

In Table 6.1 presented experimental data for water quality parameters reduction by applying aluminium dose of 25 mg/L, PAC dose of 200 mg/L at different pH level of 5.5 and 6.5. The lowest level SUVA of 0.30 L/mg-m was achieved by applying simultaneously combined 25 mgAl/L+200 mgPAC/L water treatment system at pH=6.5.

Table 6.1. Comparison of the DOC, UV_{254} and SUVA reductions at different pH of 5.5 and 6.5

Treatment Process	DOC		UV_{254}		SUVA	
	Removal, %	Remained, mg/L	Removal, %	Remained, 1/cm	Removal, %	Remained, L/mg-m
25mgAl/L+200mgPAC/L (pH=5.5)	88	1.5	95	0.022	57	1.40
25mgAl/L+200mgPAC/L (pH=6.5)	85	1.7	99	0.006	89	0.30
25mgAl/L+200mgPAC/L (pH=6.5)	83	2.1	98	0.009	87	0.40

6.7 Effect of aluminium dose on DOC, UV_{254}, and SUVA reduction

In Figure 6.10 presented the DOC, UV_{254}, and SUVA reduction values by using simultaneously combined Al+PAC process at a fixed PAC dose of 200 mg/L and pH as a function of aluminium dose of 10 to 200 mg/L. High reduction of UV_{254} and SUVA were observed by adding aluminium dose of 25 mg/L simultaneously with PAC dose of 200 mg/L at pH≤6.5.

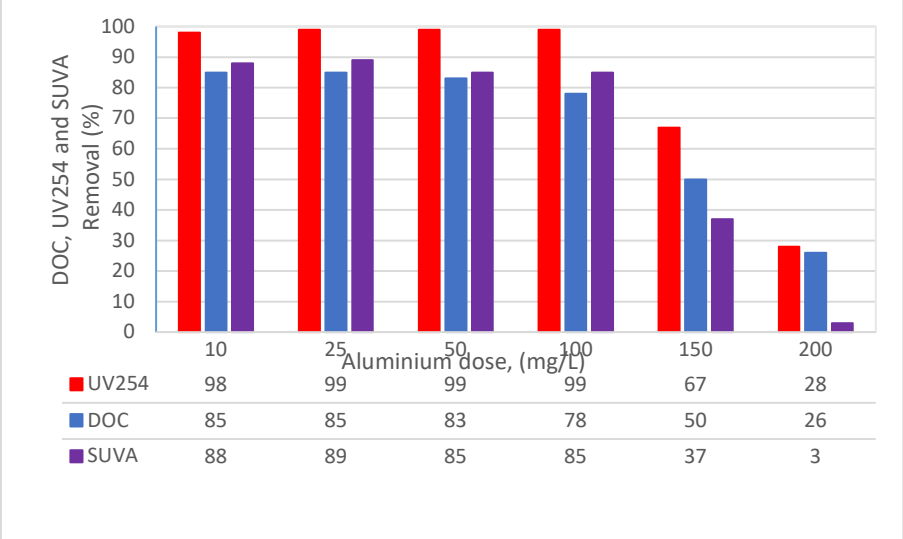


Figure 6.10. Percent removal of DOC, UV_{254}, and SUVA by simultaneous addition aluminium with PAC dose of 200 mg/L as a function of aluminium dose of 10 to 200 mg/L at pH≤6.5

According to Figure 6.10, the increased rate of aluminium dose addition from 10 to 100 mg/L had a small effect on DOC, UV_{254}, and SUVA reduction. However, aluminium dose increase from 100 to 200 mgAl/L revealed that the DOC, UV_{254}, and SUVA removal values decrease occurred. The low removal of NOM by increasing aluminium dose may be the result of competition between humic substances and OH- for Al or changes in nature of the humic substances before or following water treatment at pH ≥7.0 (Van Benschoten and Edzwald 1990). Also, Van Benschoten and Edzwald (1990) reported that at higher pH and higher aluminium dose applied bindings between humic substances and aluminium decreases, it is likely that residual humic substances have a lower complexation capacity. Based on the histogram peaks, the optimum aluminium dose rate was between of 10 and 25 mg/L. Thus, for

further reduction of chemical consumption, sludge and water treatment cost, 10 mg/L of aluminium dosage would be recommended for water treatment by using simultaneous combined Al+PAC process.

6.8 Effect of PAC dose on DOC, UV_{254}, and SUVA reduction

Simultaneously combined coagulation and PAC adsorption 25 mgAl/L+200 mgPAC/L system was investigated as a function of PAC of 0 to 480 mgPAC/L at pH=6.0, Figure 6.11.

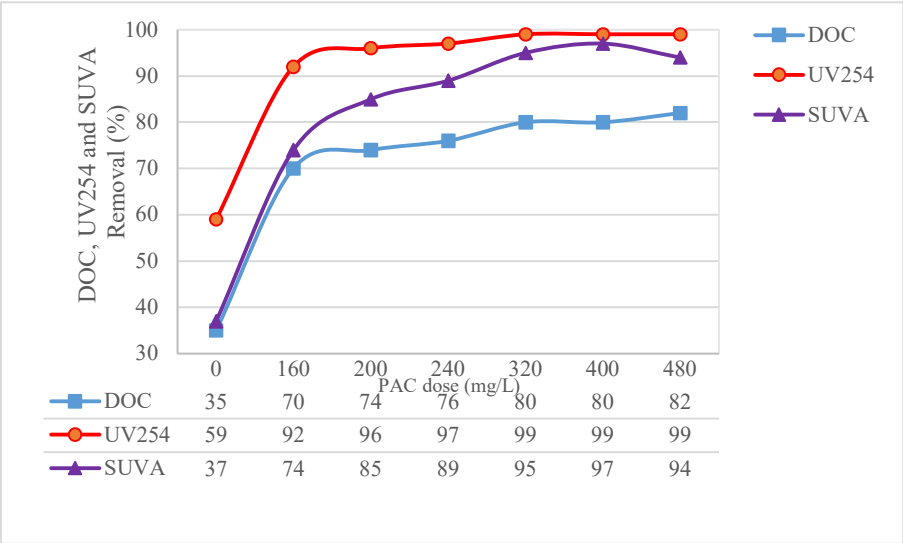


Figure 6.11. Percent removal of DOC, UV_{254}, and SUVA by simultaneous addition of an aluminium with PAC at a fixed aluminium dose of 25 mg/L as a function of PAC dose of 0 to 480 mg/L and pH=6.0

Gradually increase in DOC, UV_{254}, and SUVA reduction values were observed by increasing PAC dosage from 0 to 400 mgPAC/L. However, the UV_{254} and SUVA reduction insignificantly decreased by further PAC dose increase from 400 mg/L to 480 mg/L.

6.9 DOC correlation to UV_{254} at a fixed pH

As shown in Figure 6.12, an excellent UV_{254} correlation to DOC was defined using simultaneously combined alum coagulation with PAC adsorption water treatment process. The

defined coefficient of determination (R^2=0.998) was very close to 1 by indicating a linear relationship between UV_{254} and DOC.

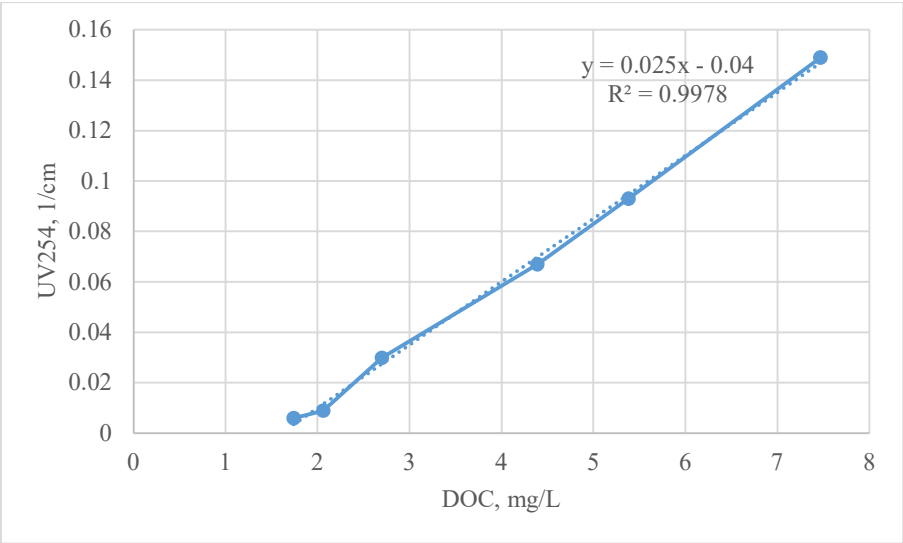


Figure 6.12. DOC correlation to UV_{254} by simultaneous addition of an aluminium dose of 25 mg/L with PAC as a function PAC dose of 0 to 200 mg/L at pH=6.5

6.9 Conclusion

The effectiveness of simultaneously combined Al+PAC process was significantly higher compared to the single alum coagulation process. For example, DOC, UV_{254}, and SUVA reduction values increased by 35%, 18%, and 25% by using the simultaneously combined 25 mgAl/L+200 mgPAC/L system. Furthermore, high levels DOC of 12 mg/L and UV_{254} of 0.404 1/cm in raw water sample were reduced to the lower levels DOC of 1.74 mg/L and UV_{254} of 0.006 1/cm. SUVA of 3.4 L/mg-cm in raw water sample was reduced to level SUVA of 0.3 after water treatment. The significant decrease of NOM in the treated water sample was explained by the complementary and synergistic effect of alum coagulant with PAC. While alum coagulant removes HMW hydrophobic natural organic matter, PAC adsorption removes LMW hydrophilic organic and uncharged NOM compounds which are cannot be removed by a single alum coagulation process (Carriere et al. 2009). It was assumed that the simultaneously combined Al+PAC coagulation-adsorption treatment removed the hydrophobic high molecular weight and low molecular weight UV_{254} absorbable NOM compounds. Also, it was suggested that the simultaneously combined Al+PAC process removed more readily

aromatic NOM fractions other than nonaromatic organic compounds. Thus, the study of the simultaneously combined Al+PAC process demonstrated that the effects of alum coagulation and PAC adsorption on the removal of NOM are complementary. DOC removal enhanced, both in terms of the overall amount and types of DOC removed (i.e. fractions with different chemical characteristics) as a result of the simultaneous addition of alum coagulant and PAC. Notably, only slightly lower reductions of DOC, UV_{254}, and SUVA were observed by applying a combined 25 mgAl/L+160 mgPAC/L system compared with the combined 25 mgAl/L+200 mgPAC/L system. The final reduction values of the water quality parameters were 88% of DOC, 99% of UV_{254}, and 89% of SUVA by using simultaneously combined 25 mgAl/L+ 200 mgPAC/L system at pH=6.5, Table 6.1.

CHAPTER SEVEN

7. THE EFFECT OF ALUM ADDITION BEFORE PAC ADSORPTION, Al—PAC PROCESS

7.1 Introduction

The effect of aluminium dosage addition prior to PAC was studied to optimise PAC dosage, pH, DOC, UV_{254}, and SUVA using combined alum coagulation before PAC adsorption Al—PAC treatment. The combined Al—PAC water treatment process was investigated at a fixed aluminium dose of 25 mg/L as a function of PAC dose of 0 to 200 mg/L at pH range of 6.0 and 6.5. Based on experimental data the pH range from 6.0 to 6.5 was chosen for the Al—PAC process study. Also, previous researchers reported that the optimum pH range is between 6.0 and 7.0 for humic NOM reduction by using alum coagulation (Yang et al., 2010). The jar test data demonstrated that maximum reduction of UV_{254} was achieved by alum coagulation and simultaneously combined Al+PAC processes at the pH 6.5, Figures (6.4 - 6.5).

7.2 Determining an optimum PAC dose and pH for DOC reduction

The experimental data for DOC reduction are presented as a function of PAC dose of 0 to 200 mg/L at pH 6.0 and 6.5 by using the combined Al—PAC process in which aluminium dose of 25 mg/L added before PAC adsorbent addition, Figure 7.1. PAC dosage increase resulted in DOC reduction increase. Also, the figure 7.1 shows that the maximum removal of DOC was observed at pH=6.5.

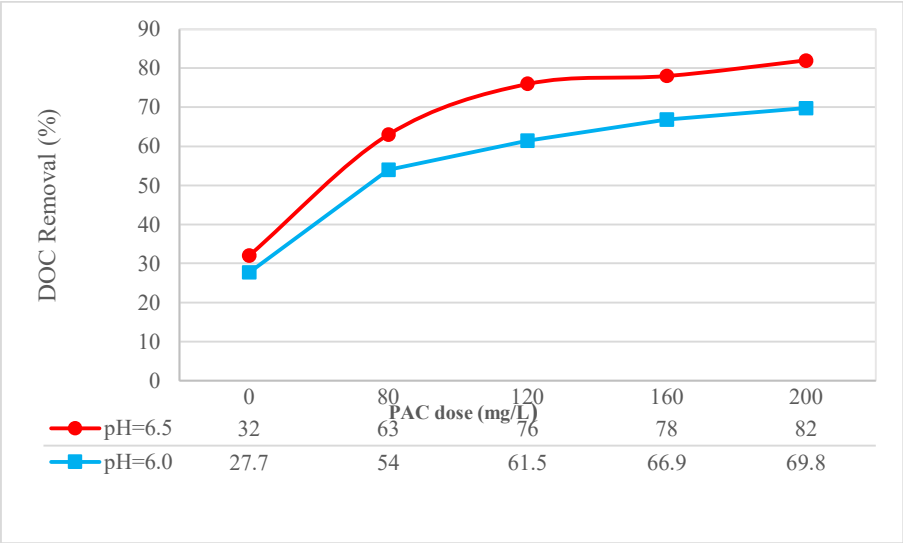


Figure 7.1. Percent removal of DOC by adding an aluminium dose of 25 mg/L before PAC as a function of PAC dose of 0 to 200 mg/L at pH of 6.0 and 6.5

Figure 7.2 demonstrates that DOC maximum reduction was observed at a fixed aluminium dose of 25 mg/L as a function of PAC dose of 0 to 200 mg/L and pH. The optimum conditions for DOC reductions indicated by a blue vertical line and blue spot, and they are: 25 mgAl/L, 200 mgPAC/L, and pH of 6.5.

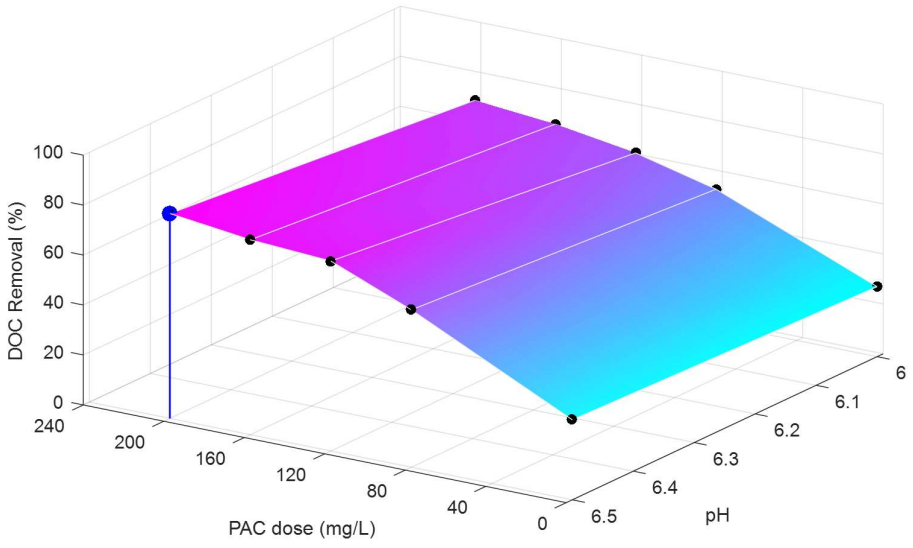


Figure 7.2. Percent removal of DOC by adding an aluminium dose of 25 mg/L before PAC as a function of PAC dose of 0 to 200 mg/L and pH of 6.0 and 6.5

The combined water treatment system at these optimum conditions was expressed as 25mgAl/L—200mgPAC/L at pH=6.5. At these optimum conditions, maximum reduction value of DOC equaled to 82%. The low level DOC of 1.6 mg/L was detected in the treated water sample which is significantly lower compared with high level DOC of 11 mg/L observed in the untreated water.

7.3 Determining an optimum PAC dose and pH for UV_{254} reduction

The maximum 98% of UV_{254} reduction value was observed by adding aluminium dose of 25 mg/L before PAC dose of 200 mg/L at pH=6.5, Figure 7.3. It appears that DOC and UV_{254} reduction values favoured at pH=6.5 by applying the combined Al—PAC water treatment process.

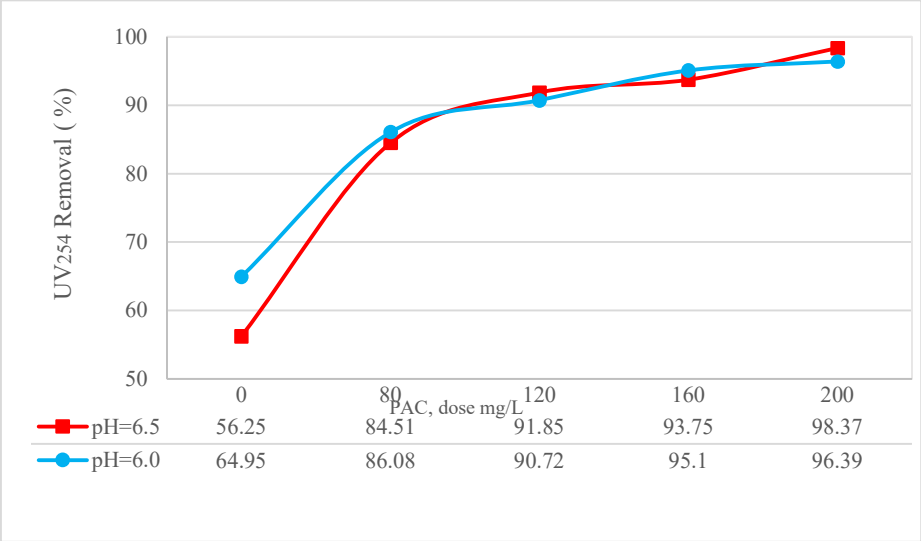


Figure 7.3. Percent removal of UV_{254} by adding an aluminium dose of 25 mg/L before PAC as a function of PAC dose of 0 to 200 mg/L and pH of 6.0 and 6.5

In 3D Figure 7.4 showed the maximum 98% of UV_{254} reduction value by red vertical line and red spot and the conditions are the same as for DOC maximum removal. The combined Al—PAC water treatment process for maximum reduction of both UV_{254} and DOC values at optimum conditions expressed as 25 mgAl/L—200 mgPAC/L at pH=6.5.

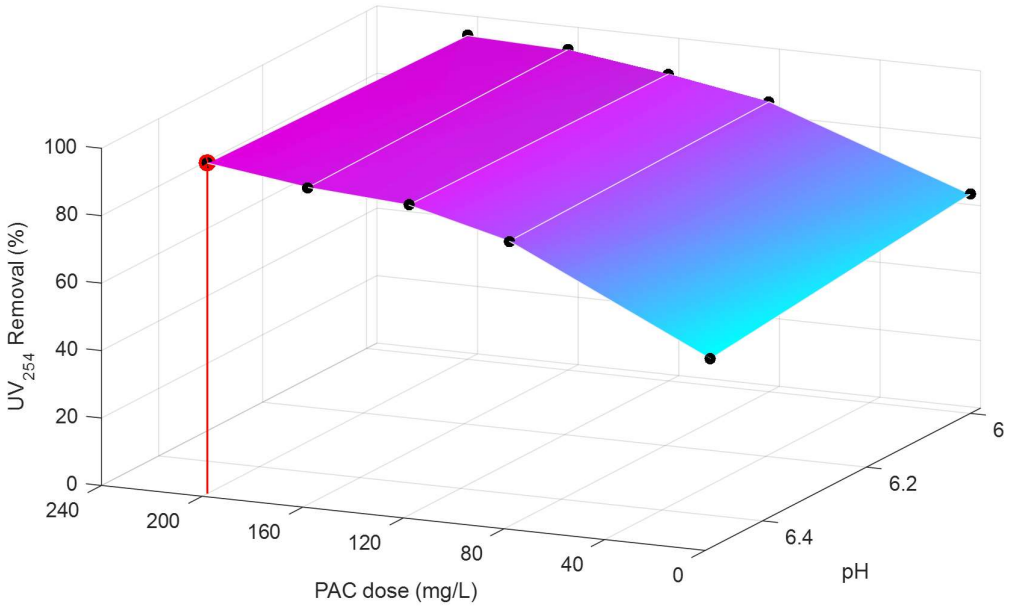


Figure 7.4. Percent removal of UV_{254} by adding an aluminium dose of 25 mg/L before PAC as a function of PAC dose of 0 to 200 mg/L and pH of 6.0 and 6.5

Also, the level UV_{254} of 0.008 1/cm was achieved in the treated water sample, while UV_{254} of 0.368 1/cm adsorbing materials were observed in the untreated water sample, Appendix Table D1.

7.4 Determining an optimum PAC dose and pH for SUVA reduction

As demonstrated in Figures (7.5-7.6), SUVA maximum removal value was observed at pH=6.0. At this pH, SUVA reduction value was reduced by 88% by applying combined coagulation-adsorption 25 mgAl/L—200 mgPAC/L water treatment system.

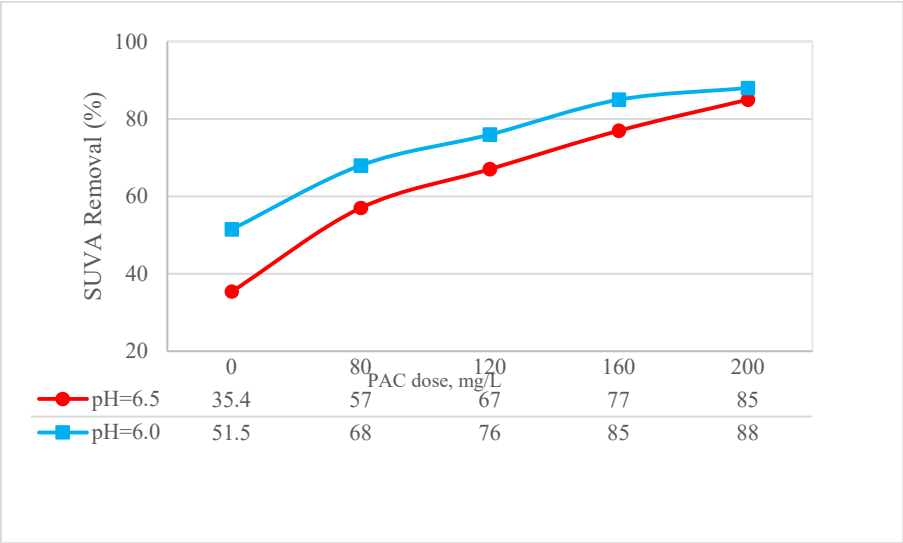


Figure 7.5. Percent removal of UV_{254} by adding an aluminium dose of 25 mg/L before PAC as a function of PAC dose of 0 to 200 mg/L and pH of 6.0 and 6.5

The optimum conditions for SUVA reduction indicated by a light green vertical line and spot, Figure 7.6. Maximum reduction of 85% of SUVA value was achieved at pH=6.0, while maximum reduction 82% of DOC and 98% of UV_{254} were observed by adding aluminium dose of 25 mg/L before PAC dose of 200 mg/L at pH=6.5. At this pH, the low level SUVA of 0.5 L/mg-cm was achieved in the treated water sample, while SUVA of 3.3 L/mg-cm was observed in the untreated water. Thus, the pH=6.5 was proposed as an optimum pH for the water quality parameters reduction by the combined Al—PAC process, Figures (7.1 and 7.3).

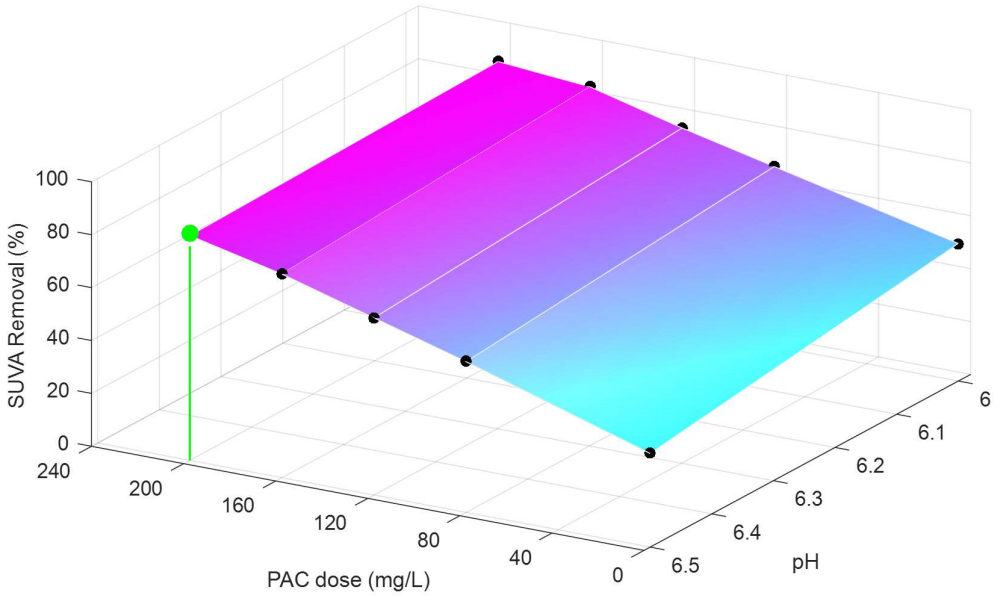


Figure 7.6. Percent removal of SUVA by adding an aluminium dose of 25 mg/L before PAC as a function of PAC dose of 0 to 200 mg/L and pH of 6.0 and6.5

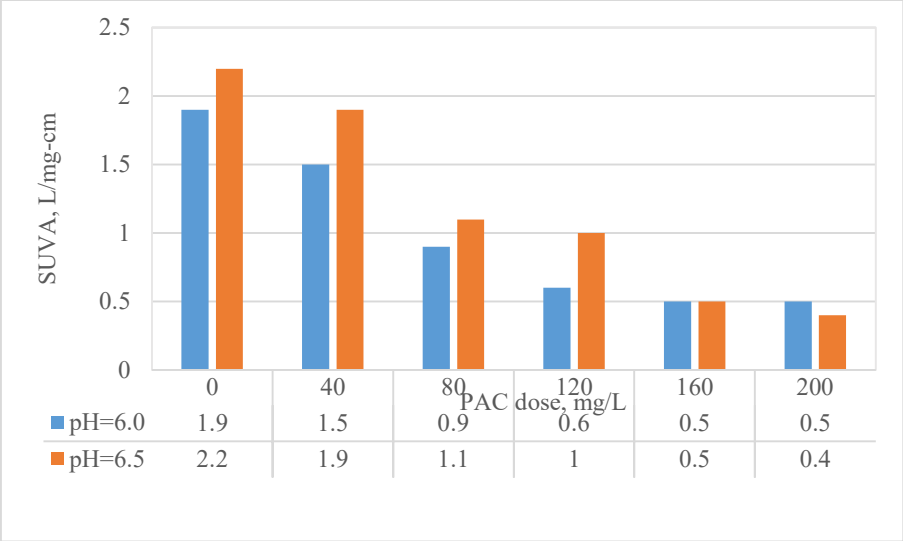


Figure 7.7. SUVA values in treated water by alum addition before PAC dose at a fixed aluminium dose of 25 mg/L as a function of PAC dose of 40 to 200 mg/L in the pH range of 6.0 to 6.5

The SUVA value of the raw surface water ranged from 3.4-3.8 (L/mg-cm). The lowest level SUVA value of 0.5 was achieved in treated water by applying PAC dose of 200 mg/L and

pH=6.5. At that PAC dose and pH the highest 82% of DOC, 98% of UV_{254}, and 85% of SUVA values were achieved, Figures (7.1, 7.3, and 7.5). The high reduction of SUVA in treated water throughout of the aluminium dose of 25mg/L addition before PAC dose of 200 mg/L demonstrated that hydrophobic humic acids were successfully removed to a very high level. This study shows that the alum addition before PAC or Al—PAC process removes almost the same amount of NOM compared with simultaneous combined Al+PAC process. Therefore, the combined Al—PAC process removed HMW hydrophobic, LMW and uncharged NOM substances as well as the combined Al+PAC process.

7.5 DOC, UV_{254}, and SUVA reduction analysis

DOC, UV_{254}, and SUVA reduction values were plotted in Figure 7.8 by adding an aluminium dose of 25 mg/L prior to PAC addition as a function of PAC dosage from 0 to 200 mg/L at pH=6.5. DOC, UV_{254}, and SUVA reduction values of 82%, 98% and 85% observed by applying the combined coagulation-adsorption 25mgAl/L—200mgPAC/L system at pH=6.5.

UV_{254} maximum removal value was 16% higher compared with the removed DOC value, suggesting that alum coagulation before PAC adsorption (Al—PAC) process was more effective in removing UV_{254} adsorbing humic fraction than other LMW non-humic fraction. The low level SUVA of 0.4 L/mg-cm was defined by using the 25 mgAl/L—200 mgPAC/L water treatment system at pH=6.5. The detected level SUVA indicates that remained in the treated water NOM fractions are mainly hydrophilic LMW dissolved organic matter species with nonhumic origin (Edzwald 1993). Besides, Edzwald (1993) reported that SUVA values of less than 3 indicate that the DOC mainly containing aquatic humic materials of LMW and low in charge density. The levels DOC of 1.6 mg/L, UV_{254} of 0.008 1/cm, and SUVA of 0.4 L/mg-cm detected by applying subsequently combined coagulation-adsorption (Al—PAC) process were comparable with the levels DOC of 1.7, UV_{254} of 0.006 and SUVA of 0.3 observed by simultaneously combined Al+PAC water treatment process. Thus, the combined coagulation-adsorption Al—PAC process was compatible with the simultaneously combined Al+PAC water treatment process in the reduction of NOM in terms of water quality parameters.

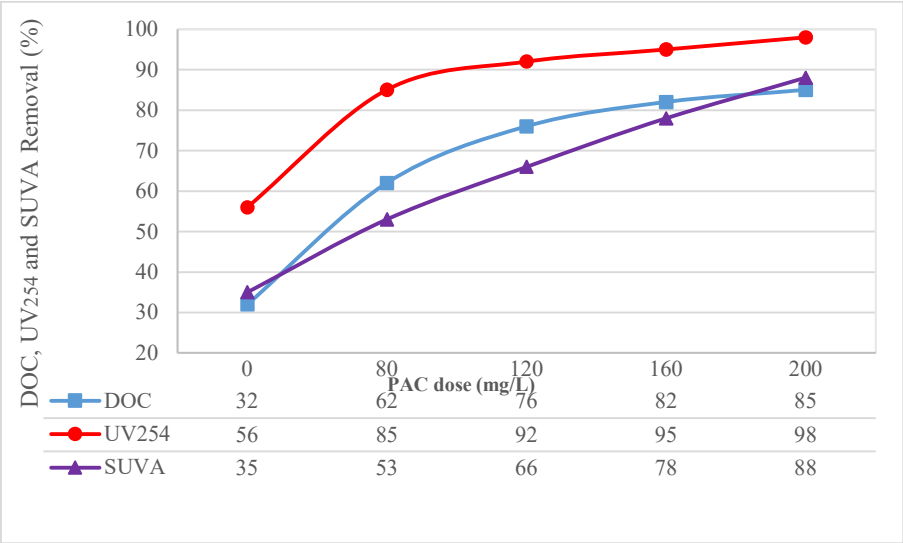


Figure 7.8. Percent removal of DOC, UV_{254} and SUVA by adding an aluminium dose of 25 mg/L before PAC as a function of PAC dose of 0 to 200 mg/L at pH=6.5

7.6 DOC correlation to UV_{254}

A good UV_{254} correlation to DOC was defined using the combined Al—PAC adsorption water treatment process, Figure 7.9. The high strength of the relationship between two variables (DOC and UV_{254}) was observed with a linear coefficient of determination (R^2 = 0.996). The degree of correlation between DOC and UV_{254} shows a positive relationship for the set of the experimental data. As one set value of DOC increases the other set of UV_{254} tends to increase as well. Moreover, DOC and UV_{254} removals improved with the increased level of PAC dosage from 20 to 200 mg/L.

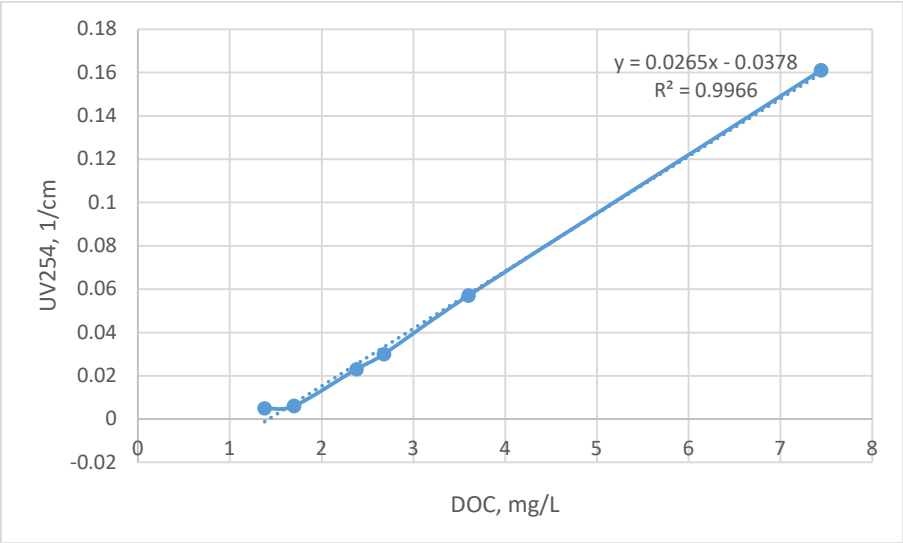


Figure 7.9. DOC correlation to UV_{254} by adding an aluminium dose of 25 mg/L before PAC as a function of PAC dose at pH=6.5

Thus, the positive correlation between UV_{254} and DOC reduction values shows that NOM contaminants in surface water sample control the requisite PAC dose for both DOC and UV_{254} – absorbing material removals in waters dominated with hydrophobic NOM.

7.7 Conclusion

According to the experimental data, maximum NOM compounds reduction in terms of DOC, UV_{254}, and SUVA **were** observed at aluminium dose of 25 mg/L addition before PAC dosage of 200 mg/L at pH=6.5 using combined Al—PAC process. According to the experimental data, the remained UV_{254} - absorbing NOM materials in the treated water sample ≤ 2%. Also, a good correlation between UV_{254} and DOC water quality parameters was observed (R^2=0.9966). The combined Al—PAC process investigation results showed preferential removal of UV_{254} absorbing fractions over DOC. The detected level SUVA of 0.3 L/mg-cm using the simultaneously combined Al+PAC process was very close to level SUVA of 0.4 L/mg-cm defined by applying the subsequent combined Al—PAC process, Appendix Table C1 and Table D1. The experimental data show that both water treatment processes removed the humic hydrophobic high and low molecular weight NOM fractions. These comparatively low SUVA values indicated that the residual DOC remaining in the treated water sample comprises mainly nonhumic, less aromatic, small molecular weight natural organic matter compounds which are less prone to DBP formation (Edzwald 1993). Thus, the combined Al—PAC process study

indicates that PAC removes low molecular weight NOM fractions which are difficult to remove by single alum coagulation because alum coagulation process preferably removes high molecular weight hydrophobic compounds of NOM.

CHAPTER EIGHT

8. PAC ADDITION BEFORE ALUM, PAC—Al PROCESS

8.1 Introduction

The combined adsorption-coagulation water treatment (PAC—Al) study aimed to estimate optimal water quality parameters in treated surface water and assess the effect of PAC before alum. This chapter examines DOC, UV_{254}, and SUVA reduction in drinking water sample using combined adsorption-coagulation treatment as a function of aluminium (10, 25, and 50 mg/L) and PAC (80; 160; 200; 240; 320; 400; 480 mg/L) doses at pH=6.0.

8.2 Determining optimum PAC dose and pH for DOC reduction

Jar test data revealed that the same 78% of DOC reduction value observed by adsorption-coagulation 200 mg PAC/L—10 mgAl/L system at pH=6.0, Figure 8.1. The PAC dosage addition increase from 80 to 200 mg/L showed that DOC reduction gradually raised. For the combined 200 mgPAC/L—10 mgAl/L system the low level DOC of 2.1 mg/L was observed in the treated water sample. While the higher levels DOC of 2.9 mg/L and DOC of 3.8 mg/L were detected in the treated water samples by applying the combined adsorption-coagulation 200 mgPAC/L—25 mgAl/L, 200 mgPAC/L—50 mgAl/L systems.

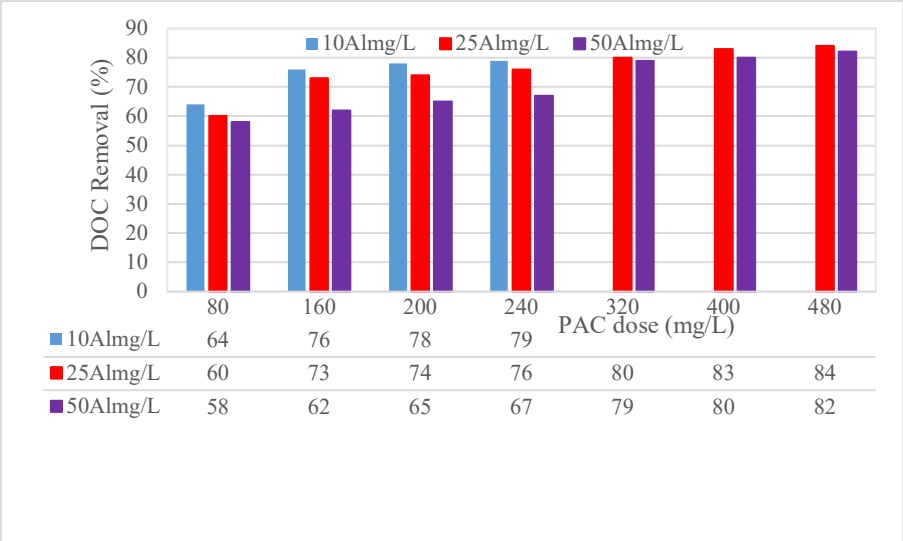


Figure 8.1. Percent removal of DOC by adding PAC before aluminium doses of 10, 25 and 50 mg/L as a function of PAC dose of 80 to 480 mg/L at pH =6.0

Based on the data the combined adsorption-coagulation water treatment by addition PAC dose of 200 mg/L before aluminium dose of 10 mg/L at pH=6.0 was proposed as optimum PAC—Al water treatment system for DOC reduction to decrease chemical consumption cost, sludge, and water treatment cost.

8.3 Determining optimum PAC dose and pH for UV_{254} reduction

UV_{254} absorbance reduction values observed at the applied aluminium dosages of 10, and 25 mg/L were close to each other using adsorption-coagulation PAC—Al water treatment as a function of PAC dosage from 80 to 200 mg/L, Figure 8.2. For both combined 200 mgPAC/L—10 mgAl/L and 200 mgPAC/L—25 mgAl/L water treatment systems, UV_{254} reduction values equaled to 95% ±1%. While the lower level UV_{254} of 0.016 was achieved by using the combined mgPAC/L—10 mgAl/L system compared with level UV_{254} of 0.021 observed in the treated water sample by applying 200 mgPAC/L—25 mgAl/L system. Therefore, the combined 200 mgPAC/L—10 mgAl/L system with aluminium dose of 10 mg/L added after PAC dose of 200 mg/L was preferred because of low cost-effectiveness compared with the combined 200 mgPAC/L—25 mgAl/L system, in which an aluminium dose of 25 mg/L added after PAC adsorption treatment, Figure 8.2.

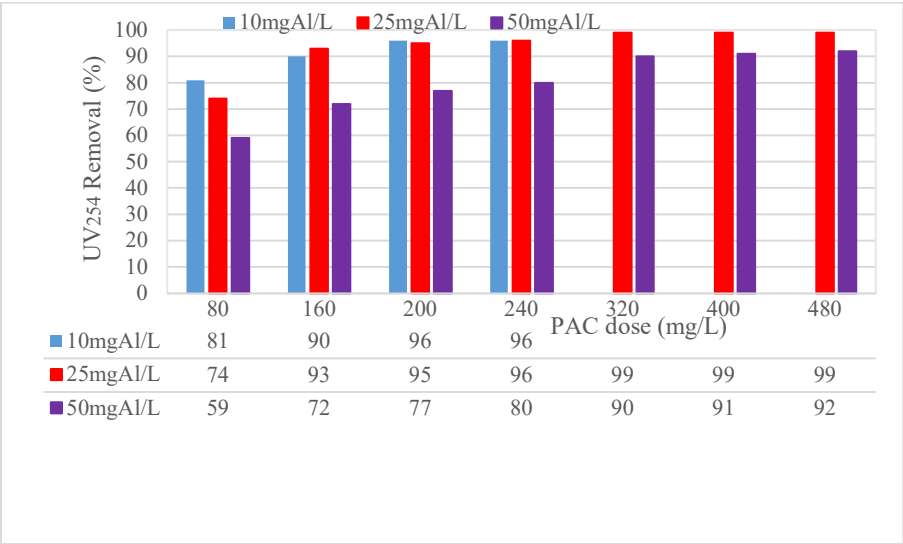


Figure 8.2. Percent removal of UV_{254} by adding PAC before an aluminium dose of 10, 25 and 50 mg/L as a function of PAC dose of 80 to 480 mg/L at pH =6.0

The lowest UV_{254} absorbance reduction values were observed by applying aluminium dosage of 50 mg/L using the combined 200 mgPAC/L—50 Almg/L system as a function of PAC dosage at pH=6.0, Figure 8.2. Therefore, the combined adsorption-coagulation 200 mgPAC/L—10 mgAl/L system was proposed as the optimum water treatment system for both UV_{254} and DOC reduction at pH=6.0, Figures (8.1-8.2).

8.4 Determining optimum PAC dose and pH for SUVA reduction

SUVA analysis indicated that the higher level SUVA of 2.1 L/mg-cm removal from treated water sample was observed by using combined 200 mgPAC/L—50 mgAl/L water treatment system, Table E1. However, the levels SUVA of 0.9 and 0.7 L/mg-cm were achieved by applying the combined adsorption-coagulation 200 mgPAC/L—10 mgAl/L and 200 mgPAC/L—25 mgAl/L systems at pH=6.0, Table E1. Thus, the combined 200 mg/L—25 mgAl/L water treatment system removes higher amount of hydrophobic high and low molecular weight NOM fractions.

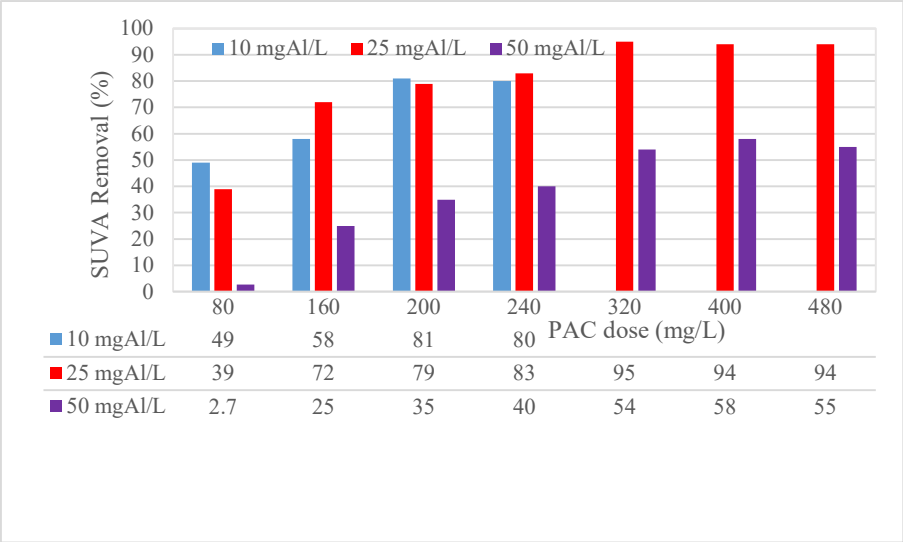


Figure 8.3. Percent removal of SUVA by adding PAC before an aluminium dose of 10, 25, and 50 mg/L as a function of PAC dose of 80 to 480 mg/L at pH=6.0

The jar test results show that by adding PAC of 200 mg/L before aluminium dose of 25 mg/L at pH=6.0 the SUVA value of 0.7 L/mg-cm was observed, Figure 8.4. The DOC, UV_{254}, and SUVA percentage values equalled to 74%, 95%, and 79% (Figures 8.1-8.3).

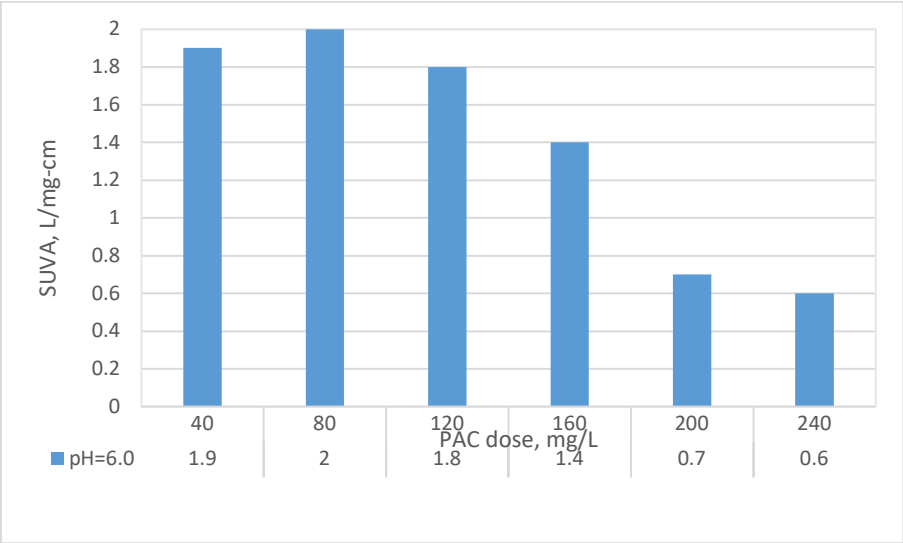


Figure 8.4 SUVA values in treated water by PAC addition before aluminium dose of 25 mg/L as a function of PAC dose of 40 to 200 mg/L at pH = 6.0

Hence, the combined 200mgPAC/L—25mgAl/L system at pH of 6.0 was comparable with the simultaneously combined 25mgAl/L+200mgPAC/L system in removing NOM at pH of 6.0, Tables (E1 and C1).

8.5 Effect of PAC dosage on DOC, UV_{254}, and SUVA reduction

Figure 8.5 shows jar test data observed for DOC, UV_{254}, and SUVA reductions by using the combined PAC—Al process as a function of PAC dosage from 40 to 240 mg/L at a fixed aluminium dosage of 10mg/L at pH = 6.0. UV_{254} reduction percentage values were very close to each other at applied PAC doses of 200 and 240 mg/L. The level UV_{254} of 0.02 1/cm was detected by adding PAC dose of 200 mg/L which was higher compared with the level UV_{254} of 0.016 observed by adding PAC dose of 240 mg/L before aluminium dose of 10 mg/L. An increase of PAC dosage of 200 to 240 mg/L had a minor effect on UV_{254} percentage removal value, Figure 8.5.

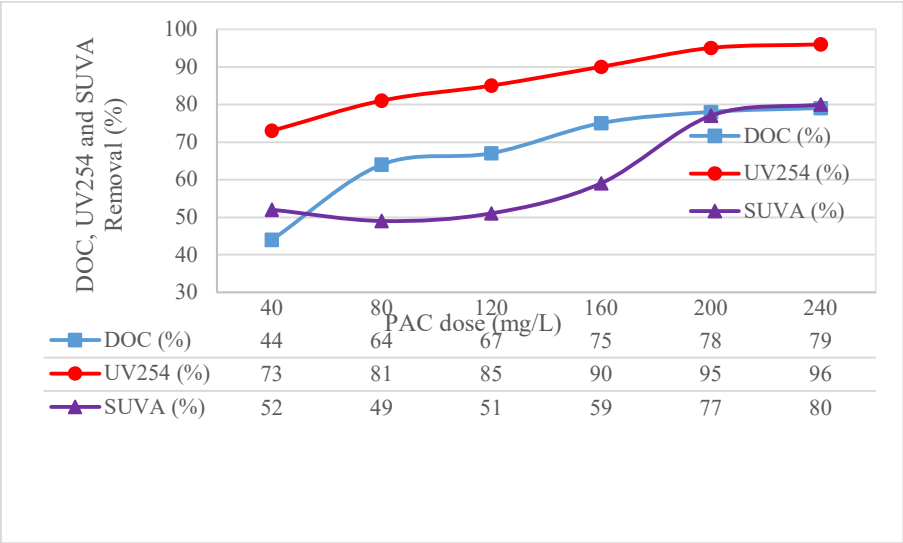


Figure 8.5. Percent removal of DOC, UV_{254}, and SUVA by adding PAC before an aluminium dose of 10 mg/L as a function of PAC dose of 40 to 240 mg/L and pH = 6.0

The higher levels DOC of 2.2 mg/L and SUVA of 0.9 were detected by applying PAC dose of 200 mg/L before aluminium dose of 10 mg/L addition compared with level DOC of 2.1 mg/L and SUVA of 0.8 L/mg-cm by applying PAC dose of 240 mg/L addition before the aluminium dose of 10 mg/L, Appendix Table E1. Based on the results, PAC dosage of 240 mg/L has a negligible advantage over the PAC dose of 200 mg/L in removing recalcitrant NOM from the surface water sample.

DOC, UV_{254}, and SUVA reduction percentage values were plotted in Figure 8.6 by using combined PAC—Al process as a function of PAC dosage of 80 to 400 mg/L at a fixed aluminium dosage of 25 mg/L and pH=6.0, Figure 8.6. The level UV_{254} of 0.016 was achieved by adding PAC dose of 240 mg/L and lower level UV_{254} of 0.004 1/cm was detected by applying PAC dose of 320 to 400 mg/L, Appendix Table E1. Further PAC dosage increase from 320 mg/L to 400 mg/L no longer reduced the UV_{254} concentration in the treated water sample, Figure 8.6.

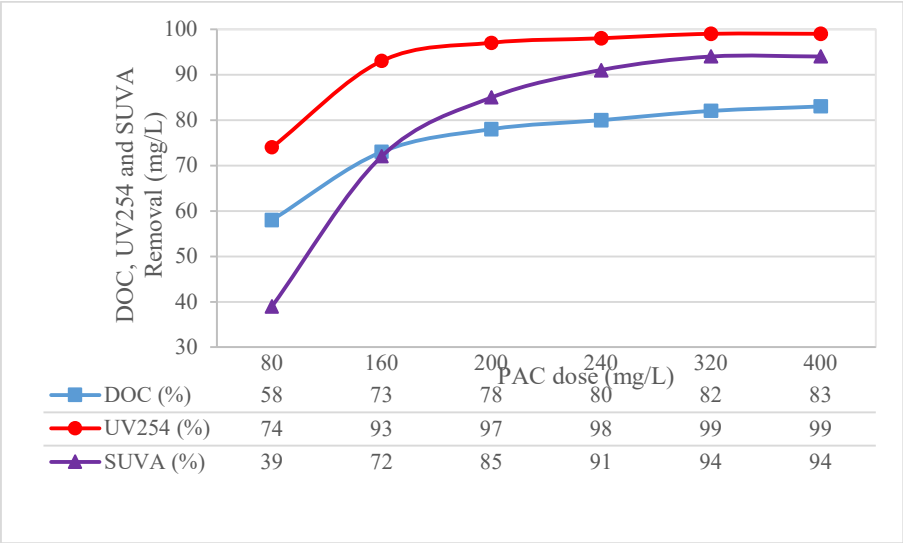


Figure 8.6. Percent removal of DOC, UV_{254}, and SUVA by adding PAC before an aluminium dose of 25 mg/L as a function of PAC dose of 80 to 480 mg/L at pH range of 5.5 to 6.0

DOC reduction values increase were observed between two combined 240 mgPAC/L—25 mgAl/L and 400 mgPAC/L—25 mgAl/L systems at pH = 6.0, Figure 8.6. The higher levels DOC of 2.73 mg/L and SUVA of 0.6 L/mg-cm were observed in a treated water sample by adding PAC dose of 240. The lower levels DOC of 1.9 mg/L and SUVA 0.2 L/mg-cm were achieved by adding PAC dose of 400 mg/L before the aluminium dose of 25 mg/L, Table E1. Therefore, the remained DOC compounds in the treated water are less aromatic and hydrophobic organic fractions because of low level SUVA. The analysed SUVA (L/mg-cm) as UV_{254} (in 1/cm) divided by DOC (in mg/L) was proposed as a predictor of aromaticity of NOM (Aaron et al., 2006). High aromaticity associated with a high content of hydrophobic and aromatic compounds, which are main recalcitrant NOM compounds with high capability to react with chlorine to form DBPs.

8.6 DOC correlation to UV_{254}

A good UV_{254} correlation to DOC was defined using combined adsorption-coagulation PAC—Al water treatment process as a function of PAC dose of 80 to 240 mg/L and an aluminium dose of 25, Figure 8.7.

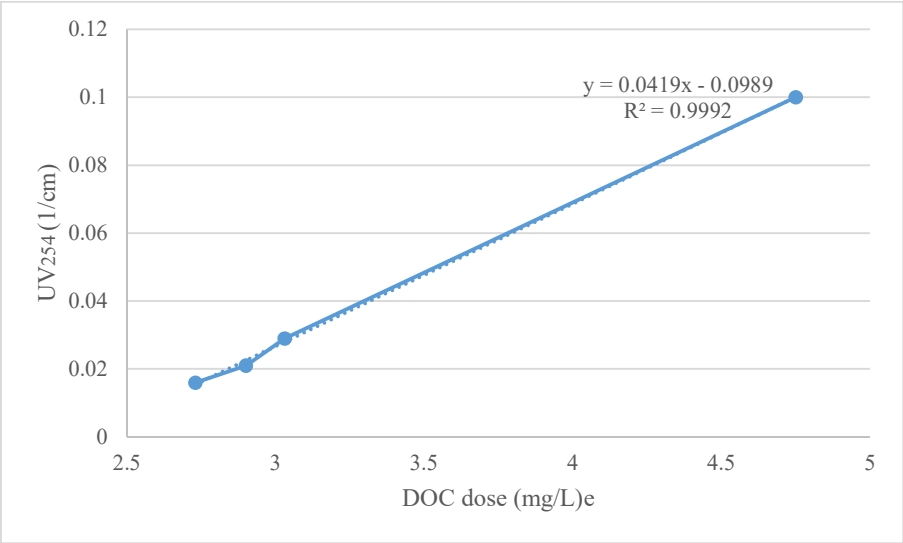


Figure 8.7. DOC correlation to UV_{254} reduction by adding PAC before an aluminium dose of 25 mg/L as a function of PAC dose of 80 to 240 mg/L at pH=6.0

The relationship between DOC and UV_{254} was very high at a fixed aluminium dose of 25 mg/L addition after PAC dose. The coefficient of determination or R-squared was very close to 1. Also, a good correlation between DOC and UV_{254} was observed by applying the combined adsorption-coagulation PAC—Al process as a function of PAC dose of 80 to 240 mg/L at a fixed aluminium dose of 10, and 50 mg/L, Appendix Figures (E1-E2). Thus, the degree of relationship between DOC and UV_{254} shows a positive correlation for one set of experimental data, Figure 8.7. As one set value of DOC increases the other set of UV_{254} tends to increase as well.

8.7 Conclusions

The combined adsorption-coagulation PAC—Al water treatment study revealed that the maximum reduction of high molecular weight hydrophobic NOM materials from surface water sample was achieved at the optimum conditions, PAC dose of 200 mg/L, aluminium dosage of 25 mg/L, and pH=6.0, Figures (8.1 and 8.4). Based on the results, the combined 200 mgPAC/L—10 mgAl/L water treatment system removes slightly less amount of NOM than the combined 200 mgPAC/L—25 mgAl/L system. However, the combined 200 mgPAC/L—10 mgAl/L system allows to reduce aluminium residue in the treated water sample by reducing the aluminium dosage from 25 to 10 mg/L. Also, aluminium dose reduction will decrease sludge and chemical cost. While aluminium dosage increase may result in raising the

concentration of carboxylic acid groups related to the hydrophobic fraction of NOM remaining in treated water. PAC addition as coagulant aid may absorb HMW humic substances as alum coagulant does and block pores of PAC to absorb LMW nonhumic fraction (Carrol 2009). The pores of PAC will not be able to absorb non-UV-absorbing compounds. Therefore, the concentration of LMW hydrophilic fractions will increase in the treated water sample. The levels DOC of 2.9 mg/L, UV_{254} of 0.021 1/cm, and SUVA of 0.7 L/mg-cm were observed by applying the combined adsorption-coagulation 200 mgPAC/L—25 mgAl/L system.

CHAPTER NINE

9. COST ESTIMATION FOR WATER TREATMENT PROCESSES USUNG ALUM AND PAC

9.1 Introduction

The defined water treatment cost to treat per megalitre raw water sample was around $898/ML by applying simultaneous and subsequent combined (25mgAl/L±200mgPAC/L) water treatment processes. The water treatment cost can be reduced further from $898/ML to $780/ML by decreasing PAC dosage from 200 to 160 mg/L at optimum pH with an appropriate reduction of DOC and UV_{254}. Hence, water treatment cost might be varied from low to high price by decreasing chemical consumption depending on raw water pollution level and water treatment requirements.

9.2 Alum coagulant and PAC consumption cost estimation

Alum and PAC consumption cost was estimated using experimental data obtained by applying alum coagulation, combined coagulation-adsorption, and adsorption-coagulation processes. The chemical consumption costs for per megalitre water treatment using either the Al+PAC, Al—PAC or PAC—Al processes for NOM reduction were found to be in the range of $595/ML -$898/ML, Table 9.1**.** The prices of the alum coagulant and PAC were defined as $1.00 and $2.95 per kilogram in Australian dollars, respectively. The alum and PAC cost presented in Table 9.1 and Figures (9.1-9.2) did not include freight costs and pH adjustment cost. The PAC cost was requested from Activated Carbon Technologies PTY LTD supplier. Alum price was estimated at approximately $1.00 per kilogram to make it easy to recalculate if a change in the market price of alum will occur. The alum coagulant consumption cost by applying alum coagulation process (25mgAl/L) was determined to be $308/ML. However, the chemical consumption cost increased from $308/ML to $603/ML by applying simultaneously combined 25mgAl/L+100mgPAC/L system. Also, NOM reduction in terms of DOC, UV_{254}, and SUVA increased as well by adding aluminium dose of 25 mg/L simultaneously with PAC dose of 100 mg/L, Table 9.1. Further increase in reductions of DOC and UV_{254} were observed by increasing PAC dosage addition from 100 to 200 mg/L or by applying the simultaneously combined 25mgAl/L+ 200mgPAC/L water treatment system, Figures (9.1-9.2). By increasing PAC dosage from 100 mg/L to 200 mg/L, the water treatment cost raised from $603/ML to $898/ML.

Table 9.1. The alum and PAC consumption cost estimation for DOC, UV_{254}, and SUVA reduction in per megalitre of raw water.

Treatment Process	Treatment Cost, AUD/ML	DOC		UV_{254}		SUVA	
		Rl	Rd	Rl	Rd	Rl	Rd
		%	mg/L	%	1/cm	%	L/mg-cm
25 mgAl/L	308	50	5.9	81	0.080	64	1.3
25mgAl/L+100mgPAC/L	603	74	-	90	-	61	-
25mgAl/L+200mgPAC/L(pH=6.5)	898	85	1.7	99	0.006	89	0.30
25mgAl/L—200mgPAC/L(pH=6.5)	898	82	-	98	0.006	85	0.58
25mgAl/L+160mgPAC/L(pH=6.5)	780	83	2.1	98	0.009	87	0.40
25mgAl/L—160mgPAC/L(pH=6.5)	780	78	2.4	94	0.023	77	1.00
160mgPAC/L—25mgAl/L(pH≥5.0)	780	73	3.0	93	0.029	72	1.00
25mgAl/L+120mgPAC/L(pH=6.5)	662	77	2.7	93	0.030	68	1.10
25mgAl/L—120mgPAC/L(pH=6.5)	662	76	2.7	92	0.030	67	1.10
5mgAl/L+160mgPAC/L(pH=6.5)	481	61	3.9	87	0.052	68	1.3
10mgAl/L+160mgPAC/L(pH=6.5)	595	64	3.9	87	0.051	63	1.3

[a] Rl=Removal. [b] Rd=Remained.

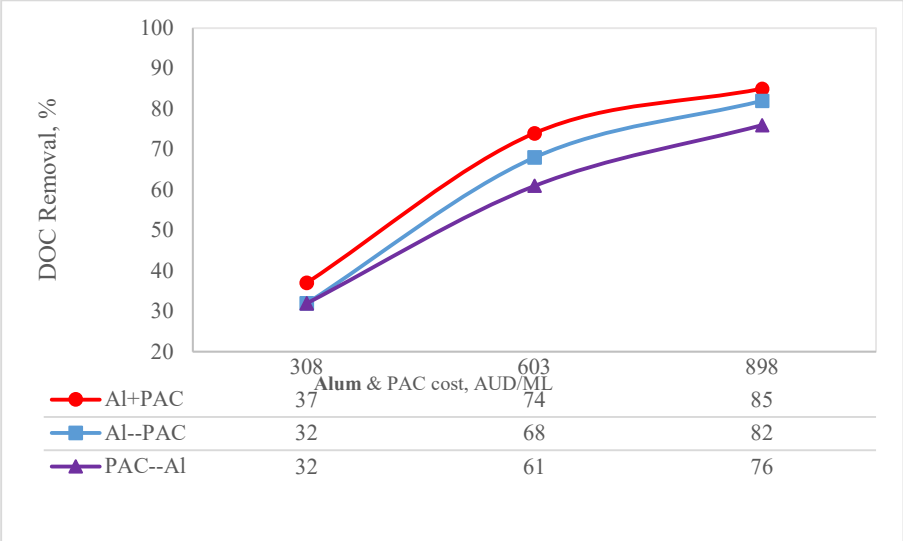


Figure 9.1. Analysis of the chemical consumption cost of alum and PAC for DOC reduction by applying simultaneous and subsequent combined Al+PAC, Al—PAC, and PAC—Al water treatment processes at a fixed aluminium dose of 25 mg/L as a function of PAC dose of 0, 100 and 200 mg/L

The percentage reduction values of DOC and UV_{254} were slightly different for the 25mgAl/L+ 200mgPAC/L and 25mgAl/L—200mgPAC/L systems. However, the maximum DOC reduction value was noticeably lower by adding PAC dose of 200 mg/L before aluminium dose of 25 mg/L. Based on experimental results, the proposed optimum water treatment system for DOC reduction was simultaneously combined water treatment system.

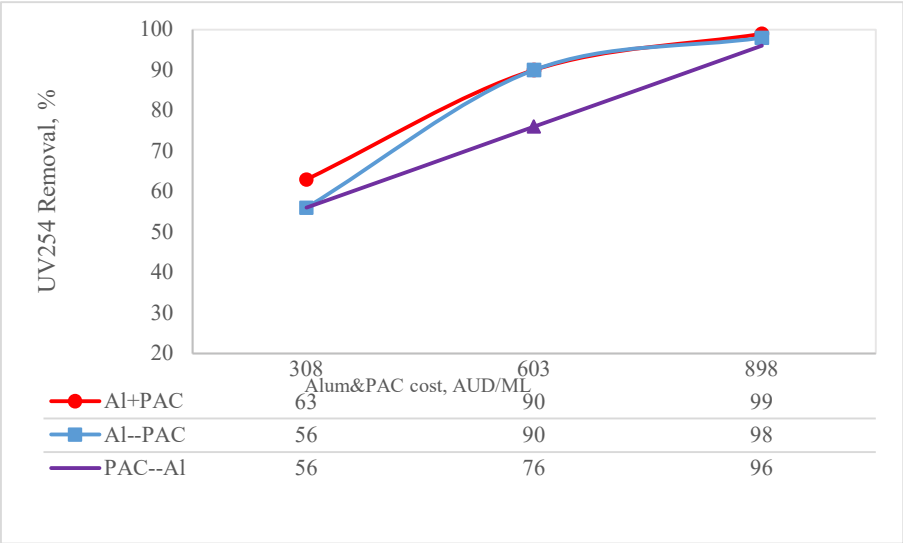


Figure 9.2. Analysis of the required cost of alum coagulant and PAC for UV_{254} removal by applying combined Al+PAC, Al—PAC, and PAC—Al water treatment processes at a fixed aluminium dose of 25mg/L as a function of PAC dose of 0, 100, and 200 mg/L

Further water treatment cost reduction was possible to be achieved by decreasing aluminium and PAC dosages. It found that 90 % of UV_{254}, 75% of DOC reductions were observed at the water treatment cost of $595/ML by applying the coagulation-adsorption combined 160 mgPAC/L—10mgAl/L water treatment system, Table 9.1 and Figure 9.3. The advantage of the water treatment processes at applied aluminium dose of 10 mg/L and PAC dose of 160 mg/L was low chemical consumption cost for noticeably high reduction of UV_{254} and DOC fractions compared with the combined system used at higher alum and PAC dose. The disadvantage of the lower-cost water treatment combined system was the lower reduction of SUVA or higher level SUVA of 1.5 (L/mg-cm) was achieved in the treated water compared with the lower level SUVA of 0.9 (L/mg-cm) observed by applying adsorption-coagulation 160 mgPAC/L—10mgAl/L system at pH=6.0, Table 9.1. The simultaneously combined 25mgAl/L+

200mgPAC/L system application allowed to increase SUVA reduction by 90% which is equals to level SUVA of 0.30 L/m-mg. The chemical consumption cost increased to $898/ML by using the simultaneously combined 25mgAl/L+ 200mgPAC/L system. However, the highest reduction of DOC (85%) and UV_{254} absorbing fractions (99%) were achieved by applying the simultaneously combined system at high chemical consumption conditions. The enhanced and combined water treatment systems have higher efficiency of the removal of high molecular weight humic, low molecular weight humic and nonhumic NOM fractions by increasing PAC dose.

The studied combination of alum with PAC at a fixed PAC dosage of 160 mg/L as a function of aluminium dose of 5, 10 and 25 mg/L revealed that no significant difference in a maximum reduction of UV_{254} values observed, Figure 9.3. The UV_{254} reduction histogram showed that the combined (Al+PAC, Al—PAC and PAC—Al) processes by applying aluminium dose of 25 mg/L slightly better than the applied processes at low aluminium concentrations of 5 and 10 mg/L.

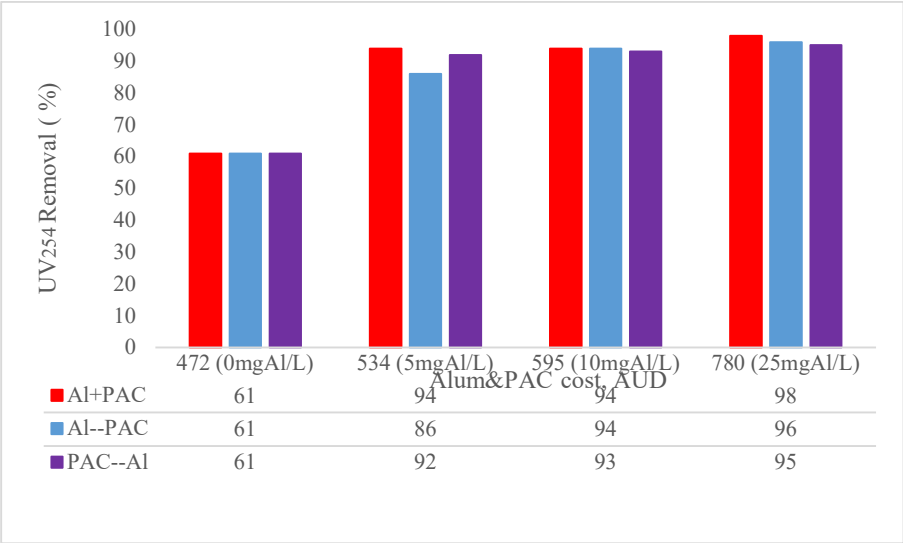


Figure 9.3. Alum coagulant and PAC cost analysis of UV_{254} reduction by applying combined Al+PAC, Al—PAC, and PAC—Al processes at a fixed PAC dose of 160 mg/L as a function of aluminium dose of 5, 10 and 25mg/L at pH=6.5

The aluminium dose of 25 mg/L was observed as the optimum dose for UV_{254} reduction by using simultaneously combined (25mgAl/L+160mgPAC/L) system, Figure 9.3. The UV_{254}

reduction values were identical by using the combined (25mgAl/L+160mgPAC/L) and (160mgPAC/L—25mgAl/L) water treatment systems, while DOC reduction was slightly higher by applying 25mgAl/L+160mgPAC/L system. Also, the simultaneously combined coagulation with PAC adsorption Al+PAC compared to the subsequent coagulation-adsorption Al—PAC process was more sophisticated to operate. Thus, the order of addition of alum and PAC study revealed that the simultaneously combined 25mgAl/L+160mgPAC/L system at pH=6.5 was a superior water treatment system for NOM reduction.

9.3 Conclusion

Depending on raw water quality characteristics and DOC, UV_{254}, and SUVA targeted reduction values the chemical consumption cost could be reduced from $898/ML to $780/ML by decreasing PAC dose from 200 mg/L to 160 mg/L, Table 9.1. The low aluminium dose of 5mg/L and PAC dose of 160mg/L addition allowed to reduce UV_{254} values by 93 and 94% by using the combined Al+PAC and Al—PAC processes. Hence, the per megalitre water treatment cost can be reduced from $898/ML to $481/ML, depending on water quality characteristics and water treatment requirements, Table 9.1.

CHAPTER TEN

10. CONCLUSIONS AND RECOMMENDATION FOR FUTURE RESEARCH

10.1 Conclusions

The impact of order addition of alum coagulant and PAC (combined Al+PAC, Al—PAC and PAC—Al processes) along with single alum coagulation and single PAC adsorption has been investigated for maximum removal of DOC, UV_{254}, and SUVA from surface water. Laboratory jar test data revealed that 81% of UV-adsorbing compounds were removed from surface water sample of the southwest of an open reservoir of Western Australia by using alum coagulation. The observed levels DOC, UV_{254}, and SUVA were 5.91 mg/L, 0.079 1/cm and 1.7 L/mg-cm by applying alum coagulation process at aluminium dose of 25 mg/L and pH=6.0 (Table A1). The reduction of UV-absorbing compounds was 70% by using PAC adsorption process by itself. The achieved levels water quality parameters were 4.86 mg/L of DOC, 0.132 1/cm of UV_{254}, and 2.7 L/mg-cm of SUVA by applying single PAC adsorption process at PAC dose of 200 mg/L and pH=6.0 (Table B1). The single alum coagulation and PAC adsorption processes study revealed that the water treatment processes have different capacity to remove UV_{254} and DOC parameters from the southwest open reservoir of Western Australia. Thus, alum coagulation and single PAC adsorption processes remove different fractions of NOM. Takdastan and Eslami (2013), Uyak et al. (2007) reported that coagulation process removes HMW hydrophobic fractions and the process ineffective on removing LMW organic materials. PAC removes LMW and uncharged NOM fractions and ineffective on removing HMW substances (Takdastan and Eslami 2013, Uyak et al. 2007). Therefore, the application of single alum coagulation with PAC adsorption process in combination will have a complementary effect on NOM reduction. Therefore, alum coagulation and PAC processes were applied in conjunction to study the impact of order addition of alum coagulant and PAC. The order of addition alum with PAC study showed that the most effective technique of ordering alum coagulant with PAC was the combination, comprising simultaneously dosing alum and PAC (or Al+PAC process) at pH range between 5.5 and 6.5. The aluminium dose of 25 mg/L was defined as optimum dose which is equaled to 308 mgAlum/L. The levels DOC, UV_{254}, and SUVA in treated water were equaled to 1.7 mg/L, 0.006 1/cm, and 0.3 L/mg-cm by applying the simultaneous combined 25mgAl/L+200mgPAC/L system at pH=6.5 (Table C1). Almost the same NOM fractions reduction were achieved by studying alum addition before PAC, Al—PAC process. At the applied alum addition before PAC process the achieved levels DOC, UV_{254}, and SUVA were 1.6 mg/L, 0.008 1/cm, and 0.5 L/mg-cm by applying 25mgAl/L—

200mgPAC/L system (Table D1). The combined two water treatment systems, 25mgAl/L+200mgPAC/L and 25mgAl/L—200mgPAC/L showed almost the same reduction in DOC (85-87%), UV_{254} (99%), and SUVA (89%) values. While the combined adsorption-coagulation 200mgPAC/L—25mgAl/L system in which PAC dose of 200 mg/L was added prior aluminium dose of 25 mg/L was less effective in DOC (76%), UV_{254} (96%), and SUVA (83%) reduction. The combined water treatment systems 25mgAl/L+200mgPAC/L and 25mgAl/L—200mgPAC/L allowed to reduce DOC from 12 mg/L to 1.6 and 1.7 mg/L at optimum conditions. The DOC (2.7 mg/L) remaining in the treated water was higher by using the combined 200mgPAC/L—25mgAl/L water treatment system. The chemical consumption cost was almost the same for both combined 25mgAl/L ±200mgPAC/L systems and equaled to $636.5/ML. PAC dose optimisation has a more considerable influence on NOM reduction than alum dose and pH.

Low NOM removal were achieved by applying aluminium dose of 200 mg/L at higher pH levels of 7.0 and 7.5. This can be explained by pH level change during the jar test experiments (fast and slow mixing) from low to high or vice versa. Therefore, the effectiveness of coagulation of NOM decreased at higher pH levels of 7.0 and 7.5 because of inability to reach the optimum pH level for coagulation of organic matter. It was assumed that a buffer agent was required to achieve steady coagulation pH at higher aluminium dose of 200 mg/L application in pH range of 7.0 and 7.5.

The chemical consumption cost was almost the same for both optimised 25mgAl/L±200mgPAC/L systems and equaled $898/ML. PAC dosage change has a more considerable influence on NOM reduction than alum dosage and pH change. The lowest surface water treatment cost was $481.3/ML with a high reduction of DOC and UV_{254} using the water treatment system of 160 mgPAC/L—5 mgAl/L at pH=5.5.

10.2. Recommendation for future research

In the future a buffer solution use is recommended for jar test experiments to achieve steady coagulation pH at higher applied aluminium dose of 200 mg/L and pH levels 7.0 and 7.5. The buffer solution use will resist a change in pH during fast and slow mixing a water sample with chemicals and increase NOM reduction in the treated water sample. Water treatment cost decrease suggested by adjusting the shear rate. Chemical consumption reduction, for example, alum and PAC doses decrease probably will allow to improve water treatment system by decreasing water treatment cost and increasing water quality parameters reduction. Also, the

research project creates a paradigm for future studies of the adsorption isotherms to characterise the adsorption process (adsorption capacity for DOC) before and after alum treatment.

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Appendices

Appendix A: Experimental data by single alum coagulation

Table A1: Coagulation experimental data observed for raw and treated surface water in southwest Western Australia

Sample Code*	Al dose (mg/L)	pH	UV_{254} (1/cm)	UV_{254}, Removal (%)	SUVA (L/mg-m)	SUVA Removal (%)	DOC (mg/L)	DOC Removal (%)
200516	10	5.0	0.256	40.0	2.5	32	10.36	12.9
		5.5	0.108	74.7	1.7	54	6.46	45.7
		6.0	0.105	75.4	1.7	54	6.25	47.4
		6.5	0.110	74.2	1.6	56	6.85	42.4
		7.0	0.109	74.5	1.7	53	6.45	45.8
		7.5	0.173	59.5	2.1	41	8.18	31.2
RW			0.427				11.89	
090616	25	5.0	0.132	69.1	1.8	50	7.35	38.1
		5.5	0.102	76.1	1.6	55	6.20	47.8
		6.0	0.079	81.5	1.3	63	5.91	50.3
		6.5	0.080	81.3	1.3	64	6.15	48.3
		7.0	0.086	79.9	1.4	61	6.05	49.1
		7.5	0.086	79.9	1.4	62	6.30	47.01
RW			0.427		3.61		11.89	
020516	50	5.0	0.106	75.5	1.4	61	7.44	37.4
		5.5	0.076	82.0	1.2	66	6.23	47.6
		6.0	0.083	80.8	1.3	63	6.13	48.4
		6.5	0.089	79.4	1.3	63	6.56	44.8
		7.0	0.097	77.5	1.4	62	7.04	40.8
		7.5	0.096	77.7	1.3	64	7.31	38.5
RW			0.432				11.89	
030516	75	5.0	0.124	71.2	1.8	50	6.91	41.9
		5.5	0.101	76.6	1.6	56	6.42	46.0
		6.0	0.099	77.0	1.5	57	6.4	46.8
		6.5	0.117	72.8	1.8	50	6.5	45.3
		7.0	0.111	74.2	1.6	54	6.7	43.6
		7.5	0.126	70.8	1.7	53	7.3	38.3
RW			0.432				11.89	
090516	100	5.0	0.174	60	2.4	34	7.27	39
		5.5	0.110	74	1.8	51	6.21	48
		6.0	0.109	75	1.9	48	5.84	51
		6.5	0.117	73	1.9	50	6.44	46
		7.0	0.119	72	1.8	50	6.64	44
		7.5	0.136	68	2.0	46	6.93	42
RW			0.431				11.89	
160616	150	5.0	0.115	73	2.0	46	5.86	51
		5.5	0.114	74	2.0	46	5.80	51
		6.0	0.124	71	1.9	46	6.34	47
		6.5	0.125	71	1.9	46	6.44	46
		7.0	0.129	70	2.0	45	6.44	46
		7.5	0.139	68	2.0	44	6.91	42
RW			0.432				11.89	
260516	200	5.0	0.304	30	3.5	4	8.73	26
		5.5	0.284	34	3.4	6	8.37	30
		6.0	0.291	33	3.2	10	8.97	24
		6.5	0.367	15	3.5	3	10.47	12
		7.0	0.429	0.7	3.7	0	11.70	1.6
		7.5	0.467	-8.1	3.6	0	12.84	-8.0
RW			0.432				11.89	

*Sample code is the experiment performance date; RW-Raw Water

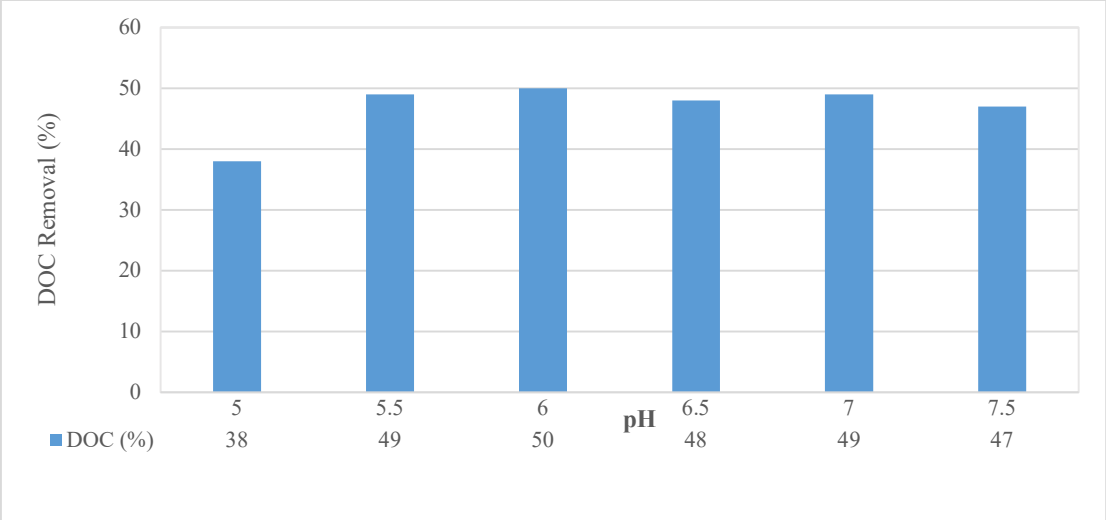

Figure A1: Percent removal of DOC as a function of pH from 5.0 to 7.5 at a fixed aluminium dose of 25 mg/L

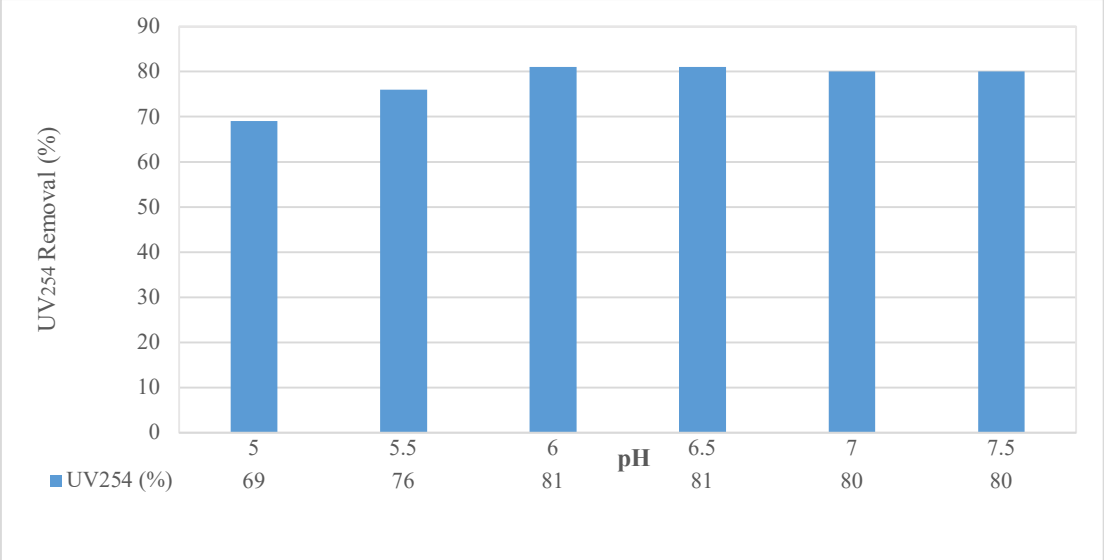

Figure A2: Percent removal of UV_{254} as a function of pH from 5.0 to 7.5 at a fixed aluminium dose of 25 mg/L

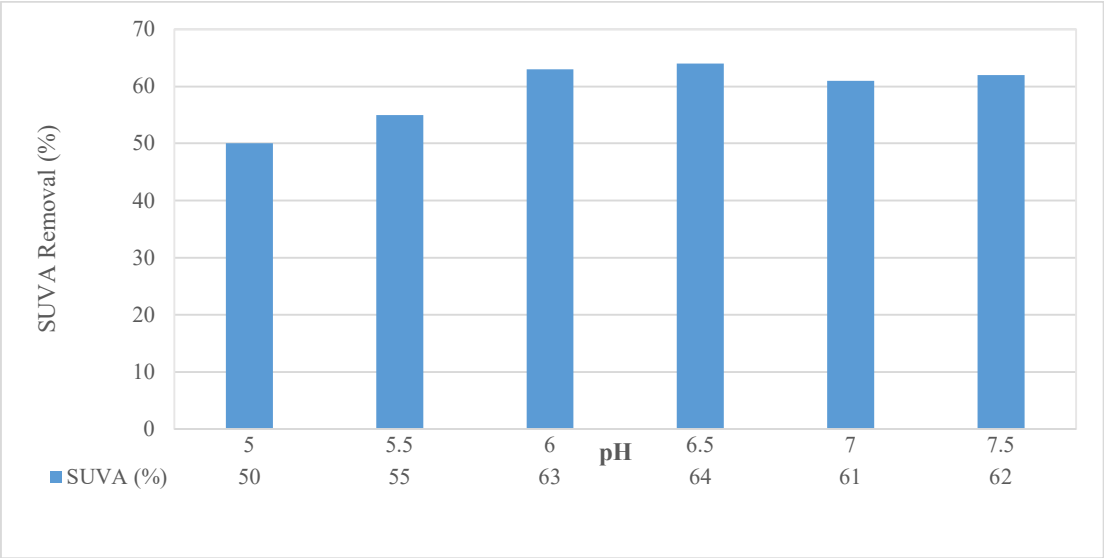

Figure A3: Percent removal of SUVA as a function of pH from 5.0 to 7.5 at a fixed aluminium dose of 25 mg/L

Appendix B: Experimental data by applying single PAC adsorption

Table B1: PAC adsorption experimental data observed for the surface water in southwest Western Australia

Sample Code*	Al dose (mg/L)	pH	UV_{254} (1/cm)	UV_{254} Removal (%)	SUVA (L/mg-m)	SUVA Removal (%)	DOC (mg/L)	DOC Removal (%)
230916	5.0	20	0.314	20	2.9	16	10.99	10
		40	0.285	27	3.0	11	9.43	23
		80	0.220	44	3.0	13	7.47	39
		120	0.170	57	2.7	21	6.32	48
		160	0.142	64	2.8	19	5.14	58
		200	0.124	68	2.7	19	4.53	63
RWPs			0.393				12.21	
220916	5.5	20	0.349	13	3.3	1.3	10.40	13
		40	0.302	25	3.3	1.5	9.02	24
		80	0.226	44	3.2	4.8	6.98	41
		120	0.187	53	2.9	6	5.85	51
		160	0.140	65	3.0	13	4.73	60
		200	0.120	70	3.4	12	4.01	66
RWPs			0.402		3.4		11.97	
160916	6.0	20	0.372	11	3.5	0	10.49	13
		40	0.320	24	3.5	0	9.12	25
		80	0.248	41	3.0	11	8.24	32
		120	0.214	49	3.0	11	7.05	42
		160	0.163	61	2.6	23	6.24	48
		200	0.132	68	2.7	20	4.86	60
RWPs			0.419		3.5		12.11	
150916	6.5	20	0.348	12	3.8	0	9.08	23
		40	0.298	25	3.4	1.2	8.87	25
		80	0.240	39	3.5	0	6.79	43
		120	0.190	52	3.4	0.39	5.61	53
		160	0.155	61	3.1	9	5.02	58
		200	0.138	65	3.2	6	4.32	63
RWPs			0.397				12	
290916	7.0	20	0.334	12	3.3	3	10.12	11
		40	0.296	22	3.7	0	8.08	29
		80	0.232	39	3.0	12	7.72	32
		120	0.186	51	3.1	10	6.05	47
		160	0.135	64	2.9	14	4.61	60
		200	0.119	69	2.0	0	5.82	49
RWPs			0.379				11.89	

*Sample code is the experiment performance date

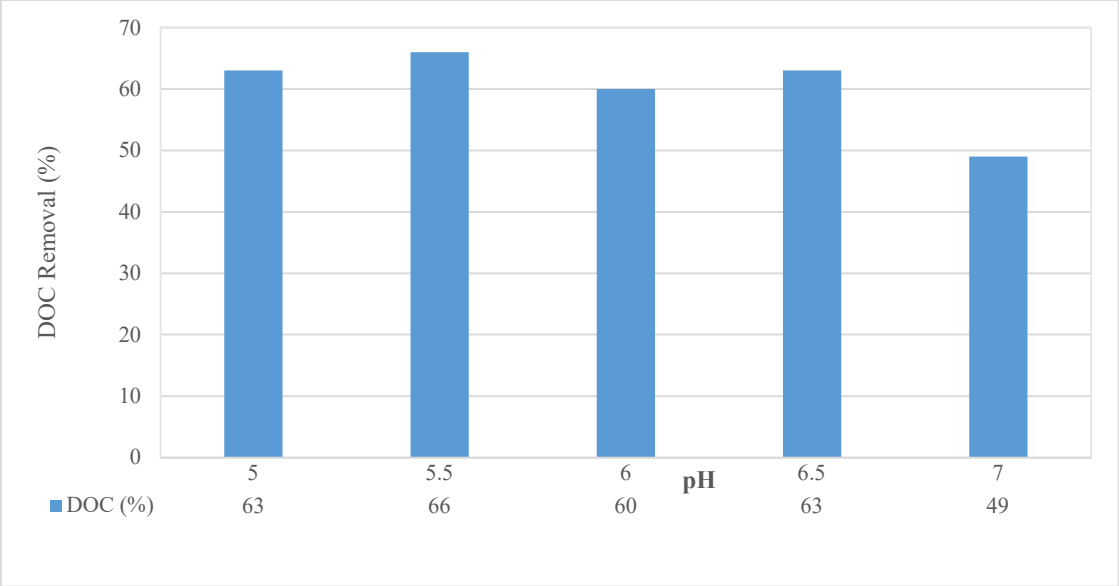

Figure B1: Percent removal of DOC as a function of pH from 5.0 to 7.0 at a fixed PAC dose of 200 mg/L

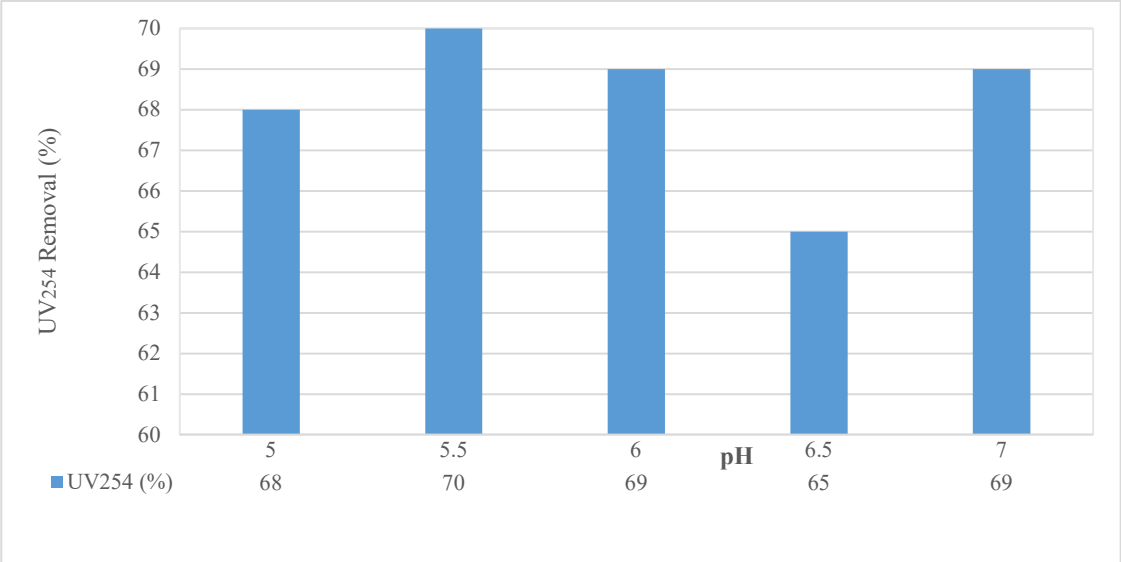

Figure B2: Percent removal of UV_{254} as a function of pH from 5.0 to 7.0 at a fixed PAC dose of 200 mg/L

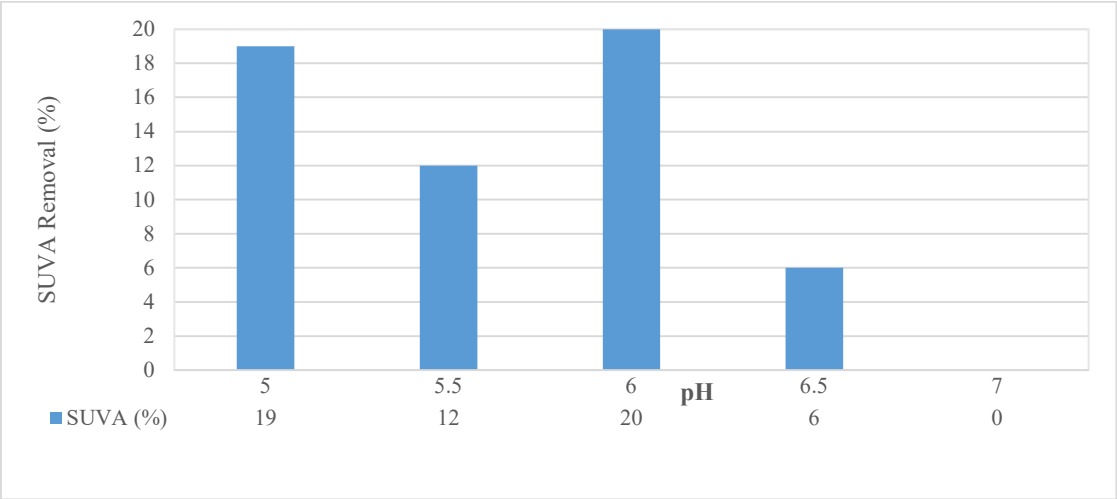

Figure B3: Percent removal of SUVA as a function of pH from 5.0 to 7.0 at a fixed PAC dose of 200 mg/L

Appendix C: Surface water treatment data by applying the simultaneously combined Al+PAC process

Table C1: Experimental data observed by applying the simultaneously combined Al+PAC process

Sample Code*	pH	Al (mg/L)	PAC (mg/L)	UV_{254} Abs (1/cm)	UV_{254} Removal (%)	SUVA (L/mg-m)	SUVA Removal (%)	DOC (mg/L)	DOC Removal (%)
310816	5.5	25	0	0.119	69	1.8	47	6.64	45
			40	0.078	82	1.5	55	5.06	58
			80	0.060	86	1.7	49	3.49	71
			120	0.035	92	1.3	61	2.64	78
			160	0.027	94	1.4	59	1.93	84
			200	0.022	95	1.5	57	1.49	88
RWPs				0.409				12	
250816	6.0	25	0	0.135	67	2.0	43	6.74	43
			40	0.089	78	1.7	52	5.33	45
			80	0.068	83	1.7	52	4.02	66
			120	0.045	89	1.3	61	3.32	72
			160	0.031	92	1.1	68	2.79	76
			200	0.025	94	0.9	73	2.61	78
RWPs				0.422		3.4		11.88	
180816	6.5	25	0	0.149	63	2.0	41	7.47	37
			40	0.093	77	1.7	49	5.38	55
			80	0.067	83	1.5	55	4.39	63
			120	0.030	93	1.1	68	2.73	77
			160	0.009	98	0.4	87	2.06	83
			200	0.006	99	0.3	89	1.74	85
RWPs				0.404		3.3		12	
190816	7.0	25	0	0.149	63	1.8	48	8.44	29
			40	0.117	71	1.6	51	7.07	40
			80	0.066	84	1.3	61	4.97	58
			120	0.043	89	0.9	72	4.49	62
			160	0.034	92	0.7	79	3.39	71
			200	0.024	94	0.5	85	4.79	70.5
RWPs				0.405				12	
260816	7.5	25	0	0.187	56	2.2	37	8.42	29
			40	0.146	65	2.3	35	6.37	46
			80	0.093	78	2.0	43	4.63	61
			120	0.090	79	2.1	41	4.36	63
			160	0.078	82	2.0	42	3.86	67.5
			200	0.060	86	2.0	44	3.04	74.4
RWPs				0.422				11.88	
270117 RWPs	6.0	5	160	0.051 0.400	87	1.3	68	3.9 11.94	61
310117 RWPs	6.0	10	160	0.052 0.400	87	1.3	63	3.9 10.95	64

*Sample code is the experiment performance date; *RWPs—Raw water parameters

Table C2: Experimental data observed by applying the simultaneously combined Al+PAC process

Sample code*	pH	PAC (mg/L)	Al (mg/L)	UV_{254} (1/cm)	UV_{254} Removal (%)	SUVA (L/mg-m)	SUVA Removal (%)	DOC (mg/L)	DOC Removal (%)
270117 RWPs	6.0	5	160	0.051 0.400	87	1.3	68	3.9 11.94	61
310117 RWPs	6.0	10	160	0.052 0.400	87	1.3	63	3.9 10.95	64

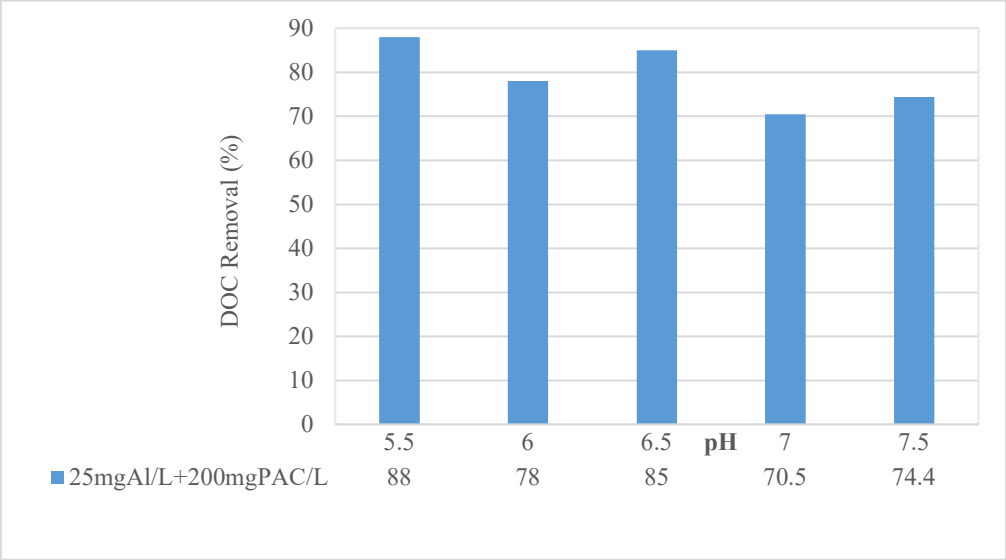

Figure C1: Percent removal of DOC as a function of pH from 5.0 to 7.0 at a fixed PAC dose of 200 mg/L by using the simultaneously combined Al+PAC process

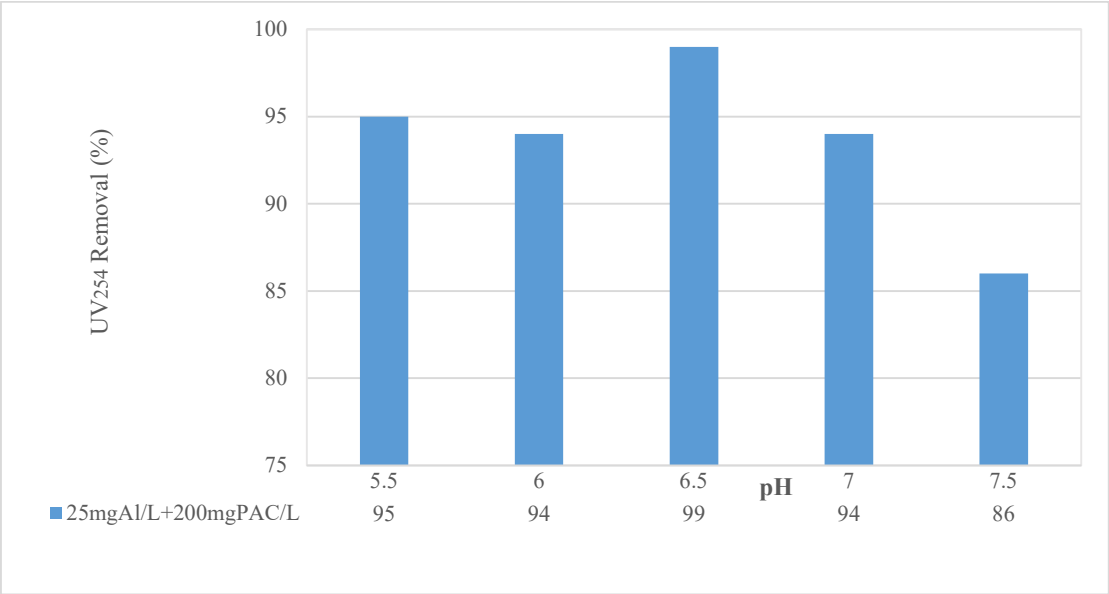

Figure C2: Percent removal of UV_{254} as a function of pH from 5.0 to 7.0 at a fixed PAC dose of 200 mg/L by the using simultaneously combined Al+PAC process

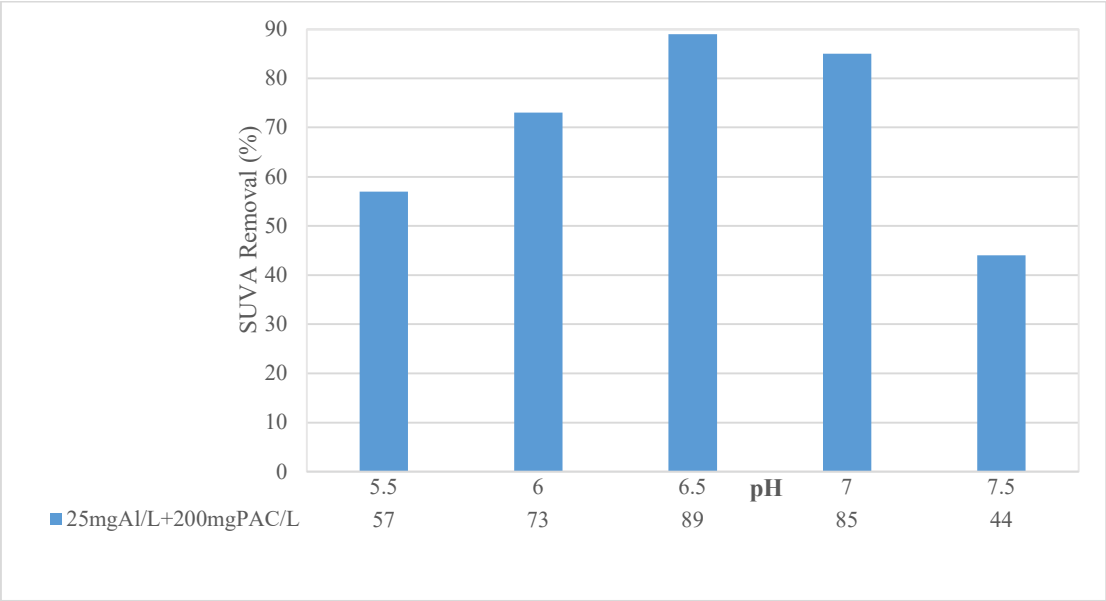

Figure C3: Percent removal of SUVA as function of pH from 5.0 to 7.0 at fixed 200 mg/L PAC dose by using the simultaneously combined Al+PAC process

Appendix D: Experimental data by adding alum before PAC, Al—PAC process

Table D1: Experimental data observed by applying the combined coagulation-adsorption Al—PAC process

Sample code*	pH	Al (mg/L)	PAC (mg//L)	UV_{254} (1/cm)	UV_{254} Removal (%)	SUVA (L/mg-m)	SUVA Removal (%)	DOC (mg/L)	DOC Removal (%)
061016	6.5	25	0	0.161	56	2.2	35	7.4	32
			80	0.057	84	1.4	59	4.2	63
			120	0.03	92	1.1	66	2.67	76
			160	0.015	96	0.75	78	2.0	78
			200	0.008	98	0.5	85	1.6	82
			240	0.005	99	0.36	89	1.38	87
RWPs				0.368		3.3		11	
201016	6.0	25	0	0.155	61	2.5	33	6.09	40
			160	0.058	85	2.5	34	2.32	77
			240	0.045	88	1.5	61	3.00	71
			320	0.033	91	1.9	50	1.73	83
			400	0.026	93	2.4	36	1.065	89
			480	0.011	98	0.6	85	1.37	86
RWPs				0.389				10.19	
030217	6.5	5	160	0.027	93	1.6	53	1.66	86
	6.0			0.053	87	2.0	42	2.64	77
	6.5	10		0.025	94	1.5	56	1.64	86
	6.0			0.049	88	2.1	38	2.29	80
	6.5	15		0.030	92	1.9		1.54	87
	6.0			0.060	85	2.5		2.43	79
RWPs									

*Sample code is the experiment performance date. *RWPs—Raw water parameters

Appendix E: Experimental data by adding PAC before alum, PAC—Al process

Table E1: Experimental data observed by applying the combined adsorption-coagulation PAC—Al process

Sample code*	pH	PAC (mg/L)	Al (mg/L)	UV_{254} (1/cm)	UV_{254} Removal (%)	SUVA (L/mg-m)	SUVA Removal (%)	DOC (mg/L)	DOC Removal (%)
200117	6.0	40	10	0.107	73	1.9	52	5.70	44
		80		0.074	81	2.0	49	3.72	64
		120		0.061	85	1.9	51	3.20	67
		160		0.040	90	1.6	59	2.50	75
		200		0.020	95	0.9	77	2.20	78
		240		0.016	96	0.8	80	2.10	79
RWPs				0.398		3.9		10.20	
271016	6.0	80	25	0.100	74	2.1	39	4.75	58
		160		0.029	93	1.0	72	3.03	73
		200		0.021	95	0.7	79	2.90	79
		240		0.016	96	0.6	83	2.73	83
		320		0.004	99	0.2	94	2.23	95
		400		0.004	99	0.2	94	1.87	94
		480		0.004	99	0.2	95	1.8	94
RWPs				0.388		3.4		11.29	
011017	6.0	80	50	0.145	59	3.1	2.6	4.6	58
		160		0.100	72	2.4	25	4.1	62
		200		0.080	77	2.1	35	3.8	65
		240		0.070	80	1.9	40	3.6	67
		320		0.034	90	1.5	54	2.3	79
		400		0.030	91	1.4	58	2.2	80
		480		0.029	92	1.4	55	2.0	81
RWPs				0.352		3.2		10.87	
070217	6.5	160	5	0.052	87	1.4	55	2.9	71
RWPs				0.400		3.9		10.00	
070217	6.5	160	10	0.029	93	1.3	60	1.8	82
070217	6.5	160	25	0.021	95	0.7	79	2.9	79

*Sample code is the experiment performance date. *RWPs—Raw water parameters

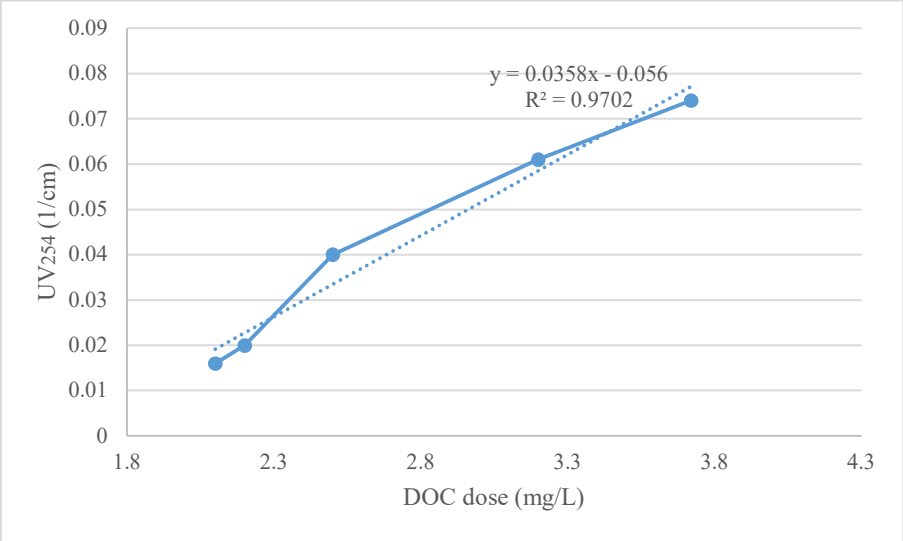

Figure E1. DOC correlation to UV_{254} reduction by adding PAC before an aluminium dose of 10 mg/L as a function of PAC dose of 80 to 240 mg/L at and pH=6.0

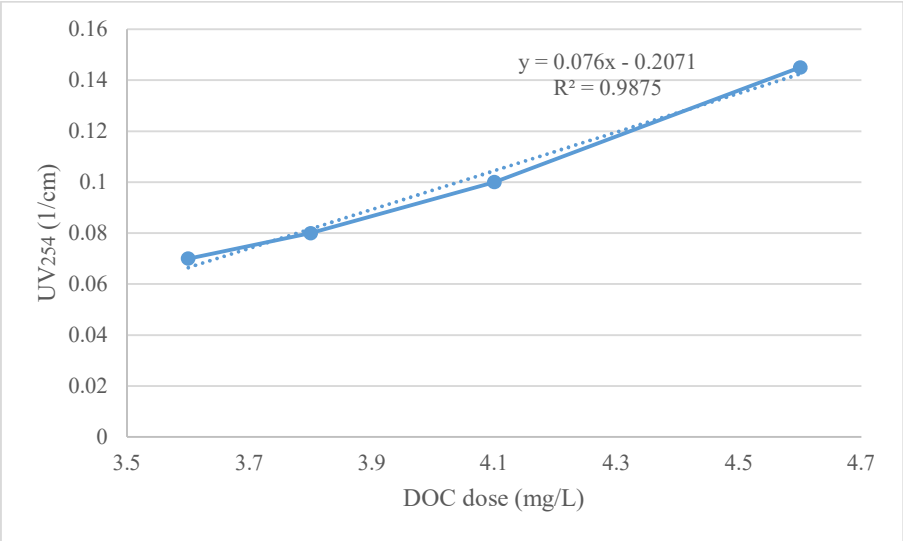

Figure E2. DOC correlation to UV_{254} reduction by adding PAC before an aluminium dose of 50 mg/L as a function of PAC dose of 80 to 240 mg/L at and pH=6.0