Development of a Novel Polysilicate Ferric Coagulant and Its Application to Coagulation-Membrane Filtration Hybrid System in Wastewater Treatment

by

Firoozeh Nateghi Ghasemian Nejad

Thesis submitted in fulfilment for the degree of

Doctor of Philosophy

School of Civil and Environmental Engineering

Faculty of Engineering and Information Technology

University of Technology, Sydney (UTS)

December 2014

CERTIFICATE OF ORIGINAL AUTHORSHIP

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of Candidate

…………………………………………………….

Firoozeh Nateghi

ABSTRACT

Coagulation is one of the effective pretreatment stages in membrane filtration of wastewater to produce clean water. Using a suitable coagulant can mitigate membrane fouling. Membrane fouling is a process where solute or particles deposit onto a membrane surface or into membrane pores in a way that degrades the membrane performance. Research in this area is currently being focused on development of improved coagulation reagents such as polysilicate ferric (PSiFe), which has a high molecular weight and large number of positive surface charges with high efficiency at low doses. In this thesis, PSiFe has prepared based on the following approaches: (a) acidification of water glass solution using HCl followed by $FeCl_3$ addition and (b) acidification of water glass solution by passing it through an acidic ion exchange resin followed by fresh $FeCl_3$ addition under different Fe/Si molar ratios. These coagulants were characterised by X-ray diffraction and scanning electron microscopy. According to coagulation jar test results, when Fe/Si=1 the best performance was achieved in terms of the turbidity, the total organic carbon (TOC) and UV_{254} removals.

In this study, a thorough experimental program has been carried out to compare the performance of three different coagulants including the existing PSiFe, $FeCl_3$ and the modified PSiFe. The results clearly indicated that in a membrane filtration system using the modified PSiFe not only reduces the required transmembrane pressure (TMP) due to lower fouling, but also improves the TOC removal efficiency.

The outcome of this research provides an efficient coagulant, which can create a sustainable coagulation-membrane filtration system with a lower consumption of chemicals compared to traditional coagulants, and lower fouling that consequently leads to minimum operating and maintenance costs. The findings of this research have also revealed that the performance of the target coagulant, PSiFe-γ, is superior to conventional reagents. Hence, this coagulant and the developed procedure in this study can be used in industry to enhance the coagulation process for achieving a more effective wastewater treatment procedure.

ACKNOWLEDGEMENT

Firstly, I would like to express my deepest gratitude to my principle supervisor, associate professor Hadi Khabbaz who gave me constructive comments and warm encouragement. The advice and comments provided by my co supervisor Dr. Ho Kyong Shon has been a great help in finding the gaps and giving me valuable feedback in my research.

I would also like to thank Centre for Technology in Water and Wastewater (CTWW) members, Professor Saravanamuthu Vigneswaran and Vinh Nguyen for helping me get started, encouraging and, guiding me through this process of developing an understanding of the subject matter.

Next, I would like to thank Dr Loga Loganathan for his advice in the chemistry section of my research and his patience in assisting me in the process of preparation of my doctoral assessment. Thank you to Jeong, Johir, Shanthini, and all of those students who have supported me in any respect during this project.

Thank to my lovely Phyllis, who for me is beyond a Research Administration Officer in UTS. Thank you for sharing the laughter and tears.

On a personal note to my loving family especially my son (Shayan) who gave me every reason to complete my PhD. Remember that you can do anything you set your mind to at any age even in the most difficult of situations. Never give up my son.

Last but not the least, my parents and siblings who continue to encourage from abroad, my heartfelt thanks to all of you. Your positive energy has helped me over the line.

TABLE of CONTENT

JOURNAL ARTICLES PUBLISHED

Nateghi, F., Shon, H. and Khabbaz, H. (2013). **“**Development of a new poly silicate ferric coagulant and its application to coagulation-membrane filtration hybrid system in wastewater treatment”, Journal of, Desalination and Water Treatment (in press).
(DOI**:**10.1080/19443994.2013.829581)

Sanghyng. J., **Nateghi, F.,** Nguyen**, T.V. and** Vigneswaran, S. (2011). “Pretreatment for seawater desalination by flocculation: Performance of modified poly ferric silicate and ferric chloride as flocculants”, *Desalination*, vol. 283, pp. 106-111.

CONFERENCE PAPER PRESENTATION

Nateghi, F., Loganathan, P., Khabbaz, H.,Nguyen, T.V., Vigneswaran, S. (2011).**“**Development of iron based coagulants and their applications to coagulation-membrane hybrid system in wastewater treatment”. In Proceedings of the 7th International Chemical Engineering Congress & Exhibition (IChEC 2011), Kish Island, Iran.

Nateghi, F., Shon, H. and Khabbaz, H. (2012).**.** New poly silicate ferric coagulant and its application to coagulation-membrane filtration hybrid system in wastewater treatment.7thChallenges in Environmental Science & Engineering (CESE 2012), Melbourne.

PRE REVIEW NOTIFICATION OF ACCEPTANCE

Nateghi, F., Shon, H. and Khabbaz, H. (2012)**,** "Polymeric Coagulation Mechanism and Its Application to Coagulation-Membrane Filtration Hybrid System in Wastewater Treatment", ICEEA 2013, Singapore

LIST OF ABBREVIATIONS

ATR-FTIR: Attenuated total reflection–Fourier transforms infrared spectroscopy

COD: Chemical oxygen demand

DI: De-ionized

DO: Dissolved oxygen

DOC: Dissolved organic carbon

DON: Dissolved organic nitrogen

EDX : Energy dispersive spectroscopy

HA: Humic acids

HOC: Hydrophobic organic carbon

HPC: Heterotrophic plate count

HPI (HF): Hydrophilic

HPO (HB): Hydrophobic

HRT: Hydraulic retention time

HS: Humic substances

MBR: Membrane bio-reactor

MF: Microfiltration

NF Nanofiltration

MQ: Mili-Q water

MW: Molecular weight

NOM: Natural organic matter

NPD: Normalized pressure drop

OM: Organic matter

PolyDADMAC: Polydiallyldimethylammonium chloride

PSA: Polysilicate acid

PSiFe: Polysilicate ferric

SS: Suspended solids

SUVA: Specific ultraviolet absorbance

SWW: Synthetic wastewater

TMP: Trans-membrane pressure

TOC: Total organic carbon

TSS: Total suspended solids

UF: Ultrafiltration

UF-MFI: Ultrafiltration-modified fouling index

UV: Ultraviolet

UV_{254}: Ultra violet at 254 nanometer absorption

XRD: X-ray diffraction

LIST OF FIGURES

LIST OF TABLES

Chapter 1

Introduction

1. Introduction

1.1 Wastewater Treatment

All untreated water, especially wastewater, contains dissolved and suspended particles, which is why coagulation and flocculation processes are used to separate the suspended solids from untreated water.

The source, composition, size, shape and density of suspended particles varies considerably, which means selecting the appropriate coagulation and flocculation processes, and the coagulants, depend on understanding the interaction between these factors, and also the fact that small particles are stabilised (held in suspension) by the physical forces acting on the particles.

Since most suspended solids possess negative charges, they have the same type of surface charge. This causes them to repel each other when they are drawn close together, and thus they remain in suspension rather than cling together and settle out of the water.

The coagulation-flocculation process is one of the most common chemical treatment methods used in water and wastewater treatment (Rizzo et al., 2005 and Nassar et al., 2009), because this process facilitates the colloidal suspension particles to aggregate and deposit as sludge wastes.

1.2 Coagulation-Flocculation Process

Coagulation and flocculation occur in successive steps that overcome the forces stabilising the suspended particles and allows them to collide and enhance the growth of flocs. The first step of coagulation and flocculation process comprises destabilisation of the particle charges. The aim of this process is adding coagulants with charges that are opposite to the suspended to neutralise the negative charges remaining on dispersed non-settling solids, such as clay and organic substances that produce colour.

Once the charge has been neutralised, the small suspended particles can stick together, and although these micro-flocs, the slightly larger particles formed by this process, are not visible, the water surrounding them should be clear. If the water is still not clear, it indicates that not all of the particle charges have been neutralised and coagulation is still incomplete, which means more coagulant may be needed. Flocculation results in the formation of larger settleable flocs by bridging the gap that can easily be settled by gravity.

1.3 Coagulant Selection

Coagulants are selected based on the conditions and specifications of the given wastewater, while the treatment facility depends on the scale volume of the wastewater and the level of the treatment needed to produce the desired results. The final selection of the coagulant (or coagulants) should be made after thorough trial testing such as jar tests.

The most commonly used coagulants in treating wastewater are aluminium (Al) and iron (Fe) salts (Adin et al., 1998 and DeWolfe et al., 2003). The toxicity of aluminium based coagulant was reported by Stauber (2005) when public worries about a connection between residual Al-salt coagulants with Alzheimer's disease were on the increase. To resolve this problem, Al-based coagulants should not be used in water and wastewater treatment plants and a safe alternative should be substitute.

1.3.1 Inorganic Coagulants

The most common coagulants used are inorganic such as aluminium and iron salts. When these highly charged ions are added to wastewater, they neutralise the suspended contaminants and the resulting hydroxides produce a chain which facilitates the formation of flocs.

Inorganic coagulants are widely available and commonly applied in industrial water treatment and are quite effective at removing unwanted particles in wastewater.

1.3.2 Polymeric Coagulants

Polymers are organic chemicals with a high molecular weight are being used more widely, especially as coagulant aids with regular inorganic coagulants. Anionic (negatively charged) polymers are often used with metal coagulants because low to medium weight positively charged (cationic) polymers may be used alone or combined with aluminium and iron type coagulants to attract suspended solids and neutralise their surface charge Zouboulis et al., 2008 and Iler,1979). A manufacturer can produce a wide range of products for various source water conditions by controlling the amount and type of charge and relative molecular weight of the polymer.

Polymers are effective over a wider pH range than inorganic coagulants. They can be applied at lower doses, and they do not consume alkalinity. They produce smaller volumes of more concentrated, rapidly settling floc. Selecting the proper polymer for a specific application requires considerable jar testing under specific conditions (MRWA, 2013)

1.3.3 Polysilicate Ferric Coagulant

Polysilicate ferric (PSiFe) is a new type of poly inorganic flocculant (PFI) that is recently undergoing extensive research. Because the silica-based coagulant is a complex reagent, different preparation methods could give different performance under the same name as polysilicate ferric, so finding the silica characters and improving them as a coagulant is a challenging process.

In a study carried out by Zouboulis (2008), polysilicate ferric (PSiFe) was prepared by starting from a known procedure, and then, after examining a wide range of different parameters, the performance of PSiFe as a coagulant was improved. That coagulant was characterised by different test methods using (Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and energy dispersive spectrometer (EDS). A series of jar tests was used to find the optimum dose for coagulation. Different ratios of Si/Fe were prepared to examine its performance and determine the optimum ratio and most efficient dosage for further investigation.

1.4 Membrane Technology

Wastewater is traditionally pre-treated before applying reverse osmosis (RO), using processes such as filtration and cartridge filters beforehand. More recently, membrane filtration has been deemed an alternative solution to these conventional pre-treatment methods. Most reported wastewater membrane clarification pre-treatment uses ultra-filtration (UF) and micro-filtration (MF) membranes (Jeong, 2013).

In recent years UF/MF membranes have gradually gained acceptance as the preferred pre-treatment to the RO process (Baig and Al-Kutbi, 1999), because they provide an absolute barrier to particles and produce a consistent quality of treated water with a variable feed source. A UF membrane plant can remove all the suspended particles and some dissolved organic compounds. It can be noted that the removal rating is dependent on the molecular mass of feed material and the mass molecular cut off of the membrane. A typical removal capability of UF that is used for general water treatment is 0.01-0.02 micron, although some new materials even provide 0.005 micron filtration. A MF membrane typically operates at a particle size in an order of magnitude that is coarser than UF, e.g. approximately 0.1–0.2 micron. UF membranes therefore have an advantage over MF, as they provide a better disinfection barrier, because the pore size of UF can exclude viruses (Baig and Al-Kutbi, 1999).

1.4.1 Membrane Fouling

Membrane fouling is a process where solute or particles deposit onto the surface of a membrane or into its pores in a way that degrades the membrane's performance. It is a major obstacle to the widespread use of this technology. Membrane fouling can cause severe flux decline and affect the quality of the water produced. There are various types of foulants: colloidal (clays, flocs), biological (bacteria, fungi), organic (oils, polyelectrolytes, humics) and scaling (mineral precipitates). Severe fouling may require intense chemical cleaning or membrane replacement, which increases the operating costs of treatment in an industrial scale (MRWA, 2013).

The main factors that affect the membrane fouling process are (Baker, 2004):

1. Membrane properties such as pore size, hydrophobicity, pore size distribution and membrane material
2. The nature of the components and particle size distribution on the water and wastewater
3. Operating conditions such as the pH, temperature, flow rate and pressure

1.5 Objectives

The main objectives of this research are: (1) to optimise the available preparation method for PSiFe coagulant as a new type of water treatment polymeric coagulant, (2) to investigate its effect and potential impact on a hybrid system, including coagulation and a submerged hollow fibre membrane, and (3) to find clogging behaviour of the PSiFe coagulant in terms of its potential of fouling on the surface of the membrane after pre-coagulation. In addition, a comparison experiment is conducted on the hybrid system to examine the effects of the modified polysilicate ferric coagulant (PSiFe-γ) with a conventionally prepared one (PSiFe-β) and another coagulant such as $FeCl_3$.

The specific objectives of this research are:

- Developing a new methodology in preparation of poly silicate ferric with considering all the affecting factors in respect of suitable coagulation
- Characterising the Poly silicate Ferric
- Investigating the optimum dosage and proper Si/Fe ratio in the coagulation process of a synthetic waste water
- Examine the hybrid coagulant system, including coagulation and hollow fibre filtration
- Comparing the performance of other convenient coagulants such as PSiFe-β and $FeCl_3$, to this new modified coagulant (PSiFe-γ)

1.6 Coagulation-Membrane Hybrid System

A bench scale hybrid system includes a coagulation dosing system where membrane filtration is arranged to find the effect of different type of the PSiFe coagulant on fouling and performance of the membrane.

Different type of coagulants named PSiFe-β and PSiFe-γ. PSiFe- β was made using a combination process of the existing acidification/

polymerisation of water glass solution procedure and partial polymerisation by ion exchange resin.

In the next modification step, water glass solution was polymeroised by ion exchange resin as well as heating and aging to have a suitable substitution of mono valiant ion (Na^+) with ferric ion which is three valiant in which lead to a high charge and high molecular weight coagulant (PSiFe- γ).

The following sequential tasks and tests are conducted to meet the objective of this study:

- Select three coagulants for the test, including polysilicate ferric with ferric chloride (FeCl3), polysilicate ferric prepared by new method (PSiFe-γ) and conventional method (PSiFe-β)
- Measuring the total organic carbon (TOC), turbidity, and UV254 in wastewater, coagulated water, and filtrated water for each of the selected coagulants
- Finding the critical trans-membrane pressure test (TMP) for each of the selected coagulants
- Conducting a membrane fouling index (MFI) test for synthetic water and coagulated synthetic water with all of the target coagulants to find their tendency to foul on the surface of the membrane

In addition to the above mentioned tests, during the implementation of these reagents as a coagulant control, the operating parameters have been optimised. They are dosing rate, speed of mixing, pH and pressure which are the key operational factors controlling the process.

1.7 Further Investigation on the Performance of the PSiFe

The effectiveness of the PSiFe has investigated in different jar experiments such as kaolin clay contaminated water to find the optimum pH flocculation range in kaolin wastewater treatment, examination of sea water to determine the potential for fouling, as well as the removal of phosphorus from raw water.

1.8 Significance of Research

The membrane filtration of wastewater treatment can handle the demand for stringent regulations quite well, but it may not be a completely efficient process due to the fouling problem. This demands an effective pre-treatment that can facilitate a faster and more durable treatment of wastewater pollutants.

Coagulation is generally known as the core process in any type of water treatment; indeed its absence would lead to an unfavourable downstream process such as membrane treatment that would in turn greatly increase the operation and maintenance costs. This would be especially so on an industrial scale where massive quantities of wastewater require thorough treatment on a daily basis. Among the all of the treatment systems, the development and implementation of coagulant is a key for the successful industrial environmental remediation (Ratajczak, 2007).

Extensive research has been carried out in this area (Zouboulis et al., 2008, Moussas et al., 2009), however due to the long time required for such work, ongoing research is imperative for possible breakthrough in this field that will contribute significantly towards successful wastewater treatment in this sustainable based industrial era.

Handling issues, together with sludge and the concerns over its environmental disposal have proven to be burning topics in those industries which form the driving force for continuous and innovative research over many years. Of all the types of inorganic poly metal silicate coagulants, polysilicate ferric is on a high research trend due to its high charge and high molecular weight, which are the main goal in the selection and preparation of a coagulant.

Until now, the hydrolysis/polymerisation of Fe-polysilicate coagulants has been investigated extensively by many chemists and water treatment specialists (Shon et al., 2005, Gao et al., 2007, and Moussas et al., 2008). Several studies were conducted using different modifications such as adding new components to polymerised silicate solution. Most studies are related to adding some modifier to increase the molecular size of polysilicate acid (PSA) and the aggregation process, as well as its stability and durability.

According to this study, there is no report, considering all the aspects needed in the preparation of PSiFe coagulant. These factors could be an acidification method, the initial concentration of silica, the temperature and suitable time of stopping the polymer aggregation of , speed of acidification, and proper pH for adding metal.

In addition, there is no evidence on using cationic resin method to prepare polysilicate ferric (PSiFe) as a water treatment coagulant. Almost all previous investigations on poly silicate ferric were based on an acidic type of polymerisation. In other words, until now, authors have not fully investigated the method of the polymerisation of silica with alternative acidification using cationic resin and aggregation characteristics to reach the main goal in coagulation of turbidity particles (high aggregation and charge). In addition, an investigation into implementing a suitable operational model, including coagulation and membrane, to find the efficiency of this coagulant (PSiFe) on performance of the membrane is another contribution in this field of research.

Obviously all these factors would directly or indirectly result in having minimum consumption of the material and high charge neutralisation ability, bridging/sweeping and all the characteristics needed for optimising coagulation and consequently steady and reliable and durable membrane treatment.

The benefits of employing the target coagulant (PSiFe-γ) and the developed procedure compared to traditional chemical treatment would be lower chemical consumption, with environmental friendly sludge material, highly efficient fouling treatment, and a more reliable and operational system on an industrial scale.

Chapter 2

Literature Review and Background

2. Literature Review and Background

2.1 Introduction

Since the early 1990s, microfiltration (MF) and ultrafiltration (UF) membrane plants have become increasingly popular alternatives to conventional water treatment technologies such as coagulation /flocculation, and sedimentation and media filtration for removing particulates, bacteria, viruses and natural organic matters (Adham et al., 2005) from surface water, wastewater and industrial water supplies. As explained by Jacangelo et al. (1997), MF and UF membrane systems can also be used as pre-treatment technologies for desalination processes such as reverse osmosis membranes.

Guerra et al. (2012) expressed that all membrane processes are subject to fouling that reduces its productivity, increases the energy consumed, shortens the maintenance intervals, increases the use of chemicals, increases the replacement of membranes, and so on. Fouling is a complex phenomenon that can be defined as the blockage of membrane pores during filtration, caused by a combination of sieving and the adsorption of particulates and compounds onto the surface of the membrane or within its pores (Li-jun et al., 2009). The composition of the feed water has a huge influence on this phenomenon because parameters such as turbidity, total organic carbon (TOC), the ultraviolet absorbance at 254 nm (UV254), as well as the polyhydroxy aromatic content, can be used to estimate the fouling potential of raw water. Many other parameters have already been investigated, based on experimental procedures and a variety of analytical techniques. However, membrane precise fouling behaviour has not been fully described or predicted by researchers yet.

A combination of coagulation with a low pressure MF membrane plant can potentially decrease many of the shortcomings encountered in conventional methods of natural organic matter (NOM) removal, e.g. coagulation/rapid media filtration and nanofiltration. Indeed, MF membranes are suitable barriers against bacteria and larger micro-organisms, with a reasonable virus retention capability depending mainly on the membrane pore sizes. Due to its excellent backwash ability and high robustness, the ceramic monolith MF configuration investigated is a promising method to counteract fouling. However, the treatment of low turbidity, low alkalinity, low buffer capacity water, and the high DOC and colour content found in Nordic countries has not been investigated in depth. Hence Crozes et al. (2001) recommended that to prove the successfulness of this type of MF membrane, an integrated process of coagulation/ceramic microfiltration must be operated such that a high permeate quality (i.e. low DOC and colour, pathogen free, no disinfection by-products, low residual metal) can be achieved with a minimum usage of chemical reagents and energy at low membrane fouling levels.

Membrane filtration makes small systems highly efficient, and is easy to operate alternative to improving the quality and of biological stability of finished water. However, the economic use of membrane filtration in small systems is often hindered by fouling which increases pressure drops applied and frequency of cleaning, as well as the associated decrease in removal efficiency as the pressure drop increases (Ratajczak, 2007).

The most common method, currently used to prevent fouling, is pre-treating the influent to the membrane by adding chemicals. However, as reported by Escobar et al. (2000), caution should be exercised, because some chemicals are incompatible for long term use, they may cause bacteria to become more resistant, and may also add impurities to the treated effluent. Pre-treating raw water with ordinary coagulation can substantially reduce the concentration of bio-degradable organic matter which can thus decrease the potential for fouling and enhance membrane rejection).

Coagulation is an indispensable pre-unit operation technology in water treatment, and it is also one of the most common and important unit processes. Polysilicate metal salt coagulant is a new type of inorganic polymer flocculent which is being researched at home and abroad, consisting of compounds of poly silicate and metal salt on the basis of traditional flocculants such as polysilicate and aluminium salt (or iron salt). Because this flocculent overcomes the defects of dosages of polysilicate flocculent for secondary treatment, and it is easy to prepare, it was a cause of great concern to the water treatment industry (Zouboulis, 2008).

Common inorganic materials were used to synthesise two poly silicate iron coagulants: polysilicate ferric chloride (PSiFe) or polysilicate aluminium chloride (PSiAl). In this study, poly silicate ferric was used as a target coagulant due to the environmental limitations of aluminium based coagulants.

2.2 Coagulation–Flocculation in Wastewater Treatment

2.2.1 Particles Destabilisation Process in Water

The suspended materials in water and wastewater mostly arise from land erosion, the dissolution of minerals and decay of vegetation, and from domestic and industrial waste discharges. According to Tzoupanos et al. (2008) for given water or wastewater, such material may comprise suspended, dissolved organic and/or inorganic matter, as well as several biological organisms such as bacteria, algae, or viruses. This material must be removed because it causes deterioration of the water quality by reducing the clarity (e.g. causing turbidity or colour), causes infection, and eventually carries toxic compounds that are adsorbed onto their surfaces. In addition, organic matter is the main precursor to the formation of disinfection by-products when chlorine is applied as a disinfection agent.

Table 2.1 Classification of particle size (Bratby, 2006)

Particle Size (mm)	Classification	Examples	Total surface area(m^2/cm^2)	Time required to settle 100 mm
10	Corse dispersion	Gravel, Corse sand	6×10^{-4}	0.1s
1	Visible to naked eye	Flocculated Particles	6×10^{-3}	1s
10^{-1}		Macro plankton	6×10^{-2}	13s
10^{-2}	Fine particulate	Mineral substances, Precipitated and flocculated particles, silt bacteria	0.6	11 min
10^{-3}	Dispersion (Visible under Microscope)		6	20 hours
10^{-4}			60	80 days
10^{-5}		Hydrolysis and precipitated products	600	2 years
10^{-6}	Colloidal dispersion	Macromolecules, biopolymers,	6000	20 years
$< 10^{-6}$	Solution	Poly electrolyte, organic molecules		

Table 2.1 classifies the common materials present in water or wastewater (Bratby, 2006) according to their size. Particles smaller than around 10^{-5} mm may be referred to as colloids and particles smaller than 10^{-6} mm are categorised as solutions. It can be noted that with decreasing size, the

time required for settling increases, up to several years for the ingredients of certain solutions. Due to their very small size, the only way they can settle and separate is to make contact and form larger particles, which can make settling easier. This procedure however, is hindered by the homonymous negative charge this material carries. The electrostatic repulsive forces constrain the particles from approaching each other and the suspension is characterised as stable, and therefore a long time period is needed for settling.

In order to accelerate the settling time, destabilisation is required, which denotes the importance of coagulation. Destabilisation can be achieved with one, or a combination of two or more of the following mechanisms, after a coagulant agent (Dulan et al., 2003; Crittenden et al., 2003) has been added:

- Compression of the electrical double layer
- Adsorption and charge neutralisation
- Adsorption and inter-particle bridging
- Enmeshment in the precipitate, using a large dose of coagulant, “sweep flocculation”

After destabilisation, flocculation promotes the aggregation and formation of flocs, but usually after the addition of an appropriate flocculent agent.

Two general types of flocculation can be identified: micro-flocculation (or peri kinetic flocculation), where particle aggregation is brought about by the thermal motion of fluid molecules (Brownian motion), and macro-flocculation (ortho kinetic flocculation), where particle aggregation is brought about by inducing velocity gradients and mixing in the suspension (Crittenden et al., 2003). Coagulation-flocculation is widely used during water or wastewater treatment, and is an integral step in the treatment of surface or underground waters indented for human consumption.

2.2.2 Coagulation-Flocculation Process

Coagulation and flocculation are defined as a process by which small particles in an aqueous solution destabilise due to the addition of chemicals, and aggregate together to form larger particles known as flocs.

Although the history of coagulation goes back three thousand years ago, the modern use of coagulants for water treatment commenced approximately 100 years ago, when aluminium sulphate and ferric chloride were used as coagulants in full scale water treatment. Since the 1980's, optimising the performance of coagulation for removing NOM has been studied systematically using various real surface and synthetic waters (Jiang, 2001). In the 1990's, NOM and other precursors of disinfectant by-products were still a primary cause of concern because earlier, the focus of coagulation was on removing particles, a topic that was addressed in the previous section.

The coagulation process is complicated, with many mass transfers and active species that take part in the reaction steps. The process can be broken down into three key steps, including the formation of coagulant, particle destabilisation (coagulation) and inter-particle collisions (flocculation). Enhanced coagulation, often referred as ‘low pH coagulation’, is often used to increase the removal of TOC and other particles by reducing the raw water pH to an optimal level, i.e., a pH between 4.5 and 5.5 for iron based coagulants and 5.5-6.5 for aluminium based coagulants (Sharp et al., 2006).

Aluminium and ferric salts are known as hydrolysing metal salt (HMS) coagulants with the active metal being Al^{3+} and Fe^{3+} for alum and ferric chloride respectively (AWWA, 1999). In solution, these small, positively charged ions form a strong bond with oxygen atoms of six surrounding water molecules, e.g., $M\ (H_2O)_6$. The hydrogen-oxygen bond is subsequently weakened and the hydrogen ions are released into solution where the resulting active metal hydroxide species are known as hydrolysis products. This process is a progressive de-protonation of water molecules in the primary hydration shell (Richens, 1997). The hydrolysis of such ions is generally represented as a sequential replacement of the water molecules by hydroxyl ions (Gregory et al., 2001).

The two main approaches in which hydrolysing coagulants act to remove particles are charge neutralisation and sweep flocculation. Charge neutralisation is a reasonably simple mechanism that involves the specific adsorption of cationic hydrolysis products from solution onto the negatively charged particles. NOM and other particles can be destabilised by small amounts of hydrolysing coagulant. Desirable destabilisation corresponds with the neutralisation of particle charge, which then leads to aggregation of the neutral particles (Gregory et al., 2001).

It is important to note that larger amounts of the positively charged coagulants (over dosing) can cause charge reversal, leaving the particles positively charged and thus re- stabilised. When charge neutralisation is the dominant mechanism, the dose of coagulant is generally considered to be proportional to the concentration of particles in the solution, although in some cases the required doses can still be dominated by the type of NOM found in the water, and not simply the concentration. In some cases a higher dose of coagulant is more effective due to extensive hydroxide precipitation and the process known as sweep flocculation (Jiang, 2001).

2.2.3 Coagulation-Flocculation Mechanism

Coagulation/flocculation is a common method used in water and wastewater treatment to remove colloidal particulate matter. Colloids are classified as hydrophobic (water hating) and hydrophilic (water loving) types. In water and wastewater treatment we deal primarily with hydrophobic colloids to increase the kinetics of the aggregation of colloids to make an effective treatment process (Hunter, 2000).

In water and wastewater treatment the terms coagulation and flocculation are often used interchangeably. Flocculation is synonymous with agglomeration and coagulation and the single term "flocculation" is used to describe both (Akers et al., 1972; McNaught et al., 1997; Hubbard, 2004 and Bratby, 2006).

According to Jiang et al. (2008), coagulation is the destabilisation of colloids by neutralising the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative zeta potential charge of the colloids. As a result, the particles collide to form larger particles (flocs). Proper mixing is required to disperse the coagulant throughout the liquid. Multivalent cations such as aluminium (Al), iron (Fe), calcium (Ca) or magnesium (Mg) salts have positively charged molecules that interact with negatively charged particles and molecules to reduce the barriers to aggregation. These chemicals, under appropriate pH and other conditions such as temperature and salinity, react with water to form insoluble hydroxides which, upon precipitating, link together to form meshes that physically trap small particles into the larger flocs. Flocculation is the action of polymers that form bridges between the flocs and bind the particles into large agglomerates or clumps. Bridging occurs when segments of the polymer chain adsorb onto different particles and help them aggregate. An anionic or cationic flocculent will react against a positively or negatively charged suspension adsorbing onto the particles and causing destabilisation either by bridging or charge neutralisation. On the other hand, coagulants could be distinguished from flocculants in terms of charge density and molecular weight. Everett (1972) and the Global Health and Education Foundation (2007), indicated that positive or negative particles may be aggregated into microscopic particles by a coagulant which may then be flocculated into macroscopic flocs with a flocculent. Thus, coagulation is the aggregation of colloidal particles in the primary energy, leading to an irreversible aggregation. Flocculation is the aggregation of colloidal particles in the secondary energy, leading to a reversible aggregation.

- Destabilisation (or Coagulation) reduces the forces acting to keep the particles apart after they come in contact with each other (i.e., lower the repulsion forces). The higher charges in the surface of the particle are beneficial for coagulation.
- Flocculation is the process of bringing destabilised colloidal particles together to allow them to aggregate to a size where they will settle by gravity. The higher molecular weight of the coagulant helps sedimentation.

Typical applications are the removal/separation of colloids and suspended particles, of NOM, or metal ions. In wastewater treatment, additional applications include the removal of toxic metals, anions (i.e. phosphates), colour, odour, etc. The removal of organic contaminants by coagulation has been studied for decades. Most of the work shows that coagulation substantially reduces the concentration of organic particles, a primary type being components of NOM (Randtke, 1988). It is difficult to predict the percentage removal of NOM from surface waters with coagulation because it depends on a variety of conditions such as the characteristics of the organic matter and the operating conditions. Removing particulate NOM is primarily achieved through colloidal destabilisation, followed by sedimentation and filtration (Randtke, 1988). As expressed by Sharp et al. (2006), NOM is traditionally removed by coagulating with the trivalent Al and/or Fe metal ions. The coagulation mechanisms that are thought to dominate with regards to removing NOM are charge neutralisation for colloidal material and charge complexion for soluble compounds.

Sharp et al. (2006) presume that the coagulation process is maximised under similar conditions and provides maximum turbidity removal, although this can also be achieved over a broader range of conditions. This occurs under acidic conditions with a pH between 4.5 and 5.5 for iron based coagulants and between 5.5 and 6.5 for aluminium based coagulants.

The performance of the membrane is characterised by the rate of increase in trans-membrane pressure required to maintain production of the plant's design flow rate. It is also based on experimental data and. used to quantify long term and short term fouling rates. According to Guerra, et al. (2012), the rate of fouling for each type of membrane depends on the operating conditions, including the trans-membrane pressure, cross flow velocity, and the frequency and efficiency of chemical cleaning. Engineering design equations govern the size and quantity of the components of a treatment plant based on the average trans-membrane pressure needed, the volume of recirculated needed, the frequency of chemical cleaning, the volume of permeate water and chemicals consumed during cleaning, daily plant downtime, total area of the membrane, and actual feed flow rate of the plant.

2.3 Common Coagulants in Wastewater Treatment

The most commonly used metal coagulants fall into two general categories: those based on Al- and those based on Fe-salts. The Al-coagulants include aluminium sulfate ($Al_2(SO_4)_3$), aluminium chloride ($AlCl_3$), and sodium aluminate ($Na_2O.Al_2O_3$). The Fe-coagulants include ferric sulfate ($Fe_2(SO_4)_3$), ferrous sulfate ($FeSO_4$), ferric chloride ($FeCl_3$) and ferric chloride sulfate ($FeClSO_4$). Other chemicals used as coagulants include hydrated lime ($Ca\ (OH)_2$) and magnesium carbonate ($MgCO_3$). The most used coagulants in wastewater treatment are Al-salts (72%) and Fe-salts (23%) (DeWolfe et al., 2003). $Al_2(SO4)_3$ is the most commonly used coagulant and is easy to handle and apply and most applicable at a wastewater pH above 5. FeCl3 is also a commonly used coagulant with a wide range of pH (Adin et al., 1998). The ferric hydroxide flocs are also heavier than the aluminium flocs, improving its settling characteristics, and reducing the size of the clarifier. However, the flocculation process using these coagulants produces large quantities of sludge which inhibit efficient wastewater treatment.

2.3.1 Metal Coagulants

The most widely used metal coagulant is probably aluminium sulfate ("alum"), which has been used for water treatment during the past decades (Zouboulis et al., 2008). It is usually manufactured from the reaction of bauxite ores with sulfuric acid.

The evaporation of water in this process results in a dry product with an approximate formula of $Al_2(SO_4)_3.18H_2O$, and with an Al content ranging from 7.4 to 9.5%. It is supplied as powder or in a liquid form and its applications includes the treatment of water or wastewater. A product prepared from alum and sulfuric acid is acidified aluminium sulfate (acid alum). It is supplied as a liquid and is used mainly in the papermaking industry. Other Al coagulants are the aluminium chloride ($AlCl_3.6H_2O$) and the sodium aluminate ($NaAlO_2$). The first one is supplied as a liquid (containing 10.5% Al) and is widely used to condition sludge, while the latter is usually supplied as a viscous, strongly alkaline, and corrosive liquid (containing 13% Al). It is rarely used alone, but generally with alum to obtain some specific results such as the treatment of highly coloured waters (Bratby, 2006; Crittenden et al., 2005).

The application of metal coagulants (conventional) is widespread, especially due to the relatively low cost and simple application route. However, Tzoupandos et al., (2008) found that they have several disadvantages such as the need to adjust the pH before or after treatment, their sensitivity to temperature changes, the need for higher dosages because the charge neutralisation is not usually enough, the sensitivity to sample specific characteristics and composition of a sample, as well as an excessive production of sludge.

2.3.1.1 Preference of Iron to Aluminum Coagulants

Coagulant reagents used for water and wastewater treatment are predominantly inorganic salts of alumimium or iron (Moussas et al., 2008), although the environmental Protection Agency (EPA) regulates a number of substances, including aluminium, in drinking water. Aluminium (Al) is clearly a powerful neurotoxic and a lot of evidence exists to show that Aluminium may play a role in the pathogenesis of Alzheimer’s disease, so the development of an Al-based coagulant is limited due to the latent toxicity for organisms of rudimental aluminium (Orme et.al., 1990; Falten, 2001). Since residual aluminium is believed to be harmful to human and living organism (Gao 2010; Letterman 1985; Orme 1990; Falten 2001), iron based coagulants have attracted more interest and attention (Edzwald 1999; Jiang et al., 2003; Lee, 2004).

2.3.2 Pre-polymerised Coagulants

Several research efforts have been devoted to improve the efficiency of the coagulation flocculation process. However, after studying aquatic chemistry and the behaviour of simple Al salts, the way to improve them seems to be associated with their (partial) polymerisation. The result of these efforts was the production of a range of pre-polymerised aluminium solutions, referred as poly-aluminium chlorides (PACl), poly-aluminium sulfates (PAS), or poly-aluminium chloro-sulfates (PACS), with variable degrees of polymerisation. These products, especially the first one (PACl), have extensively been used worldwide over the last decades, with an ever increasing demand. Their properties were examined intensively and have proven to be more efficient at lower dosages, in a wider pH, temperature, and ranges of concentrated colloids than the simpler conventional ones, leading to cost savings and more effective treatment (Sinha et al., 2004). Their superiority is related to the distribution of different species of aluminium distributed in the polymerised, rather than the non-polymerised solutions.

Aluminium exists in water solutions and at pH values < 3 as a six-coordinated Al^{3+} ion. With an increase in the pH, the aluminium ion begins to hydrolyse, and various products can be formed. The hydrolysis of the Al ion is extremely complicated; it involves hydrolysis and polymerisation reactions that lead to the formation of several polymeric species, apart from various monomeric species (Jianget al., 2004). With conventional coagulants, these reactions are entirely uncontrolled, and efficient coagulation is based more on the formation of $Al(OH)_3$ (with a pH of around 6.5-7) and less to charge neutralisation, because the hydrolysis reactions are proceeding fast and hence, the concentration of positively charged Al ions is restricted. In the case of PACl, pre-polymerisation aims to control the aforementioned reactions to a certain extent.

With the partial neutralisation of an Al solution by adding a base solution and then by ageing, these reactions may take place to some extent and various Al species can be formed. The most important reaction is supposed to be that leading the formation of $Al(OH)_4$ because this aluminium anionic form is claimed to be the precursor for the creation of polymeric Al_{13} (Parker et al., 2002). Al_{13} ($AlO_4Al_{12}(OH)_{24}(H2O)_{12}$) with an L- Keggin structure is one of many possible PACl polymeric compounds, like dimmers (e.g.$Al_2(OH)_2\ ^{4+}$), and trimmers (e.g. $Al_3(OH)_4\ 5^+$) among several others that are even larger than Al_{13} i.e. with more than 13 aluminium atoms (e.g. $Al_{30}O_8(OH)_{56}(H2O)_{24}$), which transform continuously from one form into another (Bi et al., 2000).

It can be noted that, Al_{13} is claimed to be the most stable aluminium specie in a partially neutralised aluminium solution (Wang et al., 1999). The improved coagulation properties of PACl are thought to be due to Al_{13} existence, i.e. an increased capability of charge neutralisation (coagulation) and an increased molecular size and ability to aggregate (flocculate). Furthermore, the decrease of monomeric Al in favour of Al_{13} and other polymeric compounds eliminates the hydrolysis reactions which results in the pH value having a minor impact after treatment.

The production of pre-polymerised coagulants involves the partial neutralisation of an Al solution with a base solution. Many parameters can affect the properties of the final product, i.e. the base addition rate, the stirring speed, the temperature of the synthesis, the presence of other anions (e.g. Cl^-, SO_4^-, CO_3^{2-}), and the ageing time, etc. The most important parameter however, is claimed to be the molar ratio of bound hydroxide to the concentration of metal cations (i.e. the OH/Al molar ratio). This is referred to as basicity and is also used to describe the degree of polymerisation of coagulant agents (Tzoupanos et al., 2008; Zouboulis et al., 2008).

2.3.3 New Generation of Coagulation Reagents

In spite of an improvement in the properties of pre-polymerised coagulants, their performance remains inferior compared to organic polyelectrolytes, e.g. when used in water treatment (Gao et al., 2002). In recent years the research into the field of coagulation-flocculation has focused mainly on understanding the behaviour and aquatic chemistry of pre-polymerised coagulants such as poly aluminium chloride, and to further improve their properties. The main reason why organic polymers are more efficient is their higher molecular weight (MW), which implies better flocculation properties. Thus, the increase of MW and size of the pre-polymerised coagulants is thought to be the best way for further improvement.

The general concept is to introduce various additives into the structure of a pre-polymerised coagulant in order to produce a homogenous, stable product with higher MW, and improve the coagulation-flocculation performance more than the initial reagent. The challenge is to confront the desirable combination of higher efficiency and cost effectiveness, which are the basic prerequisites for the development of new products. Various additives were examined, and they can be classified into two main categories; inorganic and organic.

2.3.3.1 Organic Additives

A suitable additive for the improvement of flocculation properties is thought to be polymerised silica. Hasegawa et al., (1990) reported that by introducing metal ions into polymerised silicic acid solution, the MW of the product increased and the respective stability and coagulation were improved. In this case the product was an inorganic metal poly silicate flocculent where silica was the main component, than a pre-polymerised inorganic coagulant. More recently, a number of researchers have focused on incorporating silica within the pre polymerised metal solutions by aiming at products with larger molecular weight using two techniques; i.e. either by introducing polymerised silica in the pre-polymerised metal solution, or by introducing polymerised silica in the metal solution, followed by polymerisation. The first method is referred to as composite polymerisation, whereas the latter one is known as co-polymerisation. Polymerised silica can be obtained when the concentration of mono silicic acid ($Si(OH)_4$) in an aqueous solution exceeds the solubility limit of amorphous silica, or otherwise, by bringing the solution temporarily into the pH-concentration range of over saturation with respect to amorphous silica. Excess monomers in the solution gradually disappear to form polymers. These polymers, or polysilicic acids, consist of silica tetrahedrons that are linked via silicon-oxygensilicon bonds (e.g. OSi-OH+ HO-SiO P OSi-O-SiO+ H2O) (Stumm et al 1967). Various species can be formed, e.g. $Si_2O_3(OH)_{42}$-, $Si_3O_5(OH)_{53-}$ etc., and the exact nature and extent of their formation is affected by the temperature, the concentration of silica, the presence of other ions, the pH value, and the ageing time. Soluble, internally hydrated, polymeric silicic acids of colloidal dimensions, or discrete particles of colloidal size, can be present.

The most important parameter that affects the kinetics of silica polymerisation is the pH value. Specifically, polymerisation is thought to be catalysed by hydroxyl anions and is very fast at the neutral or slightly alkaline pH range. At a pH value over 9 the reaction rate decreases. Furthermore, by ageing, polymerisation can lead to the formation of bigger aggregates and finally, to gel formation (amorphous $(SiO)_n$. In order to avoid gelation and preserve the poly silicates in a soluble form, the solution must be brought outside the range of insolubility by acidifying the solution to pH values 2–3. At a pH of around 2 the polymerisation rate is retarded enough and the poly silicates are stable in soluble form for several days (Chan, 1989; Stumm et al., 1967; Dietzel, 2000). Based on these observations and the use of a suitable silicic acid source, i.e. the sodium silicate solution or water glass, several efforts have been made to introduce acidified poly silicates into the structure of pre-polymerised coagulants (Tzoupanos et al., 2008).

The mixed product in the case of aluminium is called poly aluminium silicate chloride, although it should be referred to as a category of coagulation reagents because with different combinations of OH/Al or Al/Si molar ratios, various reagents can be produced. Poly aluminium silicate chloride has shown much better coagulation than the conventional or simple pre polymerised coagulants in water or wastewater treatment (Gao et al., 2002; Zouboulis et al., 2008; Cheng et al., 2005). This performance can be attributed to altering the composition of the coagulants by a specific degree. Indeed it has been proved that introducing silica chains into the structure of PACl increases the molecular weight of the components of the coagulants with the formation of alumino-silicate complexes, which in turn enhances the aggregating power and the formation of bigger denser flocs (Gao et al., 2002; Zouboulis et al., 2008; Song et al., 2003).

2.3.3.2 Inorganic additives

Organic poly-electrolytes are typical hydrophilic colloids and contain certain functional groups which may be ionisable. When these groups dissociate, the polymer molecules become charged, either positively or negatively, and are thus referred to as cationic or anionic poly electrolytes, respectively. If no ionisable groups are present, the polymers are termed as non-ionic (Bratby, 2006).

They can be classified according to their origin into two main categories, natural and or synthetic polymers. Natural polymers (bio-polymers) have long been used as flocculants (bio-flocculants). Typical examples are starch derivatives that are pre- gelatinised and soluble in water. These can be starches, anionic oxidised starches, or amine-treated cationic starches. Other classes include polysaccharides, such as guar gums, tannins, chitosan and alginates (Crittenden et al., 2005; Bache et al., 2007).

Although natural poly electrolytes have the advantage of being toxic free, the use of synthetic poly electrolytes is more widespread. They are generally more effective as flocculants, principally due to the possibility of controlling properties such as the number and type of charged units and the molecular weight. Moreover, they are much cheaper than those made from natural sources.

Synthetic organic polymers are made by either the homo-polymerisation of the monomer or by the co-polymerisation of two monomers. Polymer synthesis can be manipulated to produce polymers of varying size (MW), charge groups, number of charge groups per polymer chain (charge density), and varying structure (linear or branched). Many synthetic polyelectrolytes are based on polyacrylamide and its copolymers with poly acrylic acid. Typical examples are the hydrolysed polyacrylamides (anionic, MW 104-107 g/mole), poly di allyl di methyl ammonium chloride (poly-DADMAC, cationic, MW 104-107 g/mole) and various polyacrylamides (non-ionic, MW 105- 107 g/mole) (Bache et al., 2007).

Organic polymers are not generally used as primary coagulants. Only in certain cases will cationic poly-electrolytes be applied to destabilise colloids (coagulation), and usually in conjunction with inorganic metal salts.

The primary use of polymers is as flocculent aids, whereas non-ionic or anionic polyelectrolytes are added after the addition of an inorganic coagulant (Kim, 1995). Despite their efficiency their use is accompanied with significant drawbacks such as the increased treatment cost. Considering that apart from the cost of the product itself, which is higher than inorganic salts, polymers are usually delivered in solid form and hence, a separate dissolution set up is needed, which further increases the cost of treatment. Furthermore, the existence of remaining unreacted monomers results in residual toxicity in the treated sample (Tzoupanos et al., 2008).

The combination of an inorganic salt (coagulant) and a suitable poly-electrolyte (flocculent) into one reagent, apart from the treatment efficiency of the inorganic salt, is thought to improve the overall cost effectiveness. According to Zouboulis et al., (2008), no addition of a flocculent aid will be needed any more, whereas the introduction of a poly-electrolyte into the structure of the metal salt reduces the eventual residual toxicity quite significantly.

These suggestions lead to the production of modified inorganic coagulants with organic additives, a field that is now under investigation. All the aforementioned charged or not charged poly-electrolytes can be used for this purpose, with a different impact in the nature of the new product. For example, introducing a cationic poly-electrolyte into the structure of a pre-polymerised metal coagulant mainly improves the charge neutralisation capability, and to a less extent, the aggregating effect as well. Moreover, the use of an anionic polyelectrolyte with higher molecular weight (as compared to cationic) would further improve the aggregating ability. In this case however, the anionic polymer should have a weaker anionic charge in order not to deteriorate the charge neutralisation strength of the combined coagulant agent. A non-ionic poly-electrolyte would have a minor effect on the charge density of the coagulants (possibly negative), but would significantly increase its flocculation ability. Key factors affecting the properties of the combined (modified) coagulant are: the charge, the MW and the content of the poly-electrolyte. Some efforts regarding the combination of PACl with various anionic, cationic, and non-ionic organic polymers (Tang et al., 2002) have been reported, including the combination of PACl with poly-DADMAC (Gao et al., 2005; Gao et al., 2007). Although the research in this field is at an initial stage, promising results have been obtained from the aforementioned, investigations regarding the performance of the coagulation.

Introducing the poly-electrolyte can be accomplished by two procedures, as in the case of silica addition, i.e. with the co-polymerisation or the composite polymerisation. The content of the poly-electrolyte (PE) in the final product, usually expressed as the Al/PE ratio (mg/L), can take values between 5 and 20 and together (Xu et al., 2009) with the aforementioned parameters in the case of pre polymerised coagulants, designates the properties of the final product.

2.3.3.3 Applications of the New Generation Coagulants

Zouboulis et al., (2008) explained that poly aluminium silicate chloride was far better at treating water than conventional or simple pre-polymerised coagulants. They also showed that incorporating polymerised silica enhances aggregation because the period in which flocs grow decreases and their size increases. This enhancement compensates for the decrease in the charge neutralisation capability of flocs due to the addition of silica, because the coagulation of PASiC was clearly better, especially the residual concentration of Al. The advantages of PASiC can be summarised as treating water more efficiently due to using lower dosages of coagulants and in a wider pH range, whereas the concentration Al that remained in the treated sample was much lower.

A matter that has not yet been considered in detail is the application of poly aluminium silicate chloride in the treatment of wastewater.

lists the results of the post-treatment of biologically pre-treated landfill leachates with coagulation-flocculation (Tzoupanos et al, 2008). This kind of wastewater is difficult to treat any more, mainly due to its bio-refractory organic content (humic substances). The performance of PASiC (OH/Al =1, Al/Si = 15) was evaluated and compared with the performance of a conventional coagulant (alum, OH/Al = 0), two simple pre- polymerised coagulants, a widely used commercial product with a slightly higher degree of polymerisation ($PACl_{18}$, OH/Al = 1.2), and a laboratory prepared PACl solution with the same degree of polymerisation (PACl, OH/Al = 1). Turbidity, UV absorbance at 254 nm (corresponding to the presence of NaturalOrganic Matter / NOM) and chemical oxygen demand (COD) were among the parameters monitored during these experiments.

Table 2.2 shows that the least effective coagulant in almost all cases was alum, whereas the most effective was PASiC. The highest removal efficiencies of all the parameters examined were achieved with the new composite coagulant, with the highest dosage added (300 mg/L). What is worth noting is that the addition of alum or PACl over 200 mg/L caused the quality of the treated sample to deteriorate due to turbidity (denoted as 0% removal). Therefore, a further increase of concentration leads to overdosing, reversibility of the coagulation phenomena, and a re-stabilisation of the colloids. However, with silica based coagulants, the addition of even 300 mg of L-1 resulted in a further improvement of treated wastewater (leachate), so with these coagulants, higher doses are possible in order to obtain better treatment results. Nevertheless, it should be mentioned that in order to prepare a superior novel silica based coagulation reagent, specific attention must be given to the degree of polymerisation, the silica content, and the method of preparation because these experiments revealed that composite coagulants with different OH/Al and Al/Si molar ratios or preparation methods can be more efficient in different cases (Zouboulis et al., 2008; Tzoupanos et al., 2008).

Table 2.2 Comparison of the coagulation performance Al-based coagulants (Iler, 1979)

Coagulant	Turbidity removal %			Absorbance at 254 nm removal %			COD removal %		
	Coagulant dosage (mg/L)			Coagulant dosage (mg/L)			Coagulant dosage (mg/L)		
	50	100	300	50	100	300	50	100	300
Alum	65	72	0	16	29	39	30	51	61
PACL-18	83	88	77	18	31	70	31	46	73
PACL	84	88	0	20	32	71	35	49	63
PASiC	86	90	94	19	33	74	32	51	77

Table 2.3 Comparison of the coagulation performance polymer-based coagulants

Coagulant	Turbidity removal %			Absorbance at 254 nm removal %			Residual Al concentration (mg/L)		
	Coagulant dosage (mg/L)			Coagulant dosage (mg/L)			Coagulant dosage (mg/L)		
	2	4	6	2	4	6	2	4	6
PACL	94	97	97	70	73	79	150	172	178
PACPE	95	99	99	83	86	87	155	150	158

Table 2.3 illustrates the comparative results of kaolin-humic acid model suspension (simulated surface water) treatment with laboratory prepared PACl (OH/Al= 2) and a composite coagulant prepared with the incorporation of a non-ionic polyacrylamide (Magnaflock LT-20) in PACl (OH/Al = 2). This specific polymer has been used in water treatment facilities in Greece, whereas the respective Al/Si ratio (mg/L) in the final product, polymeric composite based coagulant (PACPE) was 15. The coagulation experiments were conducted using the same PE as

the flocculant aid in the case of PACl (in concentrations equal to 1/10 of PACl concentrations), whereas in the case of PACPE no flocculent aid was added. Both coagulants were efficient at removing turbidity.

There were significant differences in absorbance removal where PACPE performed much better; even with a relatively low dose of coagulants (2 mg/L), absorbance removal was over 80% with PACPE, whereas with PACl the respective removal was 70%.

Moreover, the residual concentration of Al was lower for PACPE, especially with doses of 4 and 6 mg/L. The most important advantage was related with the amount of PE used in both cases because it was noted that with 30% less PE, PACPE performed better than PACl. Not only were the two treatment steps (coagulation-flocculation) combined, better treatment was achieved with lower amounts of polyelectrolyte, pointing out not only a superior coagulation performance, but also the cost effectiveness related with the use of these new composite coagulation agents.

The improved properties of the composite coagulants with polyelectrolytes can be ascribed to their better flocculation properties compared to conventional coagulants, as was the case with PASiC.

2.4 Poly Silicate Base Coagulants

In general, a high dosage of monomeric or simple polymeric inorganic coagulants is required for wastewater treatment. Research results showed that a high dose of coagulants was required to treat the sewage. Using high doses of monomeric and simple polymeric inorganic coagulants will produce large volumes of sludge, which require high costs for their operation and disposal.

To overcome the limitations mentioned above, and increase the coagulant efficiency of the coagulant and prevent species of iron from precipitating, the following three types of materials might act as modifiers: (1) inorganic anions such as sulphates, phosphates, or silicates; (2) organic anions such as various organic acids and surfactants; (3) artificial or natural organic polyelectrolytes such as polyalcohol, polyose (Iler, 1979). The mechanism of their hydrolysis-precipitation inhibition might be attributed to their coordinate effects with iron monomers which influence the subsequent polymerisation process, or a direct combination with iron polymers to prevent further polymerisation. The main goals of adding a modifier are to increase the molecular size and to enhance the aggregating ability of the coagulant (Tang et al. 2002; Wang et.al, 2001).

Poly silicate has certain degrees of polymerization, and Fe^{+3} and Al^{+3} are all active species so they react with each other in a complex manner.

Fe^{+3} and Al^{+3} are positively charged and so this polysilicic acid has a positive charge which destabilises particles with a naturally negative charge (Ying et al. 2009). Many factors would affect the efficiency of coagulation, such as pH during coagulation, and the Si and Fe molar ratio (Ying et al., 2009; Wang et al., 2001; Moussas et al., 2008).

2.4.1 Poly Silicate Iron Coagulation

Poly silicate iron coagulant was the inorganic polymer with polysilicate as the basic structural unit, it was prepared under acidic conditions, and the mechanism of coagulation is different from the simple inorganic coagulants.

2.4.1.1 Preparation of Poly Silicate Ferric

The preparation of this reagent has two main steps as listed below:

- Preparation of poly silicate solution
- Adding the ferric salt to the poly silicate solution

Generally, a poly silicic acid (PSA) solution can be made by bringing water glass or sodium silicate solution and acid together in a zone of intense turbulence, and in such proportions that the mixture has a pH about 1.5-2. We can then understand this behaviour of PSA if we look at the stability curve of colloidal silica (Bratby, 2006; Iler, 1979).

Aqueous solutions of polysilicic acid are always unstable because even at low concentrations the polysilicic acid continues to polymerise. Nevertheless, if the silica concentration is not too high, polymerisation can be followed, and the solution can be used at a reproducible stage (Iler, 1979). Figure 2.1 shows the polymerisation of colloidal silica in a sequential order.

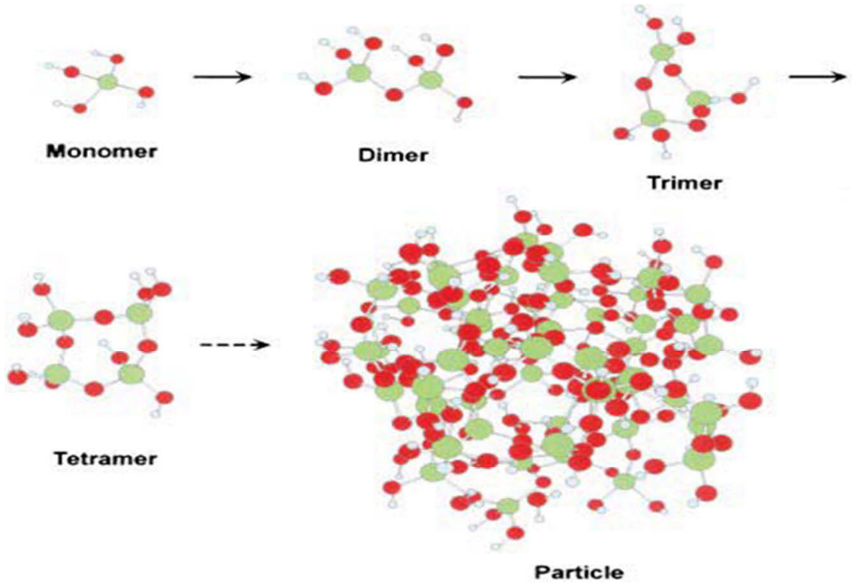


Figure.2.1 Schematic illustration of the sequential order of polymerisation of silicic acid (Iler, 1979).

Silicic acid has a strong tendency to polymerise in such a way that there is a maximum siloxane (Si-O-Si) bonds in the polymer and a minimum of uncondensed SiOH groups. Thus at the earliest stage of polymerisation, condensation quickly leads to ring structures, for example the cyclic tetramer, followed by the addition of monomer to them, and the linking together of the cyclic polymer to the three larger dimensional molecules. These condense internally into the most compact state, with SiOH groups remaining only on the outside (Figure 2.2).

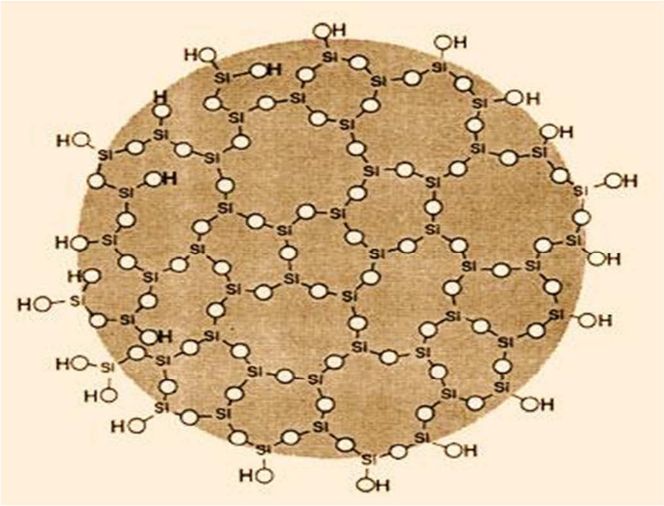


Figure 2.2 Schematic structure of silica polymer (Iler, 1979)

Additions of metal to poly silicic acid carries negative charges and consist of tetrahedrons that are linked through metal silicon-oxygen-silicon bonds, as follows (Figure 2.3).

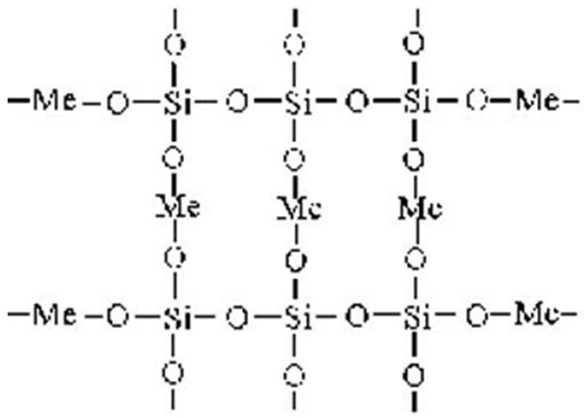


Figure 2.3 Metal in poly salicilic acid structure (Iler, 1979)

2.5 Effective Factors on Polysilicate Ferric preparation

Silica is the mystery component of the earth's crust. Its chemistry, and in particular its polymerisation and colloidal behaviour as a water treatment reagent, is not as yet understood very much, and remains to be investigated. However, it is possible to prepare a poly silicate ferric solution to use for a water coagulant, free form sodium, and high aggregation with a suitable molecular weight, by considering different factors during their preparation, as mentioned in the following sections.

2.5.1 Initial Concentration of Water Glass Solution

If the concentration of SiO_2 is more than 1% (w) such an aggregation may begin as soon as the first small particles are formed. However, at lower concentrations and acidic PH, the monomer is converted largely to discrete particles before they began to aggregate (Iler, 1979). So the initial concentration should be more than 1% (w) SiO_2; from the economic and operability points of view, the concentration should be kept between 2-3%, in order to have a clear and smooth solution of poly silicate, and it will also help to have a non-gelatine and uniform solution.

2.5.2 Level of Sodium Ion

To produce the colloidal silica dispersion, it is necessary to remove the majority of sodium ions from the polysilicate ferric polymer via ion exchange. Alexander (1956) was the first among others to follow the polymerisation of monomer in the absence of salts.

Consequently, as shown in Table 2.4 if the Na^+ is removed by the resin and a poly valiant metal such as Fe^{+3} is substituted, a more voluminous and stronger network with a lower charge and high aggregation would be formed (Iler 1979).

2.5.3 Effect of Temperature

After finalising polymerisation at a specific pH, if the solution is heated to 80-100 °C, it would grow in size and decrease the number of silica monomer (Iler, 1979).

2.5.4 Effect of Ageing

If the solution aged, the molecular weight of the silicic acid would increase, and it is generally conceded that an increase in the molecular weight on ageing is due to polymerisation (Schock et al., 1989).

2.5.5 Effect of Acid Medium on Coagulation Efficiency

Xu et al., (2009) investigated one type of acid medium of the character of PSiFe and coagulation. This investigation showed that PSiFe coagulants with different acids produced a different characterisation on stability, surface structure, microstructure, and coagulation performance.

2.5.6 Effect of pH on Polymerisation

As reported by Iler (1979), at pH 2, the number of the average molecular weight increased linearly with the square root of time. At pH 3.2 and 3.8, it increased in proportion to time. At pH 4.36 it increased linearly with the square of time, so the optimum pH for ending polymerisation was 4.36.

At higher pH (5-6), a monomer is converted rapidly to polymer particles which caused dense gelatine liquid, so that it is not possible to separate two processes, and thus controlling the process is very difficult (Iler, 1979)

2.5.7 Speed of Acidification:

Iler (1979) found that if a sample is simultaneously and instantaneously diluted and acidified, the resulting silicic acid is stable enough to permit characterisation. The problem is to ensure that acidification should be very quick hence the various silica species do not have time to polymerise as the pH is dropped from the usual region of 11-13 to 1.5-2.

Iler’s (1979) investigation showed that drop wise acidification would cause better polymerisation.

2.6 Characterisation of Poly Silicate Ferric (PSiFe)

The structure and morphology of this reagent can carried out by obtaining X-ray diffraction (XRD) and FT-infra Red spectra and Scanning Election Microscopy (SEM) microphotograph, while the destabilisation ability of the coagulant can be determined via the zeta potential measurement of the in situ product flocculation (Mouassis et al., 2008).

The most important measurement would be finding the spices by the ferron-time spectroscopy method that were reported previously (Jiang et al., 2003). The ferron reagent (8 –Hydoxy-7-iodoquinoline-5-sulphonic acid) can form complexes with single ferric ions, as well as with monomeric and dimeric species, within the reaction time of 1 min, whereas it can form complexes with medium and high MW iron polymer with increasing reaction time. The precipitated species will not react with ferron. Based on this principal, the visible absorbance at 600 nm of solution should be measured in predetermined time intervals and each absorbance would correspond to the respective concentration of ferric species.

In particular, the oligomeric (monomeric and dimeric) iron species would be determined from the absorbance reading 1 min after mixing the ferron reagent and diluted PSiF sample. The polymeric species of PSiF would be determined from the difference between readings the absorbance after 24 hours and 1 minute. The concentration of the precipitated ion was calculated by subtracting the concentration of oligomeric and polymeric species from the total concentration of iron (Zoubolis et al., 2008).

2.7 Membrane System

Membrane processes are now used in environmental, chemical, food, beverage, pharmaceutical, and various other industries for separation applications. Membrane plants applications in water and wastewater treatment as advanced physical processes for clarification and disinfection have been established and are rapidly gaining in popularity (Sethi et al., 2000). The membrane modules themselves are part of a larger system, which includes all of the operational concepts and conditions that make up a treatment system (Stauber et al., 2005).

2.7.1 Background on Membrane Treatment

Low pressure membrane systems such as microfiltration (MF) and ultrafiltration (UF) are considered to be the most reliable, cost effective, and sustainable methods in the treatment of wastewater (Fane et al., 2005). MF can be used to separate suspended solids, colloids and bacteria, and control bacterial nutrition in feed water. The UF, on the other hand, can remove viruses and some of the organic macromolecules (Pearce, 2007; Bonnélye et al., 2008).

2.7.2 History and Evolution of Membrane Treatment Processes

Micro-porous membranes were first used and patented in the 1920's (Belfort et al., 1994), although they were primarily limited to laboratory use until the 1950's. Initially, they were used for enumerating bacteria, removing micro-organisms and particles from liquid and gas streams, and fractioning and sizing macro-molecules such as proteins (MWH, 2005). In the 1950's industries began incorporating membrane filtration, primarily for the sterilisation of liquid pharmaceuticals and intravenous solutions. Membrane filtration also began to be used for industrial waste treatment in order to separate oils, fats, acids and some other impurities.

There are four main categories of membranes used in drinking water today: microfiltration (MF), ultra-filtration (UF), nano-filtration (NF) and reverse osmosis (RO). These membranes are generally classified by pore size, molecular weight cut-off (MWCO) and the applied pressure they need. Pore size is sometimes expressed as MWCO, which is a measure of the removal characteristics of a membrane in terms of atomic weight or mass, as opposed to pore size; typically measured in Daltons (AWWA, 2005). Table 2.5 and Figure 2.4 provide a concise summary of the different membrane types, as well as their applications, pore size and operating pressure:

Table 2.4: Major membrane filtration processes used in water treatment (Ratajczak, 2007)

Type	***Operating Pressure (kPa)***	***Pore size (μm)***	***Primary applications***	***Microbes removed***
MF	30-50	≥ 0.1	Removal of particles and turbidity	Algae, protozoa and most bacteria
UF	30-50	≥ 0.01	Removal of non-ionic solutes	Algae, protozoa and most bacteria
NF	500-1000	≥ 0.001	Removal of divalent ions (softening) and dissolved organic matters	Algae, protozoa, most bacteria and viruses
RO	1000-5000	≥ 0.0001	Removal of monovalent ions (desalination)	Algae, protozoa, most bacteria and viruses

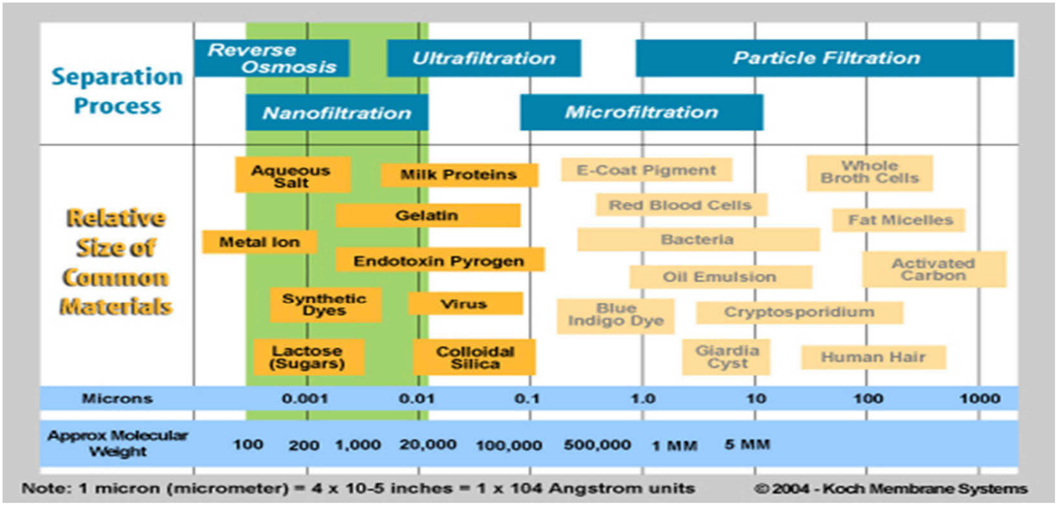


Figure 2.4 Filtration separation process range (Ratajczak, 2007)

2.7.3 Membrane Structure and Configuration

The structure of a membrane refers to the way it is constructed to optimise the surface area and reduce the degree of fouling by incoming feed water. The most common types of structures are (Schafer et al., 2005; Ratajczak, 2007):

- Spiral wound
- Hollow fibre
- Flat sheet
- Tubular/capillary

Figure 2.5 provides a summary of what the spiral wound module resembles, and highlights its most important aspects.

One of the most common structures for low pressure membranes is the spiral wound configuration' because it allows for an optimal membrane.

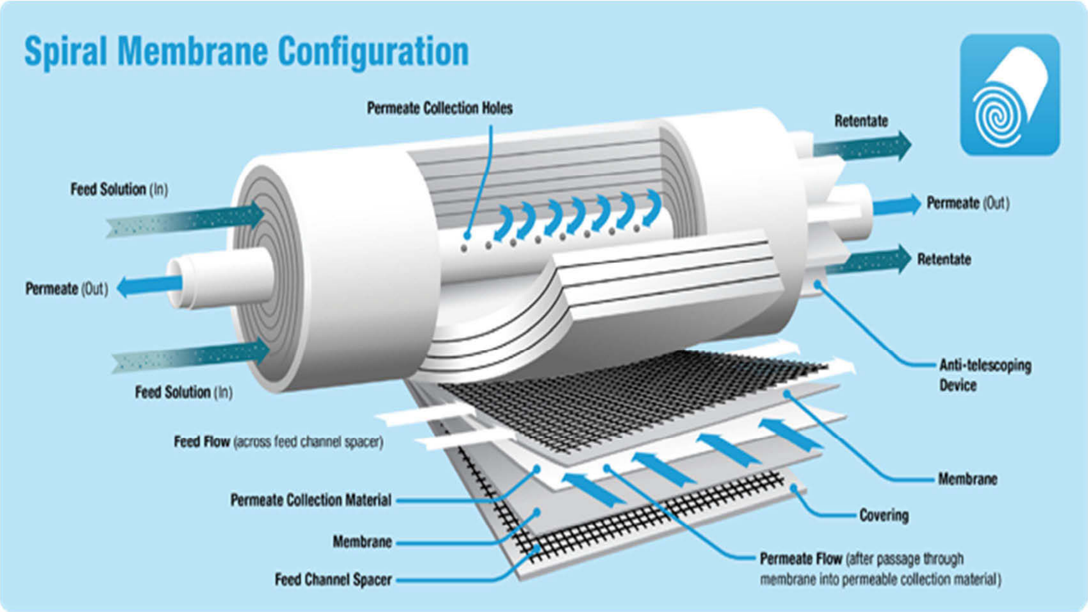


Figure 2.5 Spiral wound membrane module (www.kochmembrane.com)

The raw feed water is fed axially through the membrane module at one end, and exits in parallel at the other end. As the name depicts, the module is essentially a flat sheet membrane that is wound into a spiral shape to ensure there is enough space between the layers for the water to pass through. On this diagram one can see that the membrane support is used to ensure there is enough space between the sheets. One of the main reasons why these membrane configurations are not used on a large scale as much is because they tend to irreversibly foul. These membranes cannot generally be back flushed because of the way they are manufactured. The actual membrane modules are cast onto the interior support material so any back wash flow could potentially eliminate the membrane and expose the inner surface. For this reason these membranes rely heavily on chemical cleaning to remove any deposits from the surface, which represents a higher annual operating cost (Schafer et al., 2005; Ratajczak 2007).

Hollow fibre membranes have gained in popularity over the past decade to become the most commonly used configuration in low pressure membrane filtration (MF or UF) for water treatment (MWH, 2005). These membranes usually consist of several hundred fibres encased in a module, whether it is full scale, pilot, or bench scale. They are generally open tubes that are plug resistant and do not accumulate particles between the fibres. The diameters of the internal fibres are quite small (anywhere between 0.4 to 1.5 mm) to stop them from collapsing when exposed to high pressure (AWWA, 2005; Ratajczak, 2007). These membranes can be exposed to frequent backwash cycles, which make them an attractive module type given that fouling is the primary limitation to this technology as shown in Figure 2.6.

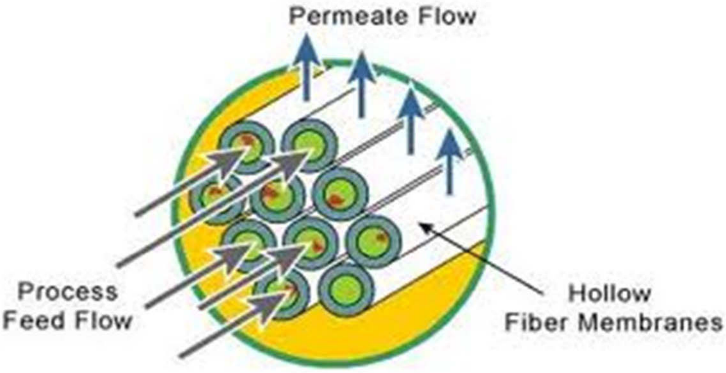


Figure 2.6 Hollow fiber membranes (Ratajczak, 2007)

Two types of flow regimes are used in practice, the first being the outside – in configuration, where the membrane is submerged into the feed water, and the untreated water is sucked in via a vacuum through the many porous fibres, where they merge and become a permeate stream.

The second configuration is the inside-out or pressure vessel configuration (Figure 2.7), where water is pumped into the membrane and filtered through the fibres and then exit into the surrounding water. The advantage of the second flow regime is that the water flows through a narrow channel, which allows for good control over module hydrodynamics. Hollow fibre membranes offer a very high specific surface area to volume ratio, because of the small inner lumens of the fibres, and therefore have the ability to treat a larger volume of water.

One of the major disadvantages of these configurations is that they are very susceptible to fouling and therefore need more backwash cycles than the spiral wound structures which cannot be backwashed at all, and are therefore much more susceptible to fouling (Lee et al., 2004). An outside-in membrane will accumulate particles on the outside surface of the membrane, which makes it easier to visually inspect the degree of fouling and much easier to backwash. The inside-out configuration will accumulate particles on the interior of the membrane module, which is a more challenging backwash and cleaning procedure. Figure 2.7 presents a schematic of a single cross flow hollow fibre membrane module:

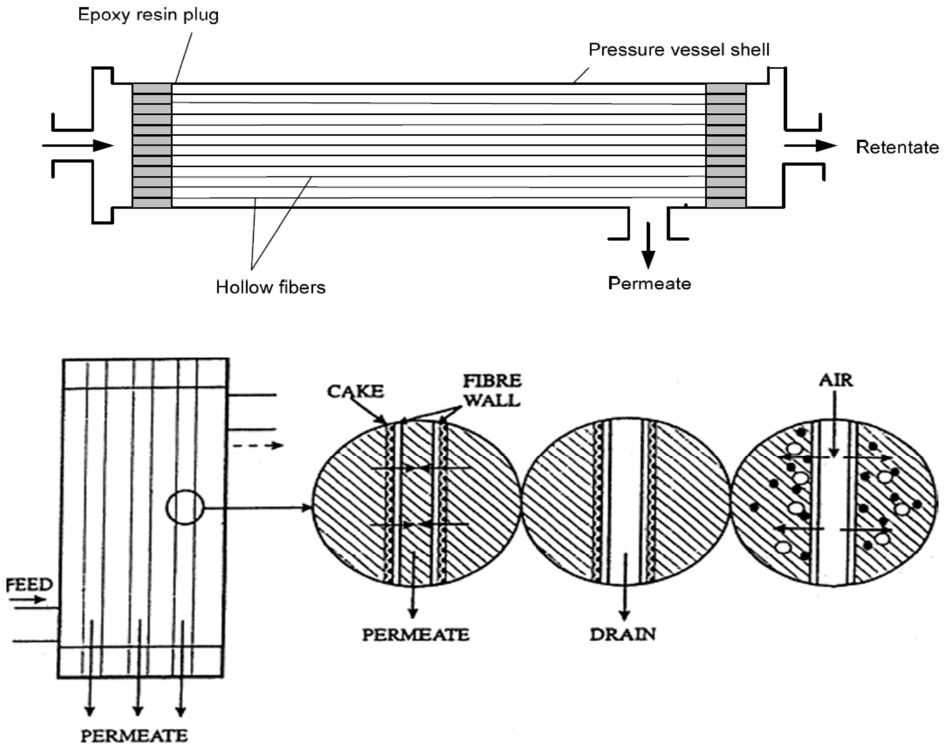


Figure 2.7 Pressure-vessel configuration of hollow fibre membrane filtration (MWH, 2005)

As Figure 2.7 shows, water enters one end of the module and is filtered through the numerous fibres, and then merges to become a permeate stream. Water that does not enter the fibres also combines to become a concentrated stream. This raises one of the few limitations to low pressure membrane systems that has not allowed for any further expansion of this technology; the concentrated stream that is generated must be disposed of accordingly because it contains a very high concentration of targeted contaminants that are being removed by the membrane.

There are four common ways of disposing of these streams: directly onto a surface water source, into domestic wastewater treatment plants, deep well injections and evaporation ponds. One of the key factors, determining which kind of disposal can be implemented, is the frequency and concentration of the chemicals used to clean the membrane modules. A concentrate that is relatively free of chemicals can generally be disposed of by discharging into large surface waters, while concentrate streams that have been discharged from membranes exposed to high frequency chemical cleaning may have to be treated further, or simply disposed of in a landfill. Another key item to note is the difference between low pressure membrane concentrate streams compared to high pressure systems like NF and RO membranes. High pressure systems often have high concentrations of dissolved solids and metal ions in the concentrate streams, which pose a threat to wildlife and habitats if disposed directly into surface waters, whereas low pressure concentrate streams are mainly composed of organic matter and micro-organisms which originate from surface waters, and therefore their disposal is less worrisome (Marcel, 2004; Ratajczak 2007).

2.7.4 Membrane Materials

Membrane performance is influenced strongly by the physical and chemical properties of the material (Ratajczak 2007; MWH, 2005). As technology is evolving, membranes are being manufactured from more sophisticated materials and with unique applications for the given source water. The most frequently used materials for membranes used in both municipal and industrial water treatment are polymer based: Cellulose acetate, acrylic, nylon, polypropylene (PP), polyamide (PA), polyamide-hydrazide (PAH), polyimide (PI), and polyethersulphone (PES). Ceramics and zirconia based materials have also gained popularity, but have not as popular as the polymer based modules. The most common polymer based materials are PA, PAH and PI's (Panglisch et al., 2000). It is difficult to identify individual applications for each membrane material because it can vary tremendously based on factors that are specific to any membrane system. Most consumer systems use cellulose acetate or nylon materials wound in a tubular cartridge. In general, cellulose acetate membranes are used with municipal water which has been disinfected with chlorine, while nylon membranes are preferred in systems that use well water. A chlorine based city water supply requires a different membrane than rural hard water well based supply because the chemical chlorine will destroy the nylon membrane (Gangloff, 2000).

Polymeric materials will continue to prosper due to their flexibility, permeability, and ability to be formed into a variety of filter components (Gangloff, 2000). However, specialty membrane materials such as ceramic and composite constructions have the potential to experience rapid growth, although on a much smaller scale, due to their higher unit cost and performance in extreme environmental applications.

Polymers are almost ideal membrane materials because they can be easily produced with pores of almost any size and are flexible enough to be configured into a wide range of constructions, including flat sheets and hollow fibre cartridge materials (Klijn et al., 2000). However, there are several drawbacks to polymer membranes; the one that stands out most is the tendency towards fouling and clogging as the result of contamination from biological growth. Nevertheless, the advantages of polymers, coupled with the growing use of cross flow designs which minimise clogging by directing fluids toward the membrane at an angle, will ensure that for the vast majority of applications, polymers will remain the material of choice for years to come.

Ceramics are another popular membrane material in the treatment of potable water, as shown in Figure 2.8. Ceramic membranes also have drawbacks such as brittleness, increased size, and higher cost on a square foot basis. These membrane types will remain limited to specific applications that require the performance characteristics offered by ceramics such as thermal stability, abrasion resistance, durability, and bacterial resistance (Gangloff, 2000).

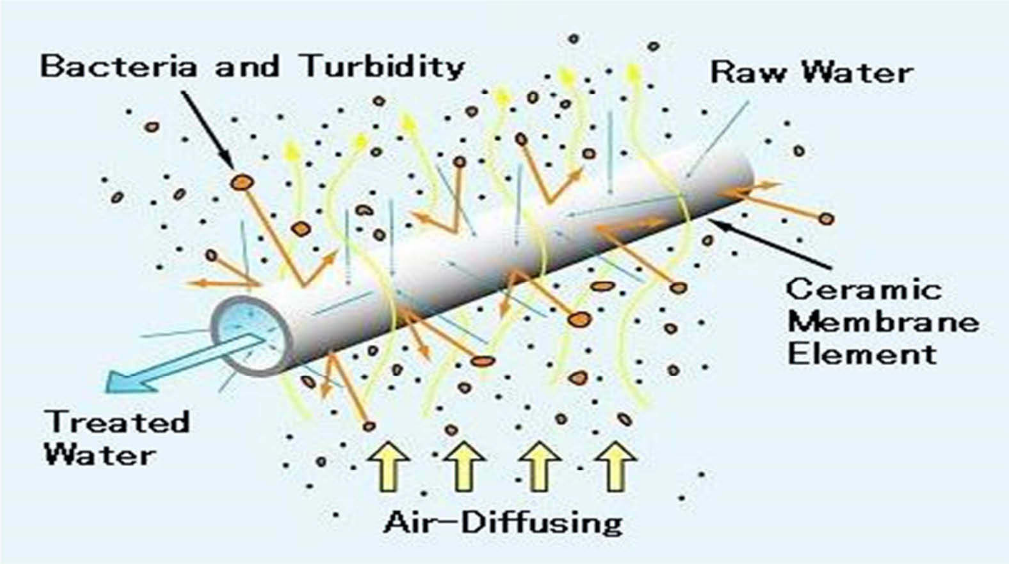


Figure 2.8 Ceramic membrane element (Ratajczak, 2007)

Ceramics can also be placed in dry storage, whereas polymer based membranes must be submerged in water to avoid damaging the material. However, new applications for ceramic membranes have been observed over the last decade, resulting in a more widely accepted usage, and subsequently leading to above average growth (Bottino et al., 2001). Ceramics will also benefit from the growing trend toward composite membranes, which combine ceramic and polymeric membranes into a single system with the advantages of both types. In the end, the advances made to ceramic and composite membranes will prolong the life spans of membranes and slow the growth in replacement sales (Gangloff, 2000).

2.7.5 Membrane Cleaning

Modular membranes are challenged during the treatment of contaminated water. It is crucial to the life of a membrane that is well maintained and cleaned otherwise it must be replaced, representing a substantial cost to the overall process. There are several ways that a membrane can be maintained in its best working order, mainly by pre-treatment, air-sparging, backwashing, and chemical cleaning (Ratajczak, 2007).

The pre-treatment of membranes has received a great deal of attention over the past decade because it is considered to have a great deal of potential in reducing the degree of fouling on the surface and inside the pores. This process entails exposing the incoming feed water to a different treatment method before the water enters the membrane module. Research has been conducted using pre-treatments such as coagulation, bio-filtration, advanced oxidation, pH adjustment, chlorination, activated carbon, and other complexing agents (Kimura et al., 2005).

Low pressure membranes have been used as pre-treatment techniques for other technologies such as NF and RO system. Such is the case for the pre-treatment of wastewater prior to RO, which has become a more common practice (Vial et al., 2002).

When using membranes, surface waters require more pre-treatment than ground waters because they have concentrations of elevated organic carbon and turbidity. Backwashing the membrane can increase its durability and remove cake from the surface that develops during the filtration cycle" (MWH, 2005). The term backwashing implies that the flow of water is reversed, and instead of raw water being pushed through the membrane, clean water is pushed in the opposite direction. Most low pressure membrane systems are set up with automatic backwash cycles, with frequencies every 30-90 min (MWH, 2005). Backwashing targets the particles that have caused reversible fouling on the surface, flushing them away to increase the permeate flux. Air sparging is another cleaning technique that is generally used in combination with the backwash cycle. This process involves pumping a constant flow of pressurised air through the membrane module which exits into the surrounding water in the form of gas bubbles. The objective of air sparging is to facilitate scour material off the surface of the membrane, and in doing so reduce the amount of particles that remain on the surface during the permeate cycle.

Backwashing coupled with air sparging would be conducted based on a set point such as time or a key performance variable such as the rate of TMP increase over time. For example, a system could be set to permeate for 40 min and then conduct a backwash/air sparging cycle before returning to the filtration mode. It could also be set to conduct a backwash every other cycle, and air sparging every cycle. Some systems are set up to trigger the backwash cycle once the TMP hits a specified maximum value. The frequency of backwash is heavily dependent on the quality of the incoming water, for instance a raw water with a high concentration of total suspended solids (TSS) will need more frequent backwashes than a raw lake water which has lower concentrations of TSS (MWH, 2005; AWWA, 2005).

Chemical cleaning is used to target the contaminants that cause the membrane to be fouled irreversibly. The frequency of chemical cleaning is different from backwashing because it varies from a few days to several months, depending on the characteristics of the membrane and the quality of the source water. When foulants can no longer be removed from the surface of the membrane by backwashing, chemical cleaning is required. This procedure typically takes several hours and involves circulating preheated cleaning solutions throughout the membrane modules, then draining the system several times and repeating. Large volumes of solution are often heated to temperatures up to 60 ºC, requiring a tremendous amount of energy, which translates into a high cost (MWH, 2005). A variety of agents can be used to chemically clean low pressure membranes: detergents, acids, bases, oxidising agents, sequestering agents, and enzymes (AWWA, 2005). Chlorine can also be used in doses ranging from 2 to 2000 mg/L; this is in addition to acting as an oxidant capable of disinfection.

It is difficult to accurately quantify the frequency of chemical cleaning needed for a given membrane system because it depends on a number of factors such as the concentration of contaminants, the volume of water treated, and required quality of effluent. Van Paasen et al. (1998), compared the frequency of chemically cleaning surface water vs. ground water treatment plants, and concluded that membranes that treat groundwater require bi-annual chemical cleaning, while surface water requires chemical cleaning 4-5 times a year. The following section provides detail of the membrane fouling phenomenon, which will help tie together the reasoning for backwashing and chemical cleaning.

2.7.6 Membrane Fouling

Fouling is the aspect of low pressure membrane systems that is receiving the most attention in water research today. It represents a very large fraction of the annual cost of a membrane system because it substantially increases the cost of a process by increasing energy requirements and frequency of replacement. One of the least understood aspects of fouling is how natural organic matter (NOM) affects the surfaces of a membrane.

The main limitation to the use of membranes in wastewater treatment is the high energy consumption that can mainly be attributed to membrane fouling, which causes the pumping action to work harder to maintain a constant flux (Kimura et al., 2005). Membrane fouling is the process by which the permeate flux through the membrane is reduced as a result of particles accumulating on the surface, forming a cake layer, or the adsorption of particles (both suspended particles and dissolved material) inside the pores of the membrane (AWWA, 2005; Ratajczak, 2007).

Preventing membranes from fouling has received a great deal of attention from water treatment research experts, as many situations show that there is no clear distinction as to whether it is the dissolved or suspended particles that contribute most to fouling. Howe and Clark (2002) concluded that more fouling occurs in the presence of small colloidal matter, ranging from about 3-20 nm in diameter. Their findings showed that the majority of dissolved organic matter (DOM) by itself does not cause fouling, but rather the actual foulant is a relatively small fraction of bulk DOM. Combe et al. (1999) found that NOM adsorbs both inside pores and on the surface, forming a gel layer which thickens over time and reduces the overall flux across the surface of the membrane.

Membrane fouling can be divided into reversible and irreversible fouling. As mentioned previously, reversible fouling can be restored by backwash cycles, while irreversible fouling requires chemical cleaning. There are four major types of fouling mechanisms that affect wastewater membranes:

- Organic fouling
- Bio-fouling
- Scaling
- Colloidal/Particulate fouling

Organic fouling is caused by dissolved and suspended particles that adsorb inside the pores and on the surface of the membrane.

Membrane scaling is the consequence of the concentration of a given water source’s solids exceeding its solubility limit, resulting in the solids precipitating on the membrane. This occurs when the concentration of the given species is too high at the surface, causing it to come out of solution and deposit itself onto the surface of the membrane. Precipitated inorganic compounds can act as scalants, which can reduce the flux, damage the surface, and cause irreversible pore blocking. When particles block the pores of the membrane, the higher concentration of dissolved molecules yield higher osmotic pressure, a higher tendency of the suspended solids to coagulate and coat the surface, and a higher likelihood of pore plugging (scaling) to occur (AWWA, 2005).

2.8 Fouling Potential of Water

It is necessary to establish a reliable method to measure and predict the potential for particulate fouling of feed water to membrane filtration systems (Boerlage et al., 2003). It can be used at the design stage to assess the pre-treatment required and to monitor the effectiveness and performance of a pre-treatment system while a plant is operating.

The silt density index (SDI) and the modified fouling index (MFI) are the most widely applied methods. Initially, a micro-filter (0.45µm) (UF-MFI) was used to evaluate the particulate fouling potential but Moueddeb et al. (1996) showed the limits of the MF-MFI for seawater. Boerlage et al. (2003) introduced the UF-MFI test as a water quality monitor which can be used to measure the fouling potential of a single given feed water type, and register a change in the quality of feedwater before the membrane has been installed.

2.9 Pre-treatment Process to Reduce Fouling in a Membrane

2.9.1 General Description

Wastewater pre-treatment is an integral part of every water treatment plant. Pre-treatment removes particulates, debris, micro-organisms, suspended solids, and silt from the seawater. Ideally, the only solids left in the seawater after pre-treatment would be the dissolved minerals. If the wastewater treatment system is operated in a manner that stops minerals from precipitating on the surface of the membrane, the membranes could operate without any cleaning for a very long time. Fouling can be averted by periodically cleaning the membrane, but in some cases the fouling could be irreversible and cleaning may not recover productivity, in which case some or all the membranes would need to be replaced. A pre-treatment strategy is therefore necessary to ensure that the feed water will not cause excessive fouling on the surface of the membrane. The main disadvantages of conventional pretreatment such as flocculation, deep bed filtration, and cartridge filter, are the intensive consumption of chemicals and inconsistency in operation (Teng et al., 2002). For example, Chua et al. (2003) reported that the quality of the filtrate produced by the deep bed filter was inferior and highly inconsistent. Leparc et al. (2007) discovered that dual media filters and cartridge filters did not reduce the content of fouling. Advanced pre-treatments such as microfiltration (MF) and ultrafiltration (UF) have recently become more important due to the negligible amounts of chemicals used. They are also operationally stable compared to conventional pretreatment.

2.9.2 Coagulation/Flocculation

Coagulation (neutralisation of the particles' charge) and destabilised particle aggregation occur during flocculation. Moreover, aggregates produced under sweep floc conditions were more compressible than for charge neutralisation conditions, resulting in compaction when the membrane filtration system was pressurised (Anthlmi et al., 2001; Cabane et al., 2002; Choi and Dempsey, 2004). Lee et al. (2000) reported that the specific resistance was smaller with charge neutralisation than with sweep floc due to the formation of less compressible and more porous cake former. Lee et al. (2000) also reported that the coagulated suspension under either charge neutralisation or sweep floc conditions showed a similar steady state flux under the cross flow microfiltration mode.

Flocculation achieves three objectives: firstly, it eliminates the penetration of colloidal particles into the pores of the membrane, secondly, it increases the critical flux, and thirdly, it modifies the characteristics of the deposit (Mietton and Ben aim, 1992; Teng et al., 2003). Conventional coagulation produced larger particles which reduced fouling during membrane filtration by reducing adsorption in the pores of the membrane, increasing cake porosity, and increasing the transport of foulants away from the surface of the membrane (Hwang and Liu, 2002). Bian et al. (1997, 1999) suggested that a combination of high flux and good water quality were achieved when a lower dose of coagulant was used prior to membrane filtration (Jeong, 2013).

Despite the high contaminants in wastewater, particles of a colloidal nature do not tend to coagulate and settle. There is enough surface-active organic matter to be adsorbed on the surface of the particles, thus keeping particles discrete. So far coagulation/flocculation combined with dual-media filtration is the most common pre-treatment in the membrane plant. Traditionally, filtration was used as a pre-treatment for the removal of particulate matter from seawater. Most plants utilise either in-line (contact) coagulation or conventional clarification as a means of destabilisation prior to the filtration step. The use of an efficient in-line flocculation strategy leads to compact treatment plant designs compared to conventional systems. In-line flocculation was found to have similar removal efficiencies at significantly shorter hydraulic retention times (HRT) compared to conventional flocculation. For either method, preliminary testing of flocculants is highly recommended (Adin et al., 1986).

2.9.3 Adsorption

Adsorption is another physico-chemical pretreatment method that can remove dissolved organic matter and reduce membrane fouling. The addition of adsorbent (such as powder activated carbon; PAC) behaved in various ways in a bulk solution, within the membrane module, or near the surface. Carbon particles can react with natural organic matter (NOM) or metals in the bulk solution. In addition, PAC forms a cake layer combined with colloids, metals, and NOM, providing an adsorption zone for further removal of NOM or a hydraulic resistance layer to permeation. Thus, the probable PAC reaction and the newly formed cake layer within the integrated membrane system are likely to improve the performance of the integrated membrane with PAC adsorption (Oh et al., 2006; Ye et al., 2010).

Suzuki et al. (1998) found that in hybrid membrane adsorption system, a large portion of organics, mainly humic substances, with a size smaller than the micro-pores in the MF membranes were absorbed by PAC, which was then completely separated by the membranes. Moreover, a decline in the permeability of the membrane was slower in this system, which may have resulted from the reduction of the organic loading to the membrane due to the adsorption of organics on PAC prior to their contact with the membrane. Fouling of membranes by NOM was further complicated by the presence of PAC particles. Although the removal of NOM was enhanced by the addition of PAC during the membrane process (Adham et al., 1991, 1993; Jacangelo et al., 1995), the presence of PAC increased the fouling problem and flux declined, as reported by some researchers (Lin et al., 1999; Carroll et al., 2000; Han et al., 2002), but it was reported to prevent the decline of flux by others (Lin et al., 1999). Overall, the importance of PAC in flux enhancement was due to a physical scouring of the surface of the membrane, lowering of specific cake resistance, or adsorption of fine colloids and dissolved organics.

The removal of PAC adsorbed organics from seawater was enhanced by a combination of adsorption and coagulation. The additional advantage of such a process is a greater effectiveness in removing humic acids compared to adsorption conducted without coagulation. The PAC added to the treated solution acts as an adsorbent for organics and also enhances the settlement of the flocs formed (Tomaszewska et al., 2004).

Conventional pretreatment technologies such as coagulation, deep bed filtration, dissolved air flotation and low pressure membrane based pretreatment methods such as ultrafiltration and microfiltration can be used according to the characteristics of the wastewater (suspended solids, turbidity, organic matters, etc.) (Bonnelye et al., 2004).

The pre- coagulation of membranes has received a great deal of attention over the past decade because it is considered to have a great deal of potential in reducing the degree of fouling on the surface and inside the pores of membranes. This process entails exposing the incoming feed water to a different treatment method prior to the water entering the membrane module. Research has been conducted using several pre-treatments, such as coagulation, bio-filtration, advanced oxidation, pH adjustment, chlorination, activated carbon and other complexing agents (Kimura et al., 2005).

2.10. Hybrid System to Control the Membrane Fouling

Low pressure driven membrane processes such as microfiltration (MF) and ultrafiltration (UF), are excellent techniques for eliminating or removing suspended solids so that colloidal particulate fouling is alleviated. Energy consumption in MF is relatively low. MF generally provides good quality feed water for RO compared to untreated seawater. Further improvements can be obtained by using UF where micro-organisms, macro-molecules and colloids can also be removed. Due to higher applied pressure, UF is more expensive than MF but it is still competitive with conventional pre-treatment. On the other hand the UF permeate used as RO feed significantly improved the performance of

RO. Recent studies proved that hybrid membrane processes (coupling coagulation/flocculation and/or adsorption and/or ion exchange resins with membranes) are efficient at simultaneously reducing membrane fouling and improving the water quality (Chinu et al., 2010; Guo et al., 2008; Shon et al., 2005).

2.10.1 Coagulation Membrane Hybrid System

In recent years, coagulation and subsequent media-filtration, as well as low pressure membrane based system such as microfiltration (MF) and ultrafiltration (UF) have been used as pretreatment methods for wastewater treatment.

Coagulation can remove colloidal matters and dissolved organic compounds which cause irreversible membrane fouling. Since membrane performance strongly depends on the quality of the wastewater, pre-treatment is generally required (Sutzkover et al., 2010). In other words, feed water with a consistent high quality is important for a successful membrane operation. A poor quality of feed water may shorten the membrane operation period and increase the cost of maintenance. It is therefore essential to remove or reduce undesirable materials in wastewater to acceptable levels prior to feeding it into the membrane (Bonnelye et al., 2004).

The addition of coagulant before the membrane reactor is often called the submerged membrane coagulation hybrid system (SMCHS).

Coagulation improves the filtration characteristics by reducing resistance of the deposit on the membrane (Cho et al., 2006). One of the expected benefits of the membrane process is a reduced demand for coagulant. Removal in membrane filtration differs from those in conventional technologies, ultimately affecting the doses of coagulant, points of application, and type of coagulant applied, etc. The combination of coagulation, flocculation, and membrane filtration is also an efficient and reliable treatment option for surface waters with high NOM concentrations at relatively low concentrations of coagulant because it enables operations under optimal pH conditions (Guigui et al., 2002).

More efficient virus retention can potentially be expected when coagulation/flocculation is combined with membrane filtration where microbes are adsorbed to or included in larger flocs that are retained by the membrane (Guo et al., 2008).

2.10.2 Powdered Activated Carbon (PAC) Membrane Hybrid System

Powdered activated carbon (PAC) adsorption has been widely applied as a pre-treatment method to assist low pressure driven membrane filtration processes such as MF to remove dissolved organic solutes from polluted water. In submerged membrane systems, air bubbles are injected into the tank to provide mixing and introduce shear at the surface of the membrane and prevent the deposition of particles. In this hybrid system the organics are adsorbed onto the PAC, and the organic laden PAC is eventually separated by the membrane (Guo et al., 2004, Jeong 2013).

The submerged membrane adsorption hybrid system (SMAHS) has many advantages when it is operated on a long term basis. PAC initially acts as an adsorbent. After the growth of micro-organisms on the PAC surface, the organic would be bio-degraded by the micro-organisms and thus the PAC can be used for a long time (Guo et al., 2008). The membrane is also free from fouling (or very little fouling) and thus can be used for a long time without cleaning. The submerged membranes do not become clogged as almost all organics are removed by the PAC and the role of the membrane is only to retain the PAC and other suspended solids.

The pre-adsorption of organics onto the PAC could help to reduce membrane fouling and maintain a consistent permeate flux. The PAC replacement in a submerged membrane adsorption bio-reactor (SMABR) could stimulate both biological activity and adsorption, as well as optimise the operation of the hybrid system. Gao et al. (2007) reported that with PAC replacement, the organic removal efficiency of the system was more than 90%.

2.11. Summary

According to the literature survey portrayed in this chapter, the implementation of several modifications on the preparation of polysilicate ferric can be a new investigation in this area of research to have a high aggregated polymer with a minimum level of sodium ion in the coagulation process in wastewater treatment.

The effect of the modified polysilicate ferric in a hybrid system process, including coagulation and membrane filtration can be another area of investigation to determine the performance of an efficient coagulant on reduction of membrane fouling and increasing the durability of the membrane performance in wastewater treatment systems.

Chapter 3

Materials and Methods

3. Materials and Methods

3.1 Introduction

The experimental procedures commenced with the preparation of poly silicate ferric (PSiFe) that included several improvements over the existing preparatory methods. The coagulant agent was prepared with different Si/Fe ratios to find the optimum ratio for water treatment processes. The selected coagulant was characterised by physical tests such as scanning electron microscopy (SEM) and X-ray diffraction (XRD).

After the preparation and characterisation stage, several experiments were carried out to assess how effectively this modified coagulant was in water treatment processes. These experiments began with a jar test in wastewater and raw water, from which the turbidity, total organic carbon

(TOC), ultra violet at a wavelength of 2,537 angstrom or 254 nm (UV_{254}), zeta-potential, phosphate, and the nitrates were measured. Furthermore an array of tests based on the membrane fouling index (MFI) was conducted to qualify the tendency for fouling. Finally, the optimum dose of silicate to the ferric ratio of the coagulant in a hybrid system was selected, which included a coagulation-flocculation system joining with a submerged hollow fibre membrane.

The sequential experimental program of this research is summarised as follows:

- Improvement in the preparation method of poly silicate ferric (PSiFe), while considering various factors, influencing the coagulation process
- Characterisation of the PSiFe
- Investigating the performance of PSiFe-γ on kaolin based wastewater
- Examining the performance of PSiFe on phosphate/nitrate removal in raw water
- Determination of the coagulation efficiency of the modified PSiFe in jar tests
- Using the modified PSiFe as a coagulant in the hybrid system of the coagulation and hollow fibre membrane filtration
- Comparing the performance of the newly modified coagulant (PSiFe-γ) with other coagulants

3.2 Material

3.2.1 Raw materials for Preparing the Coagulant

To prepare the polysilicate ferric (PSiFe) and jar tests, different materials and chemicals were used, as shown in Table 3.1. Sodium silicate, hydrochloric acid, and ferric chloride were the main materials used to prepare poly silicate ferric, and ferric chloride, sodium bicarbonate, and kaolin were used as raw materials for the jar tests.

Table 3.1 Raw materials for preparing poly silicate ferric and jar tests

Material	**Specification**
Ferric Chloride	1 M
Sodium Silicate	26% (w) SiO_2
Demineralised Water	0.1 µs/cm
Sodium Bicarbonate	1 M
Kaolin Clay	30 g/L
Hydrochloric Acid	30% (w/w)

3.2.2 Wastewater Source

The compounds and characteristics of the synthetic wastewater (SWW) used in this study, and shown in Table 3.2, represent a biologically treated sewage effluent in a wastewater treatment plant. All compounds were dissolved in one litre of distilled water. Tannic acid, sodium lignin sulfonate, sodium lauryle sulfate, peptone and poly sacharide (Arabic acid) contributed to the large MW size organic matter, while the natural organic matter (NOM) from tap water, peptone, beef extract, and humic acid consisted of the small MW organic matter.(Shon et al., 2005)

The synthetic wastewater (SWW) consisted of organic and inorganic compounds, including easily bio-degradable matter, as well as some persistent organics such as humic acid, tannic acid, lignin, and poly saccharides (Seo et al., 1997). The total organic carbon (TOC) of the synthetic wastewater was approximately 10-12 mg/l. The molecular weight distribution (MWD) ranged from 290 up to 34,100 Dalton with the highest fraction at 940-1200 Daltons. (Shon et al., 2005)

Table 3.2 Components and characteristics of synthetic wastewater (Shon et. al., 2005)

Component Name	**Concentration (mg/l)**	**MW(Dalton)**	**Fraction by DOC***
Beef Extract	**1.8**	298, 145, 65	0.065
Peptone	**2.7**	34265,128,80	0.138
Humic Acid	**4.2**	1543,298	0.082
Tannic Acid	**4.2**	6,343	0.237
Sodium Lignin	**2.4**	12,120	0.067
Sodium Lauryl	**0.94**	34,265	0.042
Acacia gum	**4.7**	925,256	0.213
Arabic Acid(Poly	**5**	38,935	0.156
$(NH_4)_2SO_2$	**7.1**	---------	------
KH_2PO_4	**7**	---------	----
NH_4 HCO_3	**19.8**	---------	----
$MgSO_4$ .3H2O	**0.71**	---------	-----

***DOC: Dissolved organic carbon**

3.2.3 Hollow Fiber Membrane

The membrane module used in this study was a poly ethylene hydrophilic membrane (Mitsubishi-Rayon, Tokyo). The surface configuration and structure of the membrane are shown in Figures 3.1 and 3.2.

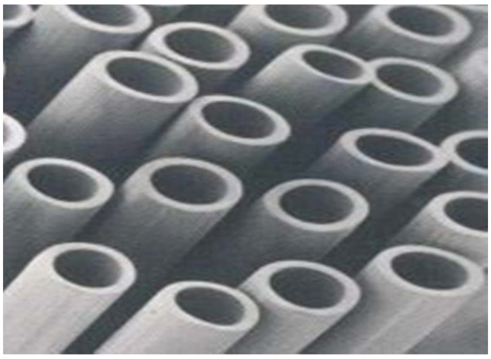


Figure 3.1 Micro-porous of fibre membrane (Mitubishi membrane, 2013)

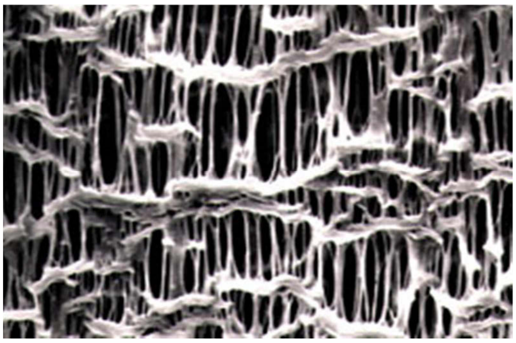


Figure 3.2 Membrane surface structure (Mitubishi membrane, 2013)

The detailed specifications of the membrane provided by the manufacturer are presented in Table 3.3.

Table 3.3 Characteristics of the hollow fiber membrane module (Mitsubishi, 2013)

Specification	Description
Material	Hydrophilic polyethylene
Nominal pore size	0.1 µm
Outer diameter	0.41 mm
Inner diameter	0.27 mm
Number of fibre	320 (16*20)
Length of fibre	12 cm
Surface area	0.1 m^2
Membrane packing density	9858 m^2/m^3
Membrane manufacturer	Mitsubishi-Rayon, Tokyo

3.2.3.1 Hydrophilic Properties of the Membrane Surface

The membrane surfaces and the micro fibre are covered with a special hydrophilic polymer (Figure 3.3)that does not dissolve in water, which means the hollow fibre is permanently hydrophilic or wettable in water. Water can flow through the hollow fibre membrane quite easily although it does not retain any liquid.

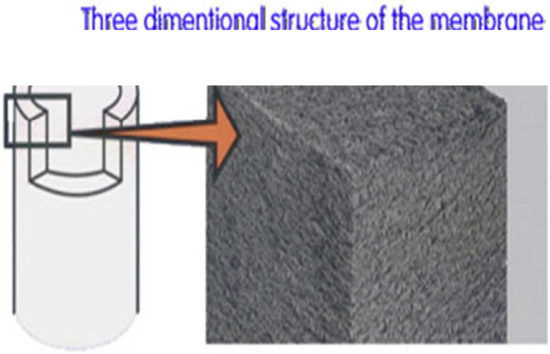


Figure 3.3 Three dimensional surface structure of the membrane

(Mitubishi membrane, 2013)

3.3 Experimental Apparatus and Equipment

3.3.1 Jar Test Apparatus (Coagulation Experiment)

A jar test is a simple device that is used to determine the required optimum coagulant dose. The device consists of 6 jars or beakers with a single stirrer and with paddle in each, as shown in Figure3.4, samples were placed in the jars or beakers, and different doses of coagulant were added simultaneously. The paddles were rotated at high speed and slow mixing in the flocculator. After the fluid settled for a few minutes, the supernatant was removed from the jars to measure their characteristics.

The most improved dose was then selected as the optimum dose of coagulant.

Figure 3.4 Photo of jar testing apparatus

3.3.1.2 Purpose

This experiment is the best way to compare how efficiently different coagulants coagulate in the treatment of wastewater.

3.3.1.3 Materials

The materials used for this test include:

- Six place gang stirrer with an rpm indicator
- Six beakers (preferably with a capacity of one litre)
- Volumetric and graduated glassware for preparing the coagulant solution
- Pipette
- A stopwatch or interval timer with seconds or fractional minutes

The analytical equipment used to verify the tests include; pH, TOC, turbidity, UV_{254}, zeta-potential.

3.3.2 Hybrid Membrane- Flocculation Bench Scale Apparatus

The first step of this phase of the research was to determine the configuration of the bench scale membrane treatment system. This arrangement included several vessels, coagulation injection pumps, a flocculator, a submerged hollow fibre membrane vessel, three transferring pumps, three different size vessels and a pressure indicator. Two branches of air from the main air header were directed to the membrane and the floccuator to ensure that the coagulant is properly mixed in the flocculator and to improve the membrane treatment process, as shown in Figure 3.5.

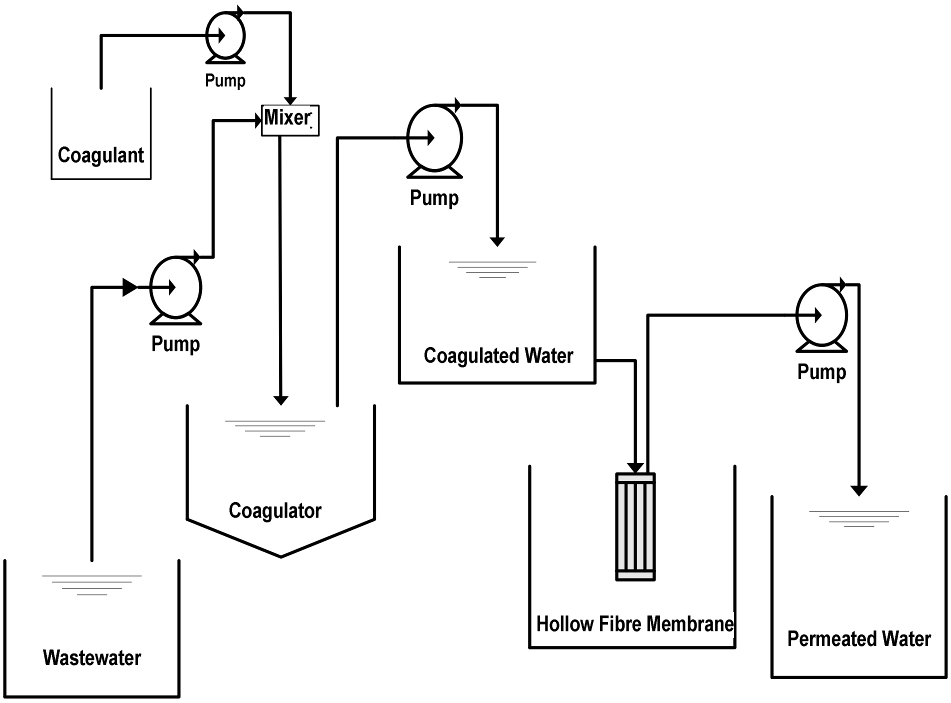


Figure 3.5 Process flow diagram of the coagulation-membrane filtration hybrid system

3.3.3 Analytical Device and Instruments

3.3.3.1 SEM and X-Ray Machine

X-ray diffraction (XRD) patterns generated with an MDI Jade 5.0 (Rigaku, Materials Data Inc., USA), were used to determine the structures of the particles. Here, samples were placed in a holder auto-sampler, and then the diffraction angles (2θ) were measured between 0 and 90° to detect the peaks in the synthesised poly ferric silicate samples.

A scanning electron microscope/energy dispersive using X-Ray (SEM/EDX, Rigaku, Japan) was used to determine the shape of the particles and the elemental composition of the Poly Silicate particles.

3.3.3.2 Dissolved Organic Carbon (DOC) and UV Absorbance

Dissolved organic carbon (DOC) concentrations were measured with a Multi N/C 2000 analyser (Analytical Jena AG, Japan) equipped with an auto sampler. The total organic carbon (TOC) analyser measured the gaseous carbon dioxide (CO_2) that formed an oxidised organic carbon and an acidified inorganic carbon. Once the CO_2 gas was formed, it was measured by a non-dispersive infrared (NDIR) cell detector. All of the samples were filtered through a 0.45 µm filter prior to the TOC measurement, which means that the TOC values were, in fact, DOC values.

The DOC of initial and flocculated SWW was analysed with a TOC analyser. The TOC standard solutions were prepared from a potassium hydrogen Phosphate solution, and a standard calibration curve was also prepared. The inorganic carbon(IC) and total carbon (TC) were measured with the TOC analyser, and then the DOC was computed from the difference between TC and IC. The calibration curve was in- built (calibrated regularly) and the TOC value was computed directly by the instrument. Acidified samples ($H_3 PO_4$) were placed in an auto-sampler and results were obtained. This procedure has been detailed by Jeong et al., 2013.

3.3.3.3UV Meter

The UV-absorbance of the initial and flocculated SWW was monitored by measuring the absorbance with a UV-vis spectrophotometer (N 595, Shimadzu, Kyoto, Japan) in a 1 cm quartz cell at λ of 254 nm. The data was generated using computer software provided by Shimadzu Scientific Instruments Pty Ltd (Figure3.6). The UV-vis spectrophotometer was calibrated using Mili-Q water. The samples were filtered by 0.45 µm membrane, and then each sample was placed in a standard square 1 cm quartz cell and inserted in the cell holder of the UV-vis spectrophotometer. A calibration curve was plotted for the initial concentration of pollutant and the analogous absorbance data, and then the obtained equation was used to calculate the concentration of pollutant at any absorbance dada taken. This procedure has been stated previously by Jeong et al., 2013

Figure3.6. UV-vis spectrophotometer (N 595, Shimadzu, Kyoto)

3.3.3.4 Turbidity

A turbidity meter (2100N HACH, USA) and a pH meter (TPS 90FLMV) were used to measure the turbidity and the pH of the initial and flocculated SWW, respectively (Figure 3.7). Two pH buffer solutions were used to calibrate the instrument (pH = 6.88, TPS 121380 and pH = 4, TPS 121382 solutions).

Figure3.7 Turbidity meter (2100N HACH)

3.3.3.5 Pressure Gauge for Transmembrane Pressure (TMP)

Trans-membrane pressure (TMP) is a physical operational factor that is the difference between the inlet and outlet membrane pressures. This factor was measured by a pressure gauge device. The scale was kPa and it was located at the outlet water from membrane. Since the inlet pressure is atmospheric, the pressure gauge shows the drop in pressure across the membrane as kPa.

3.3.3.6 Zeta Potential

The zeta potential of the supernatants was measured with a Zetasizer Nano Series-Zs Malvern, UK as shown in Figure 3.8. Particles in a colloidal suspension or emulsion usually carry an electrical charge, which may arise in a number of ways, and is more often negative than positive. The zeta potential is the overall charge that a particle acquires in a specific medium. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If all particles have a large negative or positive zeta potential they will repel each other, and then a dispersion stability condition will be present. If the particles have low zeta potential values then there is no force to prevent the particles coming towards each other and hence there will be an unstable dispersion.

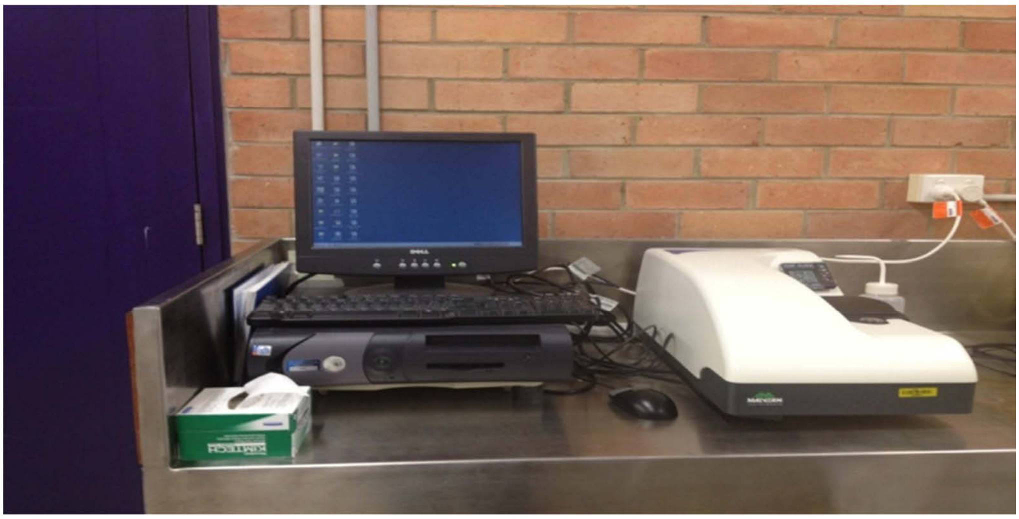


Figure 3.8 Zetasizer Nano Series-Zs Malvern, UK

3.3.3.7 Modified Fouling Index (MFI)

The modified fouling index (MFI) was established by Schippers and Verdouw (1980) to evaluate membrane fouling mechanism. A schematic diagram of the MFI experimental set up is shown in Figure 3.9. The MFI was determined at standard reference values of 207±3 kPa trans-membrane pressure (TMP), a feed water temperature of 20 °C and an ultra-filter (UF) with a 47 mm diameter and molecular cut-off of 17.5 kDa. The modified fouling index (UF-MFI) can indicate whether pre-treatment could reduce the fouling potential of the membrane (Jeong et al., 2013)

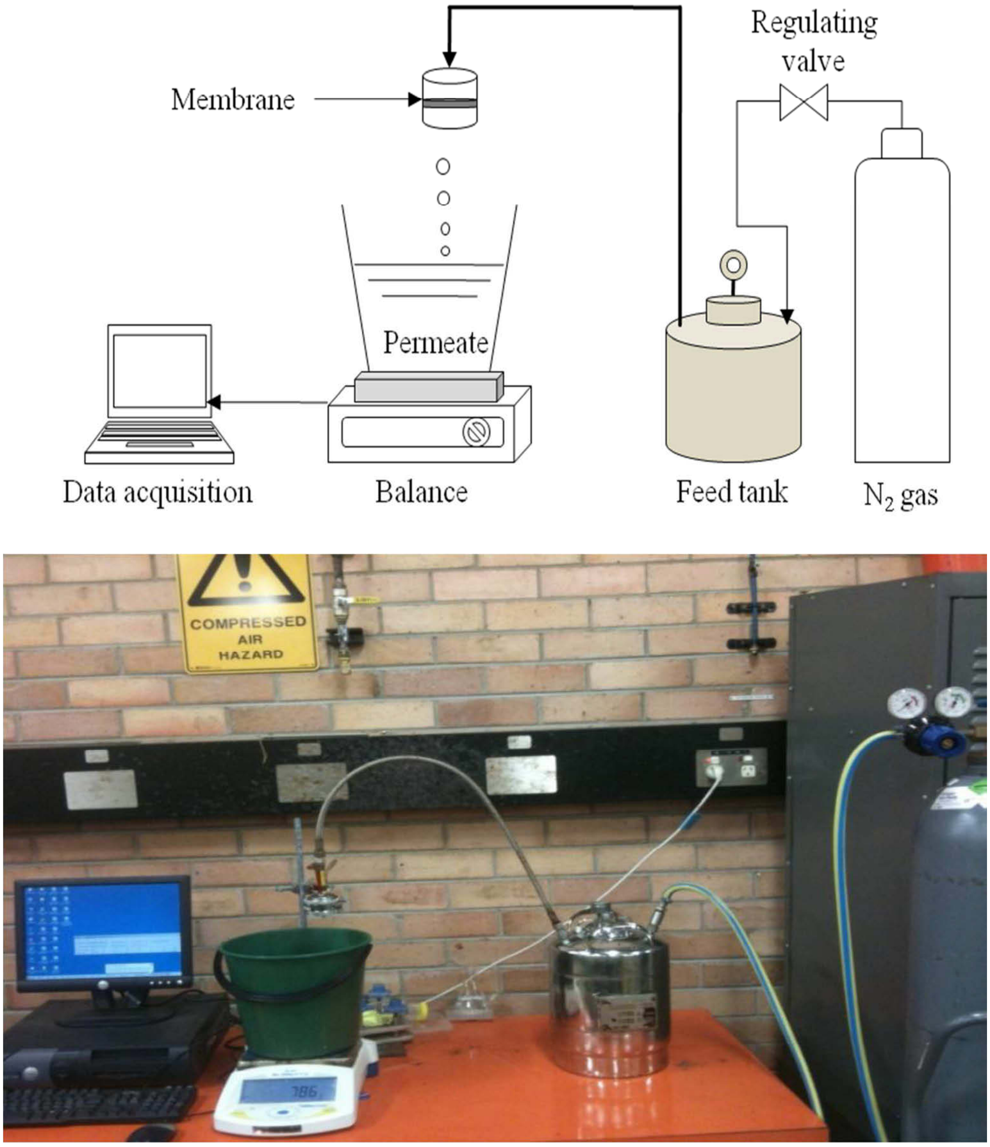


Figure 3.9. UF-MFI experimental set-up photo (Jeong et al., 2013)

3.4 Proposed Experiment

3.4.1 Improving the Method Available for Preparing PSiFe

As per the procedure suggested by Wang (2001), the first step was to prepare the poly silicate ferric (PSiFe) using his procedure. This method includes the polymerisation of diluted water glass solution 26% w/w

(SiO_2) with an acid or ion exchange resin, or both, followed by the addition of metal. This improvement was carried out in three different procedures, and the final coagulants were called PSiFe-α, PSiFe-β, and PSiFe-γ.

3.4.1.1 PSiFe-α

The first coagulant reagent was prepared by slowly adding hydrochloric acid to a diluted (6% w/w of SiO_2) water glass solution while stirring vigorously, followed by adding four different doses of 1M $FeCl_3$ solution to prepare four different Si/Fe ratios (i.e. 0.2, 0.5, 1, and 2). The results showed that using this coagulant (PSiFe-α) resulted in high contents of sodium and chloride in treated water and a maximum percentage of turbidity removal in the synthetic wastewater.

3.4.1.2 PSiFe-β

In order to reduce the content of sodium chloride from the previous preparation, this coagulant was prepared for polymerisation by passing the diluted water glass solution through a strong acidic ion exchange resin (DOWEX Ion Exchange Resins) up to a pH of 6; the remaining polymerisation was by hydrochloric acid, and at the final stage, different doses of ferric chloride 1M were added to prepare four different Si/Fe ratios (0.2, 0.5, 1, and 2). This chemical reagent showed a slight improvement in some specific ferric chloride dosing, but some samples still had high chloride content, which was an issue.

3.4.1.4 PSiFe-γ

After conducting a comprehensive literature survey on silica and its characteristics in polymerisation, the following modification was applied to the protocol for preparing Poly Silicate Ferric, while the reason for each change was referred to a related study on the background section as follows:

- Dilution of the water glass solution to 6% w/w of SiO_2 (Iler et al.,1956; Iler, 1979a)
- Heating the diluted water glass solution to 80-100 ºC for 10 min to improve its ability to aggregate (Mahulkar et al., 2006)
- Passing the solution through an acidic ion exchange resin to prepare Poly Silicate acid (PSiA) without Na^+; this causes dispersion instead of aggregation and improves the stability of the solution (Hasegawa et al. 1993 ; Robert, 1998)
- Heating the PSiA to between 80 ºC and 100ºC for 10 min and then ageing it for 24 hours to increase the molecular size of the polymer (Gao et al., 2011; Roberts, 1998)
- Adding different amounts of $FeCl_3$ (1M) to a specific volume of PSiA to prepare four samples with Si/Fe ratios of 0.2, 0.5, 1 and 2 (Iler, 1979; Wang et al., 2001; Yokoyama et al., 1980)

Every step in this modification is summarised in Table 3.4

Table3.4 Summary of improvement procedure of poly silicate ferric (PSiFe)

PSiFe Type	***Preparation Method***	***Remark***
PSiFe -α	Polymerisation of water glass solution(6%SiO_2)with hydrochloric acid and adding the ferric chloride at the final stage.	TOC machine could not function because of high ion content (Cl^-/Fe^{+3}/Na^+).
PSiFe -β	Polymerisation of water glass solution(26.6% SiO_2) by strong acidic ion exchange resin and hydrochloric acid at the final polymerisation stage and adding the ferric chloride at final polymerisation stage.	Polymerisation with acid changed partially to ion exchange procedure in order to remove Na^+&Cl^- content
PSiFe -γ	• Polymerisation of diluted water glass solution by the high strong acidic ion exchange resin continue • The polymerisation by ferric chloride addition until reaching a proper pH. • Increase pH by poly silicate acid • Aging, heating and control the speed of the addition	Result in low Na^+&Cl^-, high polymerisation rate, suitable iron citation. Solve TOC machine alarm. In addition to basicity in preparation in during the coagulation stage consider some adjustment to compare the effect of this factor

3.4.2 Characterisation of PSiFe

The structure and morphology of PSiFe were determined by using X-ray diffraction (XRD), and Scanning Election Microscopy (SEM). The XRD tests had already included the two main steps in preparing the sample, and the computer setup.

For SEM machine, the samples were dried in oven at 100 °C to remove the moisture prior to imaging. The samples were then sprinkled on a carbon tape. The images were taken using computer image software.

3.4.3 Coagulation Experiments (Jar test)

Jar test experiments were conducted based on the following steps:

3.4.3.1 Determine the Poly Silicateferric dose

The dose of coagulant was calculated based on the content of ferric chloride as an active ingredient in polysilicate ferric for the requirements of synthetic wastewater. It ranged from 5 mg/l to 30 mg/L of $FeCl_3$ with a 5 mg/L interval for each beaker.

3.4.3.2 Addition of the Poly Silicateferric to each Beaker

Various doses of the stock coagulants with 4 different Si/Fe and different Si/Fe ratio solutions were quickly injected into each jars with a measuring pipette. Jar #1 had the lowest dose (5 mg/l of calculated $FeCl_3$

in PSiFe) while Jar #6 was allocated the highest dose (30 mg/l of calculated $FeCl_3$ in PSiFe).

3.5.3.3 Flash Mixing

With the stirring paddles lowered into the jars, the stirring apparatus was operated for a short period of time at a high speed. It was adjusted to specific mixing conditions in the workplace. The mixing speed set to 90 rpm for 10 minutes.

3.4.3.4 Flocculation Mixing

This step was similar to flash mixing, but with a longer operating time (20 minutes) and a slower speed (30 rpm). It was adjusted to represent the actual mixing conditions in the workplace. Evaluating and interpreting the quality of the flocs at the end of this mixing period was an important task for this stage.

3.4.3.5 Settling Time

In this step the stirring apparatus was stopped and the samples in the jars were allowed to settle for 30 min. The samples were then withdrawn from their position 20 mm below the surface and then used for analysis in the following tests:

- Measuring the turbidity of the suspended solids
- Dissolved organic carbon (DOC)

- UV_{254} to measure the dissolved organic compounds by UV light absorbance at 254nm. Low absorbance corresponds to a high removal of dissolved organic matter
- Zeta –Potential at the sedimentation stage of the jar test to determine the relationship between the particle charge characteristics and the tendency towards flocculation.

Acceptable results would show that the flocs were dense, well formed, and with a process liquid between individual particles, while a hazy sample would suggest poor coagulation. The results were described as poor, fair, good, or excellent.

Alkalinity was monitored by measuring the pH after the section where the coagulant was added, and in some experiments was adjusted by adding sodium bicarbonate solution (1 M) to have a solution with a pH of 8 to ensure that enough alkalinity was presented for the coagulation process to work effectively.

The measured UV_{254}, DOC, and turbidity, were compared with the synthetic wastewater (SWW) specifications using the following formula (Equation.3.1):

$$\%\ of\ DOC\ Removal = \frac{Sample\ Result - SWW\ Result}{SWW\ Result} * 100$$

(Equation. 3.1)

3.4. 4 Performance of PSiFe on Kaolin Based Wastewater

In order to compare the effectiveness of PSiFe compared to the ferric chloride coagulant, a specific dose of kaolin clay (30 g/l) was added to the wastewater and tap water, and then the turbidity, UV_{254}, and zeta – Potential were measured.

At the end of the experiment, the optimum dose of each coagulant was selected and the performance of the coagulant was compared with ferric chloride.

3.4.5 Phaphate /Nitrate Removal of PSiFe in Raw water

The effect of ferric chloride on the removal of nitrogen /phosphate from raw water was investigated experimentally with a jar test, where the measuring apparatus was a nitrogen /phosphate measurement device. The dosage of coagulants commenced from 500 ppm to 3000 ppm (500 ppm interval of each beaker) and then the concentration of nitrogen /phosphate was measured. The removal of phosphate and nitrate was compared with the raw water, before adding the chemical as a percentage of the treatment.

3.4.6 Bench Scale Coagulation-Membrane System

After determining the optimum Si/Fe ratio and optimum dose of PSiFe with the jar test, a hybrid system consisting of a combination of coagulation and submerged membrane (hollow fibre) was prepared to determine how the new coagulant would affect the performance of the membrane system (Figure 3.5). The main analyses involved were DOC, turbidity, and TMP. Here, TMP was measured using a pressure gauge at the outlet of the membrane, DOC was measured after coagulation but before membrane filtration, and the second sample point was measured after membrane filtration.

The wastewater tank had a capacity of approximately 75 L. The synthetic water was set in flow via a pump joined by an injected stream of coagulant that was injected via a low flow gear pump, where the dose rate was calculated with the amount of wastewater in order to meet the jar test best dose criteria. The coagulant tank had 1 L capacity and contained a diluted coagulant in a ratio of 1:10. In order to be mixed properly, two streams were combined and fed into a long plastic pipe screwed into a cylinder, as shown in Figure 3.10.

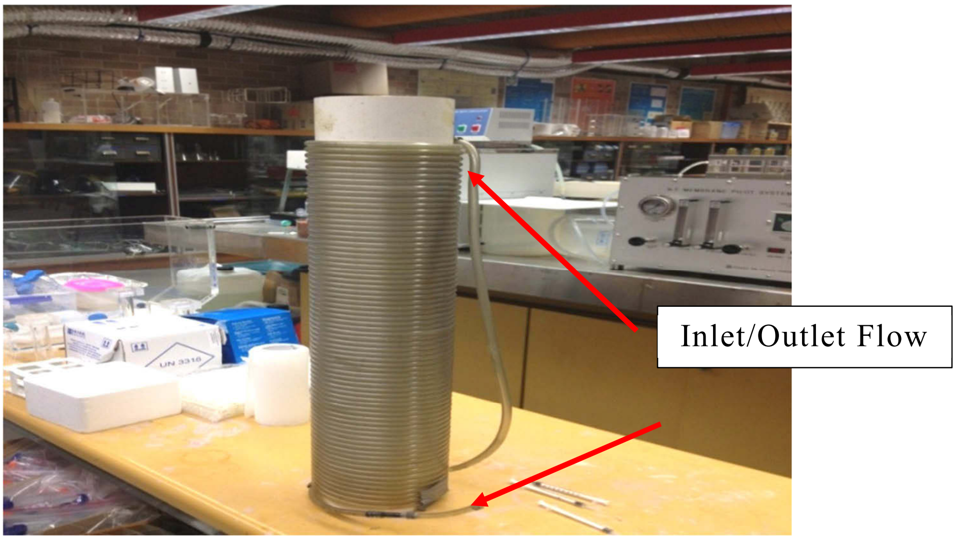


Figure 3.10 Screw type mixer of bench scale hybrid coagulation/membrane

The concept behind the arrangement of the plastic pipe was simple: two fluids (water and coagulant) flowing through a pipe that was wound around a cylinder would be enough to ensure that the coagulant was mixed properly before entering into the 15 L flocculation tank.

All the trials were conducted with a flocculation tank influent flow of 90 mL/min, which ensure a hydraulic retention time (HRT) of 16.1 min. The fluid mixture was then fed into the top of the flocculation tank and exited via an overflow port at the top of the tank, while the flocs accumulated at the bottom of the tank.

The coagulated water was pumped into the membrane tank designed specifically for this application. As Figure 3.11 shows, there was a pressure gauge at the exit line of the membrane. Since the inlet pressure of the inlet line to the membrane was atmospheric, the gauge showed the difference in pressure between the inlet and outlet lines as a trans-membrane pressure (TMP). The treated water from the membrane was transferred to a 15 L tank, and a port at the top of membrane vessel would allow water to flow into the sink if the membrane became blocked. The simple arrangement of a valve, an overflow, and tank allowed us to have a continuous coagulation/ membrane treatment for a specific time with minimal supervision.

An incoming flow of 90 mL/min and a permeate flow of 45 mL/min meant that 45 mL of water was restricted in the treatment of coagulated water every minute. This large difference between the feed and permeate flow was attributed to the aim of minimising the fill time of the membrane tank after drainage. If the feed flow was similar to the permeate it would take approximately 20 minutes to fill the membrane tank, so the ratio of permeate to fill time would be the same, but with an increased feed flow the fill time was reduced to 10 min and the ratio increased twice. According to this ratio the result was reasonable and remained constant throughout all of the membrane trials.

Figure 3.11 Bench scale membrane system

3.4. 7 Modified Fouling Index (MFI)

The modified fouling index (MFI) has been proven to have a perfect linear relationship with the feed concentration and it could reasonably represent the actual behaviour of fouling influenced by the feed concentration (Boerlage et.al., 2003 and Yiantsios et.al., 1998). A standard MFI involves a complex test analysis where its value is defined as the slope of the linear region of a plotted graph (Javeed et.al., 2009 and Brauns et.al., 2002). The MFI is determined from the gradient of the general cake filtration equation at constant pressure by plotting t (time)/V (volume) using Equation 3.2. (Schippers, 1980)

$$\frac{T}{V} = \frac{\eta \mathrm{Rm}}{\Delta PA} + \frac{\eta\alpha\ \mathrm{Cb}}{2\Delta P\mathrm{A}^2} \times \mathrm{V}$$

(Equation 3.2)

Where:

V = total permeate volume (l)

R_m = membrane resistance (-)

t = filtration time (s)

ΔP = applied trans-membrane pressure (Pa)

η = water viscosity at 20 ^{o}C (N.s/m^2)

α = the specific resistance of the cake deposited (-)

C_b = the concentration of particles in a feed water (mg/L)

A = the membrane surface area (m^2)

At this stage two volumes of approximately 2 L of coagulated water were collected. The first one was treated with 30 mg/L of ferric chloride and the second was treated with poly silicate ferric (Si/Fe=1). When the MFI tests were conducted the performance of both samples and their tendency towards fouling were compared to synthetic wastewater.

The samples were then transferred to the feed tank which was under constant pressure from nitrogen. As soon as the nitrogen valve was opened the water samples (coagulated or synthetic wastewater) began to move through the micro filter and water was collected in a calibrated vessel that was located on top of the electronic scale. The mass of treated water was measured by the scale and the time interval, both of which could be adjusted by the user, and then the measurements were transferred to the computer and converted into volume.

At the end of the experiment, three graphs were prepared for a sample of synthetic water and two samples of coagulated water, such that the volume was in an x-axis and time /(volume)^2 was on the y-axis. The slope of each line is an index for analysing the tendency of the membrane towards fouling.

A plot of t/V versus V was constructed, as shown in Figure 3.12(Schippers et al., 1998), and then divided into three regions: (I) the pore blocking region, (II) cake formation without compression, and (III) cake formation with compression to differentiate the fouling mechanisms over the filtration period. The membrane fouling index (MFI) was then defined as the gradient of the plot of t/V versus V of region II, and the modified fouling index (MFI) can be determined using the following equation:

$$\mathbf{MFI = \alpha \times C_b} \qquad \textbf{(Equation 3.3)}$$

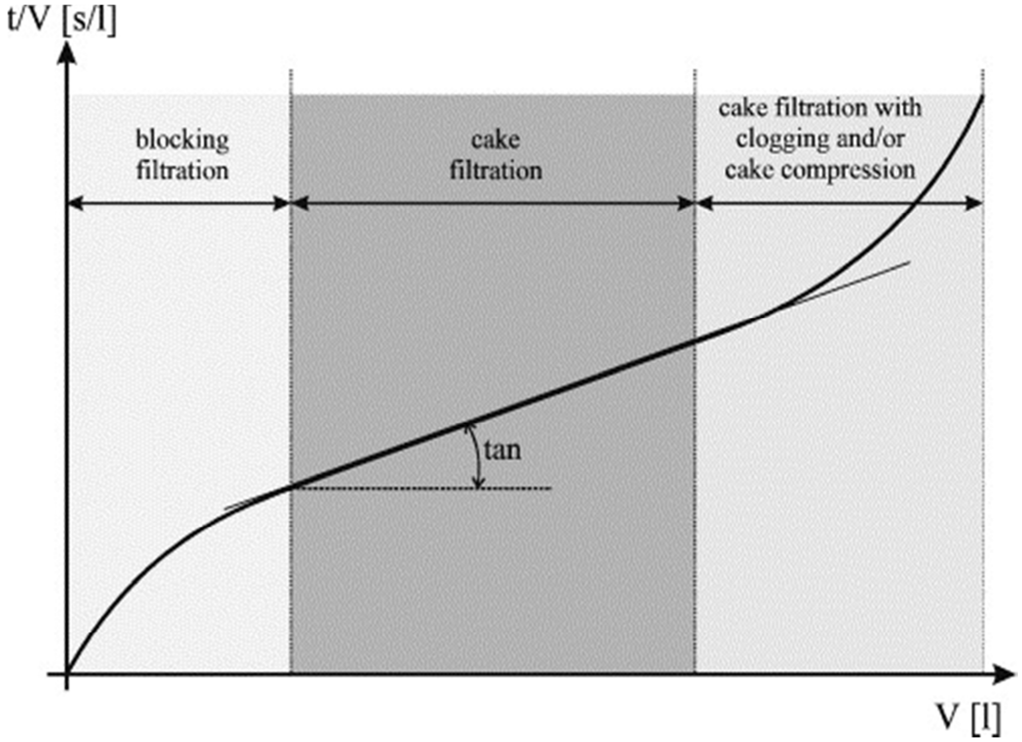


Figure 3.12 Cake filtration curve (Boerlage et. al., 2003)

Chapter 4

Results and Discussions

4. Results and Discussions

4.1 Introduction

In this chapter the performance of the target coagulant, which is a poly silicate ferric (PSiFe) based coagulant has been evaluated. Through several experiments the efficiency of this modified coagulant in the treatment of water and wastewater was determined. The current method for preparing PSiFe was modified to improve its coagulation in terms of organic removal, coagulant dose, and turbidity removal. Every method for preparing poly silicate ferric consists of two main processes: (i) acidification of water glass solution (PSiA), and (ii) the addition of iron to the polymer (PSiFe). These two straightforward processes can be prepared using different approaches. However, to ensure having a suitable polymeric chemical with a high molecular weight and a proper surface, suitable for water coagulation, it is necessary to have appropriate silica aggregation during acidification, high valiant metal ion substitution, a bridge with a metal ion, a proper temperature, and a pH and ageing time.

Based on this explanation the method for preparing the coagulant was modified as follows:

- Preparing a dilute solution of silica in order to have smaller particles with a higher speed of aggregation and better flow ability for the next steps in the process. Using cation exchange resin instead of acid for polymerisation to have mono valiant salt to tri valiant. This means there will be a higher surface area, a high molecular weight, and more charge for the coagulation procedure
- Finalise polymerisation at specific acidic pH
- Add the dilute silica and increase the specific pH to have silanol SiOH at the surface of the molecule in order to stabilise the solution and prepare for the addition of iron
- Low heating in order to have a large size and reduce the pH by adding ferric chloride salt up to a specific pH
- Ageing for a few hours to neutralise and increase the surface due to SiOH being converted to SiO
- After the coagulant was prepared using this method this procedure was called PSiFe-γ, while the existing procedure was called PSiFe-β

The following section describes the results, obtained from a series of characteristic tests, jar tests, a determination of the modified fouling index (MFI), and bench scale hybrid system tests with PSiFe-β, PSiFe-γ, and $FeCl_3$.

At the beginning of the experimental program, an array of jar tests with different Si/Fe ratios (i.e. 0.2, 0.5, 1, and 2) was carried out on PSiFe-γ to find the optimum ratio and dosage of this coagulant in wastewater treatment. Afterwards, comparisons between PSiFe-γ and PSife-β were conducted by characterising both coagulants. In addition, different experiments were performed to find the functionality of PSiFe coagulants in different processes of water/wastewater treatment.

4.2 Objectives

The main objectives of this phase of the research are summarised as follows:

- Evaluation and characterising of the silicate base coagulants
- Finding the optimum ratio of silicate to iron
- Understanding how these coagulants behave when exposed to various treatment processes

- Establishing an optimum dose of coagulant that yields the maximum TOC and turbidity removal for each of the three coagulants ($FeCl_3$, PSiFe-β, and PSiFe-γ)
- Finding a reference point to identify the fouling potential of feed water using a hollow fibre membrane system
- Describing the effects of the coagulants based on a bench scale hybrid membrane coagulation/filtration system
- Evaluating their level of phosphate removal in raw water, and the TOC and turbidity removal in kaolin based water treatment
- Determining the efficiency of the modified coagulant (PSiFe-γ) in sea water treatment

4.3 Characteristics of PSiFe

4.3.1 Fourier Transforms Spectroscopy (FTIR) Spectra Analysis

Fourier transform spectroscopy (FTIR) analyses were conducted with the functional groups in the PSiFe. The solid coagulants were analysed by FTIR with the spectrophotometer and potassium bromide (KBr) pellet method. The spectra were in the range of 4000-400 cm^{-1}. In the first step the PSiFe sample was dried in an oven at 105 ℃ and then ground into powder. The KBr disc method was then used to analyse the structure of sample on an infrared spectrometer.

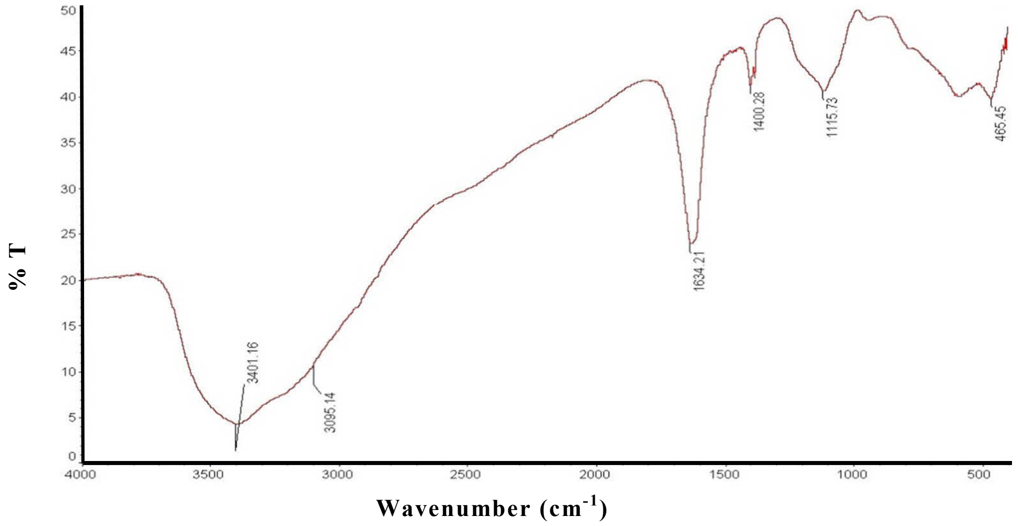


Figure 4.1. FTIR Spectra of PSiFe Sample

Figure 4.1 presents the FTIR spectra of PSiFe. All of the absorption bands in FTIR spectra are in three different areas, Si-O bond (400-1400) and O-H bond in various hydroxyl group, which reveals the presence of functional groups (3800-3000 cm^{-1}), and (1700-1600 cm^{-1}) (Ilin, et al., 1978). As can be seen, absorption peaked at 3401 cm^{-1} and 1634 cm^{-1}. Accordingly it can be inferred that PSiFe, whose changes in structure are directly affected by water molecules, is still a kind of ferric poly-hydroxylated polymer (Guojun Du et al, 2008). The appearance of all these peaks suggests that the composite PSiFe was prepared successfully, as explained by Zeng et.al 2009 and Zouboulis et.al. 2008.

It is worth mentioning that the different intensity and area of peak at 1080 cm^{-1} indicated the existence of an interaction between Fe and Si. Moreover, the three intensity peaks of PSiFe showed that Si can strengthen absorption at the three wave lengths (Li-jun et.al., 2009). According to the absorption peak caused by the bending vibration of Si−O−Fe, namely an oxygen cross linked substance with a silicon-oxygen tetrahedron and oxygen-ferrite tetrahedron, we can determine that a non-ionic bond reaction occurred between the poly-Fe ions and poly-Si ions, and produced an Fe-Si polymer, i.e. PSiFe (Shi-Qian, 2011).

The peaks at 465 cm^{-1} and 1115 cm^{-1} were assigned to the characteristic bands for the Fe–O bond and Si–O bond (Li-jun et.al, 2009), respectively, and they also exhibited these characteristic peaks at 954 cm^{-1}, which was attributed to the bending vibration of Si–OH–Fe bonds (Nakamoto, 1964). The position of the absorption bands corresponding to the Si-O-Si (1400-954 cm^{-1}) and absorption peaks around 600 cm^{-1} and 470 cm^{-1} that were regarded as peaks caused by the stretching vibration of Fe−O (Guojun Du et al, 2008) and bending (400-500 $cm^{-1)}$ vibration, indicates that PSiFe has a structure that is highly condensed between silicon hydroxyl and ferric in three dimensional types of the compound (Ilin, et.al. 1978).

The presence of some other peaks in figure 4.1 can be attributed to a new chemical compound, although the peak was not meant to be positive with regards to the formation of a new chemical compound.

4.3.2 XRD Analysis

Figures 4.2, 4.3, and 4.4, illustrate the XRD patterns of solid PSiFe-β (polymerisation partially with acid) and PSiFe-γ (Polymerisation with acid and passing through the ion exchange resins) where the last figure is a combination of both figures in order to have a better comparison between these two polymers. To perform this test, the PSiFe samples must be dried in an oven at 105 ℃ and then compressed into one solid sample, after which its structure must be analysed on an infrared spectrometer.

The pattern shows that in polysilicates, the diffuse amorphous cells gradually weaken and multiple small diffractions peak, which shows that the coexisting multiple crystal phases are growing (Moussas, 2009). Hence it can be concluded that PSiFe is not a substance with a crystal structure or a substance like amorphous PSi, it is an amorphous polymer. Both samples have an amorphous pattern and in the first sample the sample includes a high intensity obscure peak of sodium chloride with equally broad shoulders, and no characteristic diffraction peak with the amorphous pattern.

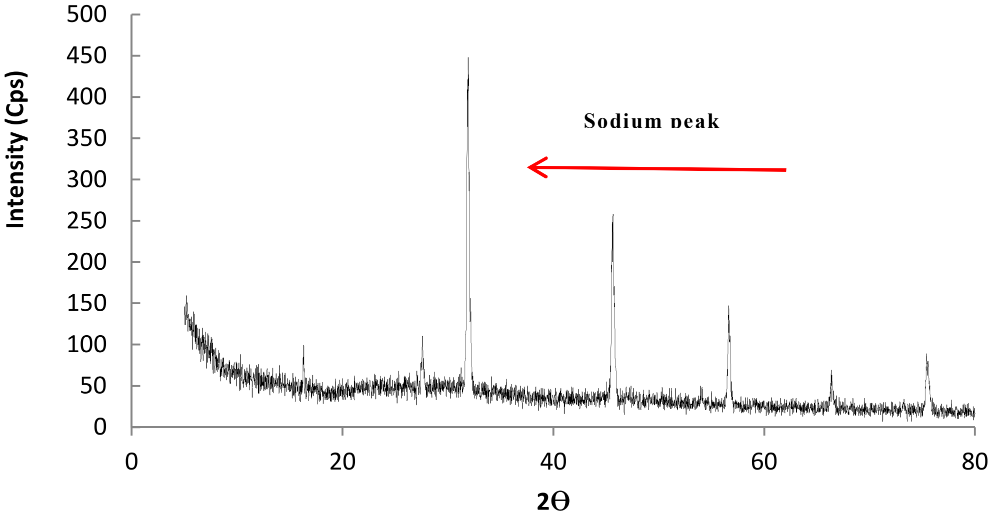


Figure 4.2 X-Ray diffractometer scan of PSiFe-β

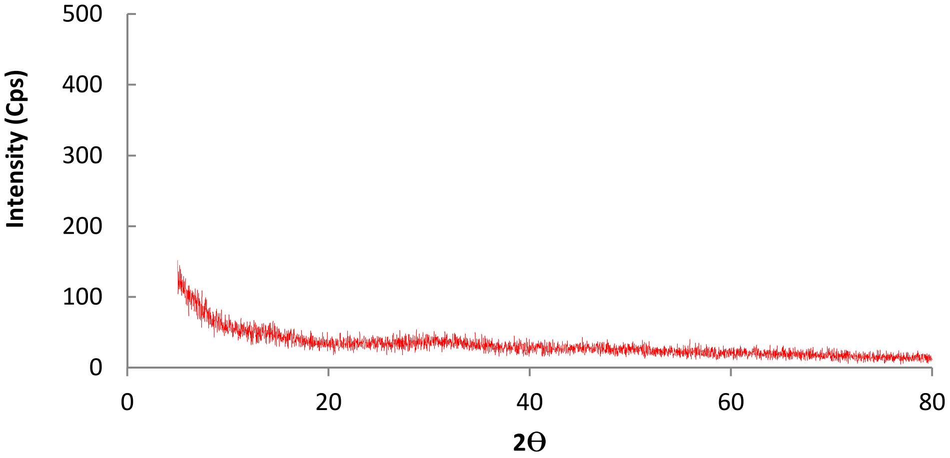


Figure 4.3 X-Ray diffractometer scan of PSiFe-γ

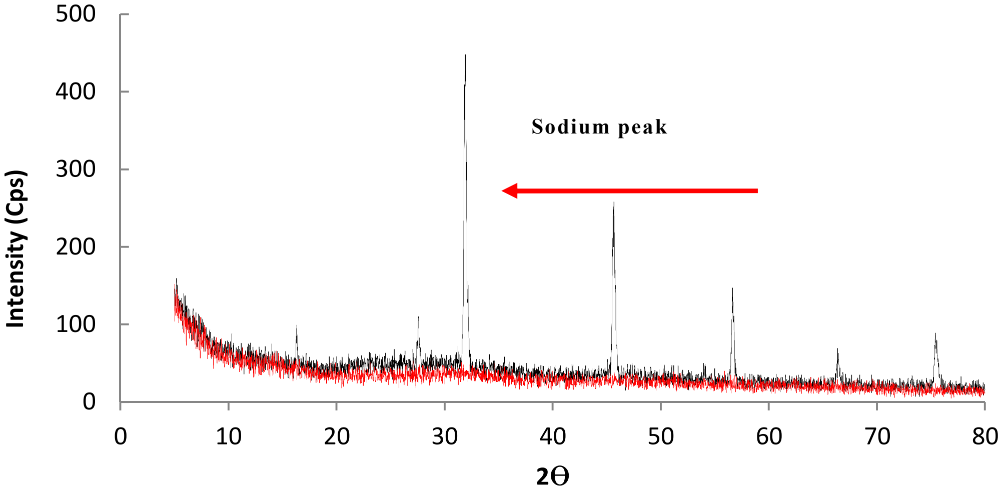


Figure 4. 4 X-Ray diffractometer scan Comparison Chart

4.3.3 SEM and EDS Analysis of Samples

Surface analyses, chemical analysis, and imaging on a variety of materials can be conducted using a scanning electron microscope (SEM). The SEM used in this study was equipped with an energy dispersive spectrometer (EDS). SEM was specifically used to observe the surface morphology of the freeze dried coagulated flocs. The EDS test was also measured with the same machine. The difference in energy between the higher energy shell and the lower energy shell is released in the form of an X-ray. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

This test was conducted for PSiF-β and PSiF-γ. In both cases the Si/Fe molar ratio was kept to be equal to 1. The SEM and EDS test machine used for this test was XL30ESEM. The analysis was performed in a variable pressure (VP mode) at 0.3 Torr pressure, 20 kV accelerating voltage, 10 mm working distance, and with the EDAX EDS system.

Figures 4.5 and 4.6 show the SEM and EDS pictures or surface morphology of the polysilicate iron coagulants. The SEM images show randomly forming aggregates that are largely in an amorphous structure. The results showed that the addition of polysilicate changed the Fe^{3+} three dimensional model and formed poly ferrosilicon with a reasonable stability and a higher molecular weight. As Figures 4.5 and 4.6 shows, the surfaces of poly silicate iron coagulants were rougher than other polymeric metals such as polyferric chloride (Figure 4.7), and possessed a larger specific surface area. Therefore, the polysilicate iron coagulant had a better adsorption performance, and as a result the removal rate of pollutants increased.

The SEM results for PSiFe-β showed the presence of some white salts (sodium chloride), whereas the SEM micro-photograph of PSiFe-γ indicated there was no sign of sodium salts (Figures 4.5 and 4.6).

The EDS results (Figures 4.5 and 4.6) confirmed that PSiF-β, prepared by existing preparation method, included the NaCl contaminant. A long peak of sodium salt can be clearly seen among other components such as chloride and silicate.

Since ion exchange resin was used in the preparation of PSiF-γ, it was expected to have only a short sodium peak. The peak for sodium salt in PSiF-γ was significantly less than PSiF-β and the EDS graph was in good agreement with this line of reasoning

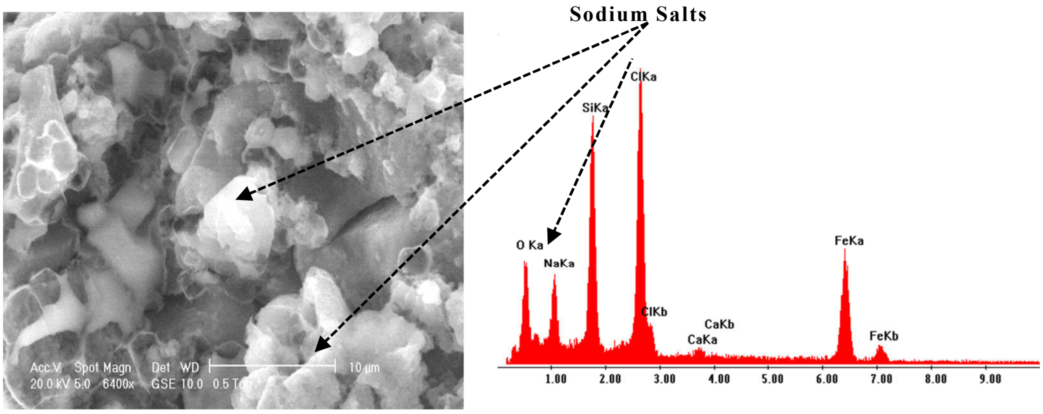


Figure 4.5 SEM microphotograph and EDS spectrum of the PSiFe-β

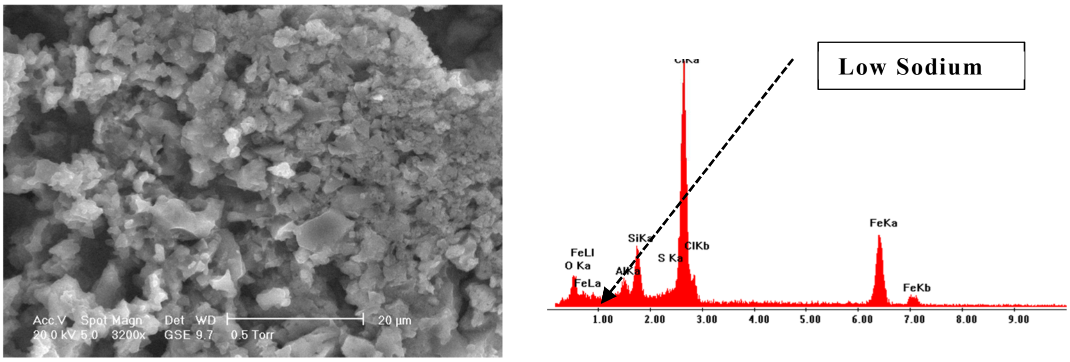


Figure 4.6 SEM microphotograph and EDS spectrum of the PSiFe-γ

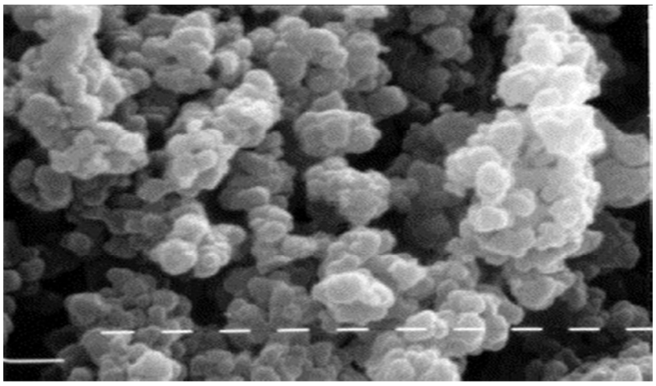


Figure 4.7 SEM micro photograph of poly ferric chloride (Wang et al., 2011)

4.3.4 Determination of Polymerised Iron Concentration

The measurement of the Fe species by the ferron-timed spectroscopy method has been reported previously (Jiang et al., 2008). The ferron test reagent (8-hydroxy-7-iodoquinoline-5-sulphonic acid) can form complexes with single ferric ions, as well as with monomeric and dimeric species, within a reaction time of 1 min, whereas it confirms complexes to medium and high molecular weight iron polymers when the reaction time increases. It can be noted that the precipitated ferric species does react with ferron, so based on this principle, the visible absorbance at 600 nm of solutions was measured at pre-determined time intervals and each absorbance corresponded to the respective ferric species concentration. In particular, the oligomeric (monomeric and dimeric) iron species were determined from the absorbance reading taken 1 min after the ferron reagent and diluted PFS sample were mixed together. The polymeric species of PFS were determined from the difference between the 24 h and 1 min absorbance readings. The concentration of precipitated iron species was calculated by subtracting the concentration of oligomeric and polymeric species from the total concentration of iron.

4.4 Coagulation Experiments

4.4.1 Jar Test by PSiFe-γ in Synthetic Wastewater

To obtain four different Si/Fe ratios from PSiFe-γ, four equal amounts of polysilicate acid (PSiA) solutions were measured and kept in different beakers by calculating the content of silicate. Then four different amounts of 1 M $FeCl_3$ solution were mixed rapidly one by one, with the PSiA solutions at 40-60 °C. The ratios of Si to Fe were kept at 0.2, 0.5, 1, and 2. The calculation was based on 5 mg/L of Fe^{3+} to 30 mg/L of Fe^{3+} with a 5-mg/L interval.

4.4.1.1 PSiFe-γ with Si/Fe Ratio of 1:2

As Figure 4.8 shows, the coagulation performance of PSiFe-γ with Si/Fe=0.2 was evaluated for measuring the TOC, turbidity, and UV_{254}. The doses began with 5 mg/L in the first jar, and with a 5-mg/L interval, ended with 30 mg/L in the sixth jar.

The results indicated that the maximum treatment occurred with 30 mg/L Fe^{3+} under the slightly acidic condition (pH=6). The first four samples become cloudy after the coagulant was added, but the last beaker was slightly clearer as can be seen in Figure 4.9. The flocs had formed, but they did not have sufficient weigh and charge to settle down (Figure

4.8). The percentage of turbidity removal in the first 5 samples was minus, indicating that turbidity was higher than the synthetic wastewater. However, turbidity removal was 45.61% in the last sample, which was a substantial improvement in improving turbidity.

For this ratio the TOC removal was at very low percentage in the low coagulant dose (5 mg/L Fe^{3+}), and on the last sample when the dosage of coagulant was increased to 30 mg/L Fe^{3+} it rose to 80%. From the first to the second sample, by increasing 5 mg/L Fe^{3+}, the TOC removal improved by 45.5%. The UV_{254} had an increasing trend from 25% to 40%. All of the data are tabulated in Table 4.1 for the sake of comparison.

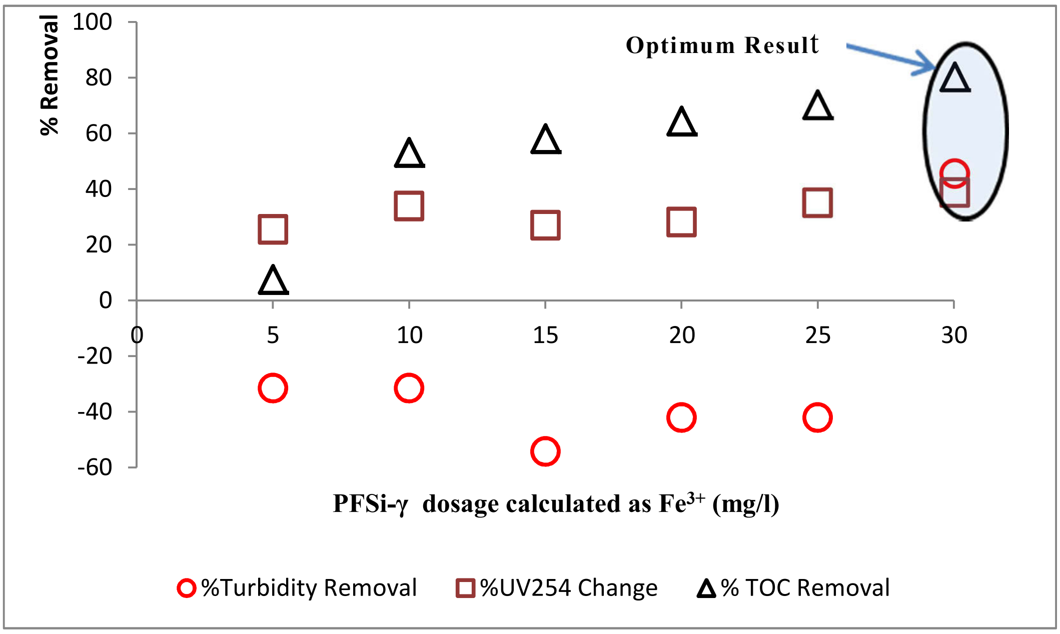


Figure 4.8 Treatment of synthetic wastewater with different PSiFe-γ (Si/Fe=0.2) dosage

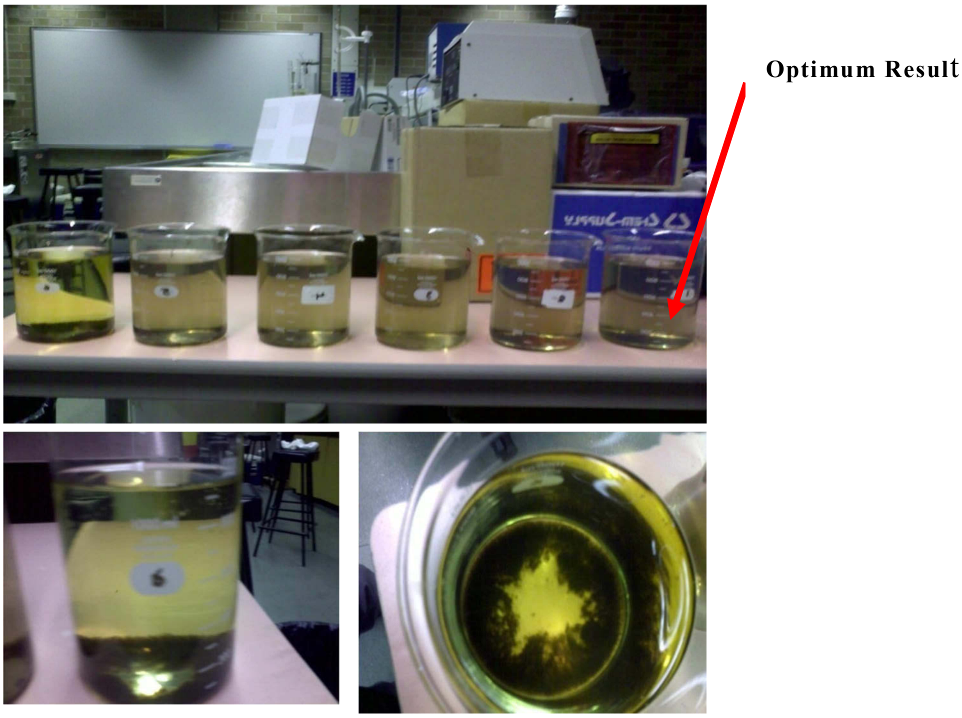


Figure 4.9 Jar Test Experiment Photo for PSiFe-γ (Si/Fe=0.2)

Table 4.1 Jar test data PSiFe-γ (Si/Fe=0.2)

mg Fe^{3+}/L	pH	Turbidity NTU	UV254 (/cm)	Zeta mV	TOC (mg/L)	%Turbidity NTU	%UV254 NTU	%TOC (mg/L)	Zeta Diff.
5	7.01	7.50	0.785	264.3	7.12	-31.58	25.47	7.53	-28.3
10	6.91	7.50	0.697	240.0	3.61	-31.58	33.80	53.12	-4.0
15	6.81	8.80	0.770	236.7	3.23	-54.39	26.91	58.05	9.9
20	6.69	8.10	0.757	235.3	2.74	-42.11	28.08	64.42	0.7
25	6.56	8.10	0.682	231.1	2.29	-42.11	35.23	70.26	4.9
30	6.42	3.10	0.643	218.2	1.52	45.61	38.93	80.26	17.8

The zeta potential measurement is important because its value can be associated with the stability of colloidal dispersions. The zeta potential indicates the degree of repulsion between adjacent similarly charged particles (the vitamins) in dispersion. For molecules and particles that are small enough, a high zeta potential will confer stability, i.e., the solution or dispersion will resist aggregation. When the zeta potential is low, attraction exceeds repulsion and the dispersion will break and flocculate. Hence, colloids with a high zeta potential (negative or positive) are electrically stabilised, while colloids with low zeta potential tend to coagulate or flocculate as outlined in Table 4.2 (Greenwood, 1999 and Hanaor 2012).

Table 4.2 Relationship between stability of a colloid and zeta potential (Hanaor 2011)

Zeta potential (mV)	**Stability behaviour of the colloid**
from 0 to ±5,	Rapid coagulation or flocculation
from ±10 to ±30	Incipient instability
from ±30 to ±40	Moderate stability
from ±40 to ±60	Good stability
more than ±61	Excellent stability

Figure 4.10 represents the relationship of pH with the zeta potential difference between synthetic water and each jar. Since the pH of the coagulant was in the acidic range, by adding the coagulant in each jar, the pH began to reduce. By adding a higher dose of coagulant the zeta potential began to reduce by slightly linear phenomena. In the first sample with a pH 7.01, the zeta potential was 264.3 mV and in the last sample (sixth beaker) the pH had reduced to 6.42 and the zeta potential had reduced to 218.2 mV. The zeta potential in wastewater was 236 mV. The maximum positive difference in the zeta potential was at the best dose, which was the sixth beaker.

Based on Table 4.2, the colloids in all of the jars have excellent stability but not enough weight to have acceptable sedimentation (Greenwood, 1999 and Hanaor 2012).

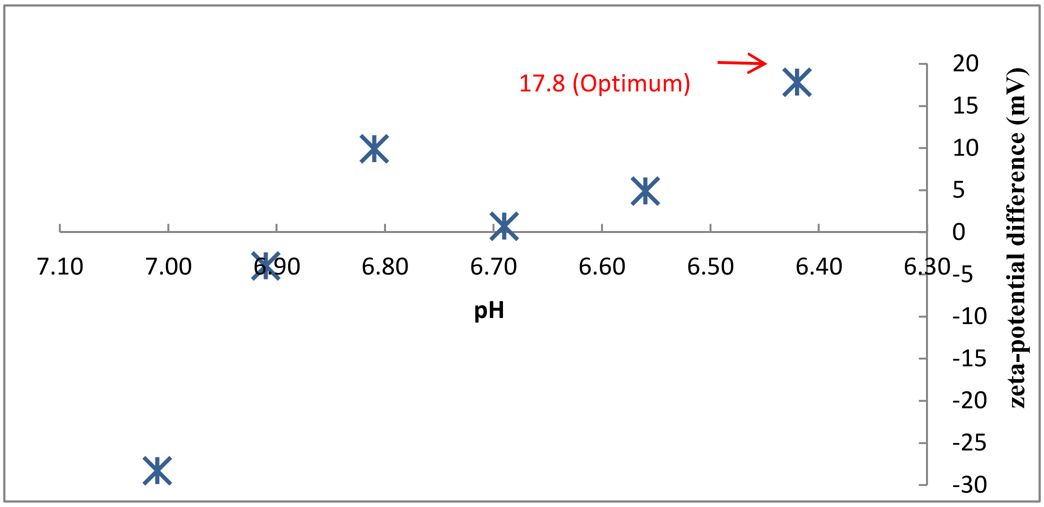


Figure 4.10 Relation between pH and zeta-potential, Si/Fe=0.2

4.4.1.2 PSiFe-γ with Si/Fe Ratio of 1:2

The trend of the wastewater treatment by PSiFe-γ with Si/Fe=0.5 can be observed in Figure 4.11. For this experiment, by a visual check (Figure 4.12), the last two samples were clear with suitable sedimentation. In the actual data it was observed there was a slight improvement in the first two samples but there was a sharp negative change in Sample 3, and again, improvement from Samples 4-6. The best result was from sample 5 with 90% improvement in turbidity, 95.56% in TOC, and 84.46% improvement in UV_{254}. In samples 3 and 6, after adding the coagulant, the beaker clarity reduced and visually showed a negative change in turbidity. In Figure 4.11 the numerical data for these two samples were -12% and -24%, which matched with a visual check of the samples.

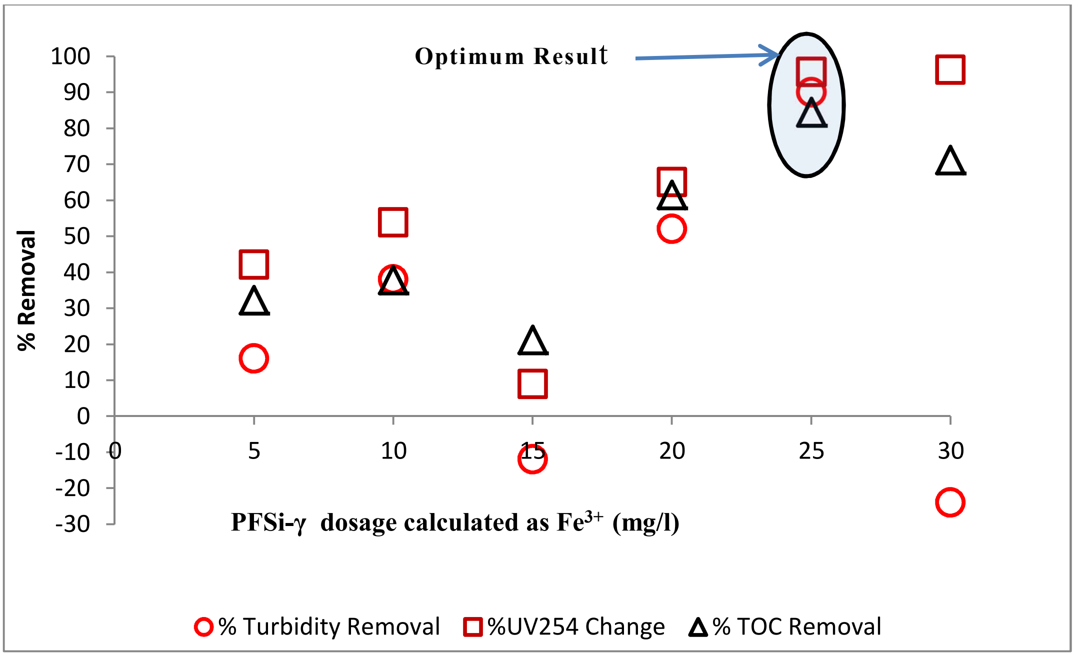


Figure 4.11 Performance curve of PFSi-γ, with Si/Fe=0.5

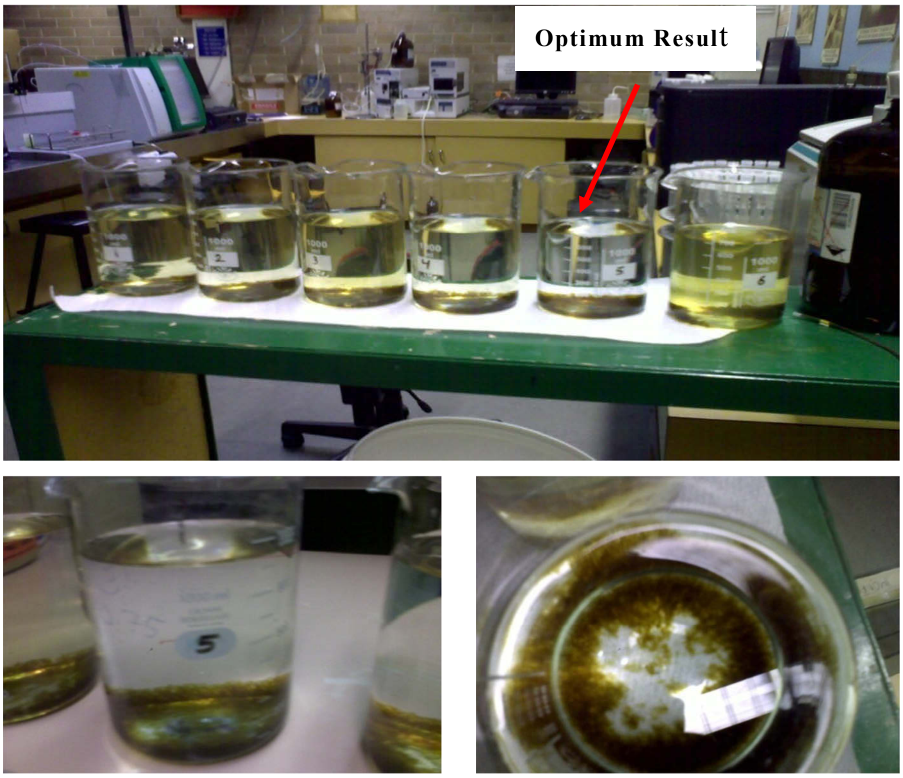


Figure 4.12 Jar test experiment Photo for PSiFe-γ (Si/Fe=0.5)

All data for the jar test by this ratio (Si/Fe=0.5) are summarised in Table 4.3.

Table 4.3 Jar test data for PSiFe-γ (Si/Fe=0.5)

mg Fe^{3+}/L	pH	Turbidity NTU	UV254 (/cm)	Zeta mV	TOC (mg/L)	%Turbidity NTU	%UV254 NTU	%TOC (mg/L)	Zeta Diff.
5	6.14	4.20	0.3552	238.20	3.270	16	42.07	32.16	25.8
10	6.00	3.10	0.2832	233.60	3.00	38	53.82	37.76	30.4
15	5.71	5.60	0.5585	239.20	3.80	-12	8.92	21.16	24.8
20	5.33	2.40	0.2148	247.10	1.857	52	64.97	61.47	16.9
25	5.25	0.50	0.0272	270.40	0.749	90	95.56	84.46	6.4
30	4.60	6.20	0.0231	293.70	1.390	-24	96.23	71.16	29.7

In the zeta potential experiment (Figure 4.13)the optimum dose with the maximum improvement can be recognised based on the minimum zeta potential difference (6.4 mV) with slightly acidic pH (5.25). This means that the optimum treatment of TOC and turbidity happened with the lowest difference in zeta potential and wastewater.

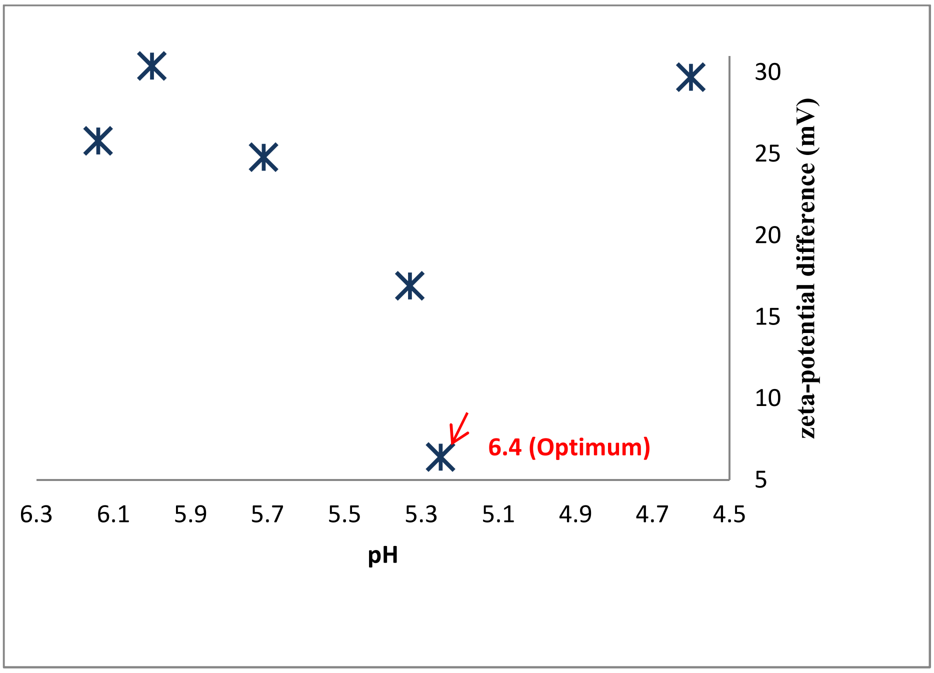


Figure 4.13 Relation between pH and zeta-potential, with Si/Fe=0.5

4.4.1.3 PSiFe-γ with Si/Fe ratio of=1:1

In the jar test, the trend of the wastewater treatment with PSiFe-γ with Si/Fe=1 can be observed in Figure 4.14, and the associated data are summarised in Table 4.4. In this experiment Jars 5 and 6 were clear and their data were very close to each other. The trend of improvement in turbidity, TOC, and UV was linear (with the exception of UV for samples 3 and 4). The visual appearance of Jars 1-4 was yellowish

(Figure 4.14), optimal flocculation was in Jars 5 and 6 with about a 91-93% notable improvement in turbidity, 34-35% in UV 254, and 72-74 % in TOC, respectively.

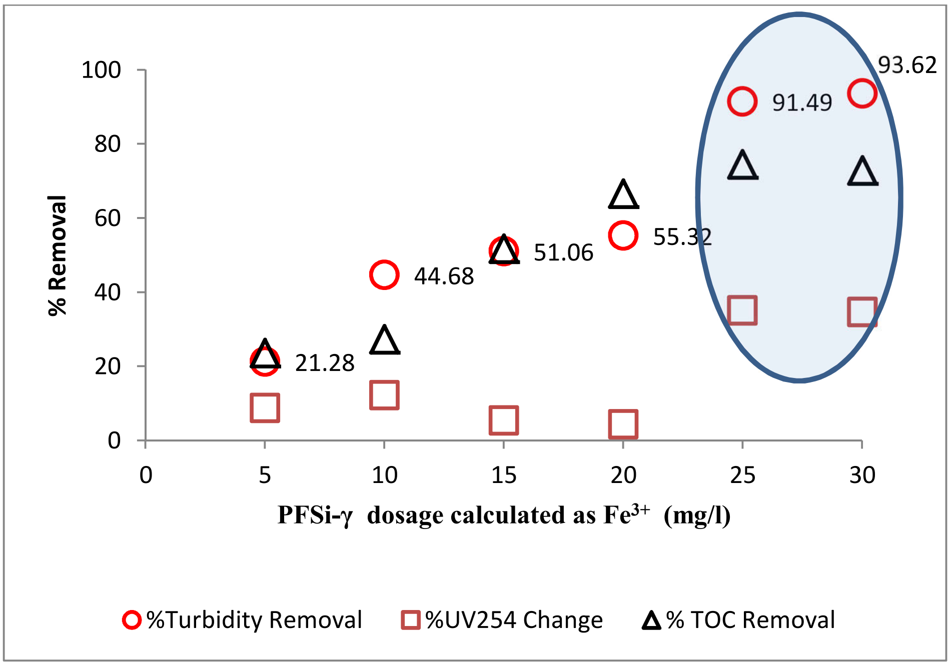


Figure 4.14 Performances curve of PFSi-γ, with Si/Fe=1

Figure 4.15 Jar test experiment photo for PSiFe-γ (Si/Fe=1)

All data for the jar test with this ratio (Si/Fe=1) are summarised in Table 4.4.

Table 4.4 Jar test data for PSiFe-γ (Si/Fe=1)

mg Fe^{3+}/L	pH	Turbidity NTU	UV254 (/cm)	Zeta mV	TOC (mg/L)	%Turbidity NTU	%UV254 NTU	%TOC (mg/L)	Zeta Diff.
5	6.34	3.70	0.5309	406	1.230	21.28	8.75	23.60	48
10	6.14	2.6	0.5106	412	1.170	44.68	12.24	27.33	42
15	6.04	2.30	0.5503	426	0.777	51.06	5.41	51.75	28
20	5.95	2.1	0.5566	437	0.537	55.32	4.33	66.65	17
25	5.65	0.40	0.3773	453	0.409	91.49	35.15	74.60	1
30	5.4	0.3	0.3798	482	0.435	93.62	34.72	72.96	-28

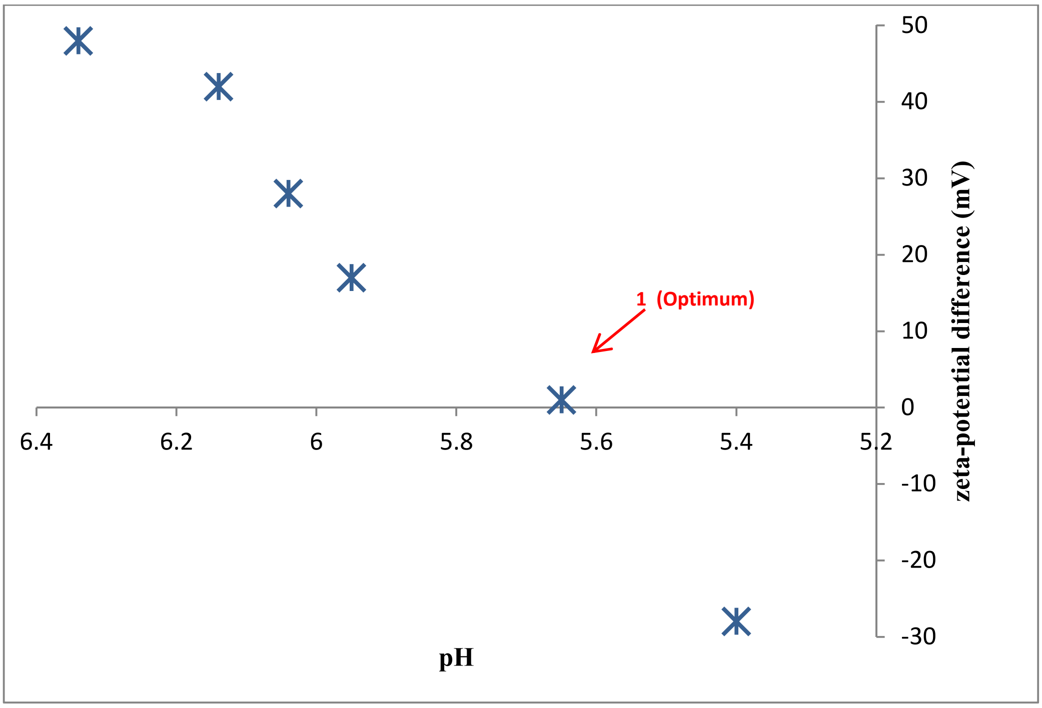


Figure 4.16 Relatioship between pH and zeta-potential with Si/Fe=1

The results of the zeta potential difference between the sample and wastewater for PSiFe-γ with Si/Fe=1 are depicted in Figure 4.16. It is of interest to note that there is a positive relationship with decreasing the pH and reduction of the zeta potential.

The best results of TOC and turbidity treatment were associated with Samples 5 and 6. However, when considering the zeta potential, Sample 5, with the minimum positive difference with synthetic water, was in the category of excellent coagulation flocculation. Accordingly, both Jars (5 and 6) with 25 and 30 mg Fe^{3+} /L were the best dose among all four Si/Fe ratios and therefore this dose and ratio are considered to be the optimum dose for further MFI, Phosphate and hybrid system tests.

4.4.1.4 PSiFe-γ with Si/Fe Ratio of 2:1

The results of the jar test of synthetic water with PSiFe-γ Si/Fe=2 as the coagulant are given in Figure 4.17 and Table 4.5. By means of a visual check it can be found that Sample 5 had a very clear liquid, as shown in the photographs in Figure 4.18. In this experiment the turbidity of Jar 1to Jar 5 increased by increasing the dose of coagulant (5- 25 mgFe^{3+}/L). In Jar 5 all of the treatment factors decreased compared to the previous ones, and therefore the optimum treatment for this experiment was achieved in Jar 5 with 83.33% improvement in turbidity, 92.9% enhancement in UV254, and 79.05% improvement in TOC removal.

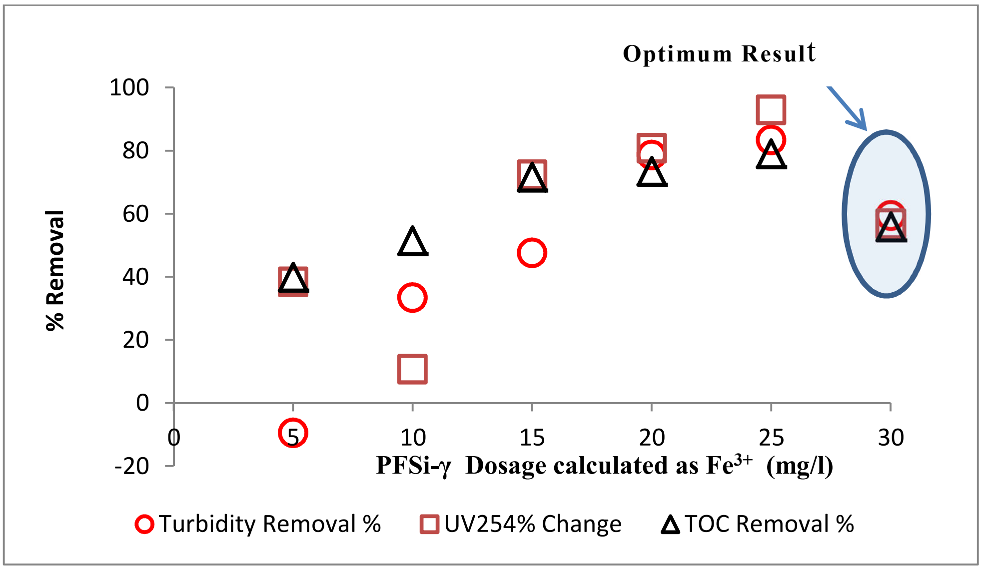


Figure 4.17 Performance curve of PFSi-γ, Si/Fe=2

Figure 4.18 Jar test experiment photo for PSiFe-γ(Si/Fe=2)

Table 4.5 Jar test data for PSiFe-γ with Si/Fe=2

mg Fe^{3+} /L	pH	Turbidity NTU	UV254 (/cm)	Zeta mV	TOC (mg/L)	%Turbidity NTU	%UV254 NTU	%TOC (mg/L)	Zeta Difference
5	6.69	4.60	0.2950	223	2.90	-9.52	38.40	39.83	3
10	6.22	2.80	0.4279	231	2.34	33.33	10.65	51.45	11
15	5.90	2.20	0.1324	241	1.37	47.62	72.35	71.58	21
20	5.60	0.90	0.0925	254	1.28	78.57	80.68	73.44	34
25	5.42	0.70	0.0340	264	1.01	83.33	92.90	79.05	44
30	4.33	1.70	0.2063	291	2.12	59.52	56.92	56.02	71

As Figure 4.19 shows, the zeta potential almost follows a linear relationship with the pH. According to the TOC and turbidity data, the optimum dose was at 25 mg Fe^{3+} /L. At this point (Jar 5), the zeta potential difference was in the category of excellent stability.

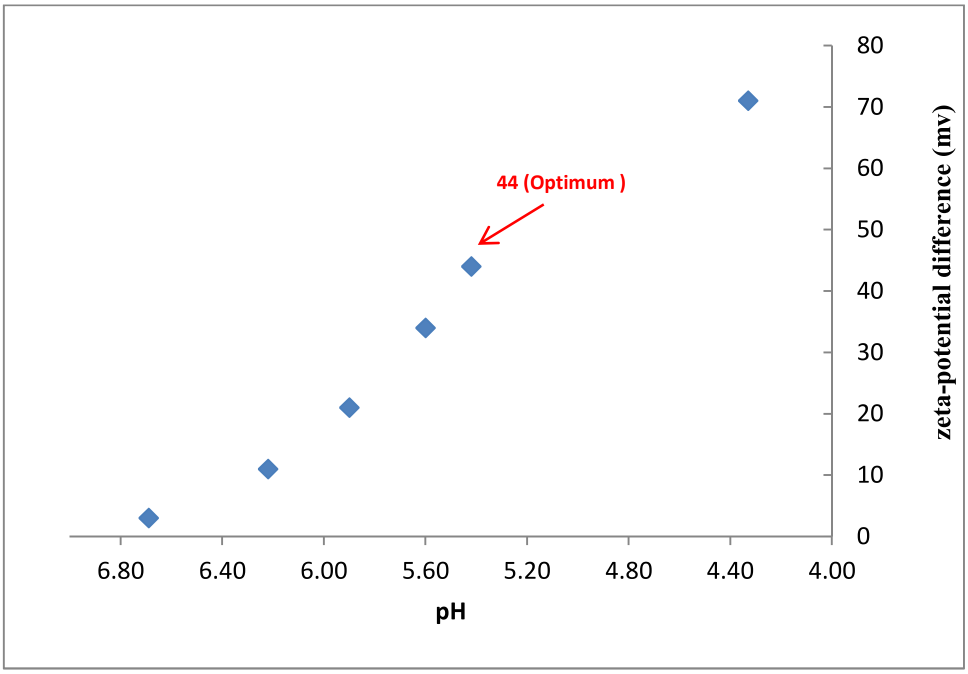


Figure 4.19 Relationship between pH and zeta-potential with Si/Fe=2

4.5 Performance of PSiFe-γ on Kaolin Based Water Treatment

4.5.1 Coagulation with PSiFe-γ on Kaolin Contaminated Wastewater

These coagulation experiments were carried out using the target coagulant PSiFe-γ, and kaolin in distilled water as contaminated wastewater according to the existing experiment with titanium sulphate coagulation.

Distilled water was used for kaolin preparation to define the flocculation and suspension region. In order to measure the removal of turbidity, a predetermined dose of kaolin clay was prepared (30 g/L) with distilled water and agitated vigorously. The mixture was then allowed to settle for 6 hours in order to have a uniform stock kaolin clay suspension with a specific concentration for the coagulation experiments. The stock suspension was adjusted by diluting it to 138-185 NTU.

The jar test included rapid mixing for 45 seconds, quick stirring for 10 minutes, moderate stirring for 10 minutes, and slow stirring for 10 minutes. The water temperature was between 17 ºC and 19 ºC. The flocculation samples were allowed to settle for 30 min before any measurements were taken. Predetermined doses of 1 mol/L sodium hydroxide (NaOH) were usually added together with polysilicate ferric to provide a proper pH environment that is required for flocculation.

Five jar tests with different dosages from 1 to 5 mL/L of PSiFe were carried out. In each jar the pH was increased by adding sodium hydroxide (NaOH), so there were 5 samples with the same dosage of coagulant and content of kaolin, but with a different pH value. The turbidity and TOC of each beaker was measured after the jar test and then all data were compared to the base kaolin sample as a form of control.

4.5.2 Analysis of the Flocculation Region

After completing five different jar tests with different PSiFe dosages (1-5 mL/L) and different pH values, 30 samples were classified into four categories, (a) visible liquid sample with no perceivable hydrolysis, (b) turbid samples with obvious hydrolysis but no visible flocs, (c) a good sample with good suspended floc but slightly cloudy and no sedimentation, and (d) a clear sample with good flocculation and sedimentation.

The data for each category are shown in Figure 4.20 and illustrates that almost all good performing flocculation samples were form dosage 3 and 4 mL/L of PSiFe, with a pH value between 4 and 7.5. Therefore this area was nominated as the most effective area for flocculation or the flocculation region. The turbid sample with no flocs happened mostly with low doses (i.e. between 1 and 2 mL/L) and low pH (below 5), or high pH (above 8) in different dosages of PSiFe (1-4 mL/L)

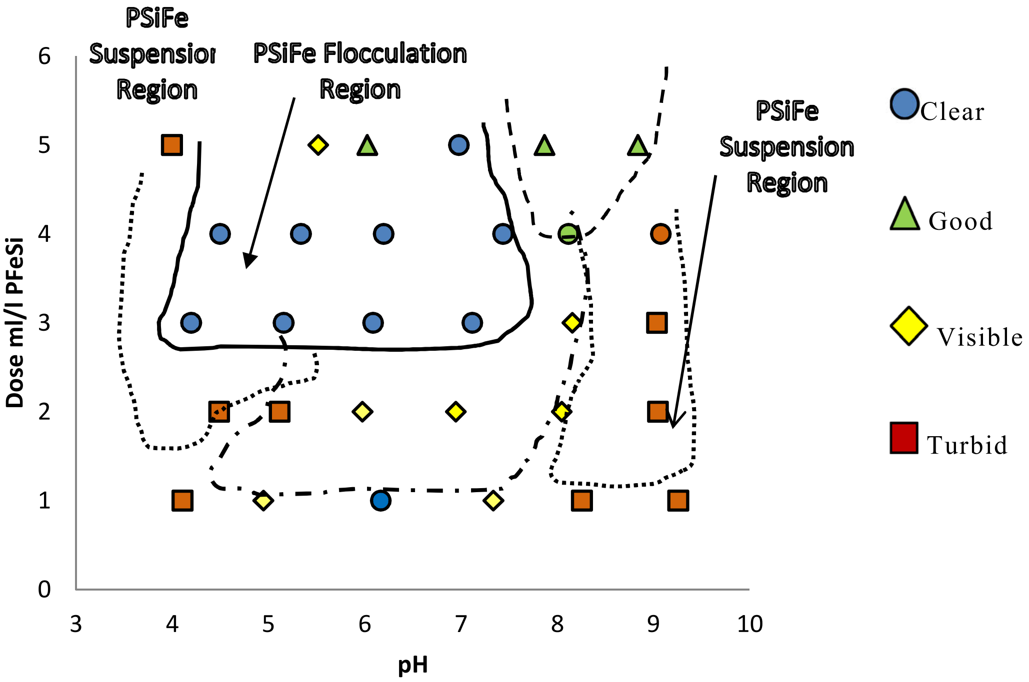


Figure 4.20 Flocculation zone experiment for PSiFe-γ

Apart from a visual check for suitable flocculation in terms of turbidity and TOC removal, Figures 4.21 and 4.22 show that the specific conditions, with low alkalinity and a high dosage of coagulant, improved UV_{254} better, whereas high alkalinity with a moderate dosage of coagulant resulted in a very high turbidity treatment. Generally, the turbidity treatment showed that a high turbidity removal was achieved with a minimum dosage of chemical in a wide pH range. This means that turbidity treatment and hydrolysing of this coagulant is suitable for water contaminated with kaolin clay.

By considering 99.4% of the turbidity removal, it can readily be concluded that during the coagulation process most PSiFe hydrolyses to produce settling precipitates and filterable colloids that can be conveniently removed by any further simple sedimentation and filtration process. After this coagulation/ filtration process, treated water will be ready for further physical or biological treatment. As illustrated in Figures 4.21 and 4.22, PSiFe can work effectively in a wide range of pH, in fact to a large extent this physical treatment process will work operationally and economically. In contrast with turbidity, TOC removal was 43.6% at a slightly acidic pH.

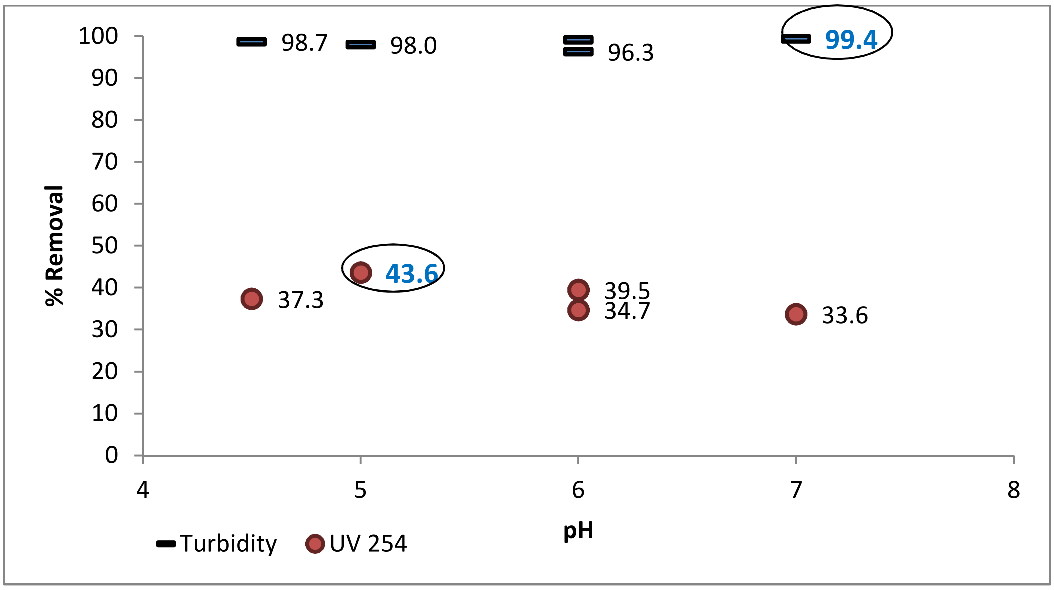


Figure 4.21 Removal of turbidity and UV 254 improvement with 30 mg/l of PSiFe-γ vs pH

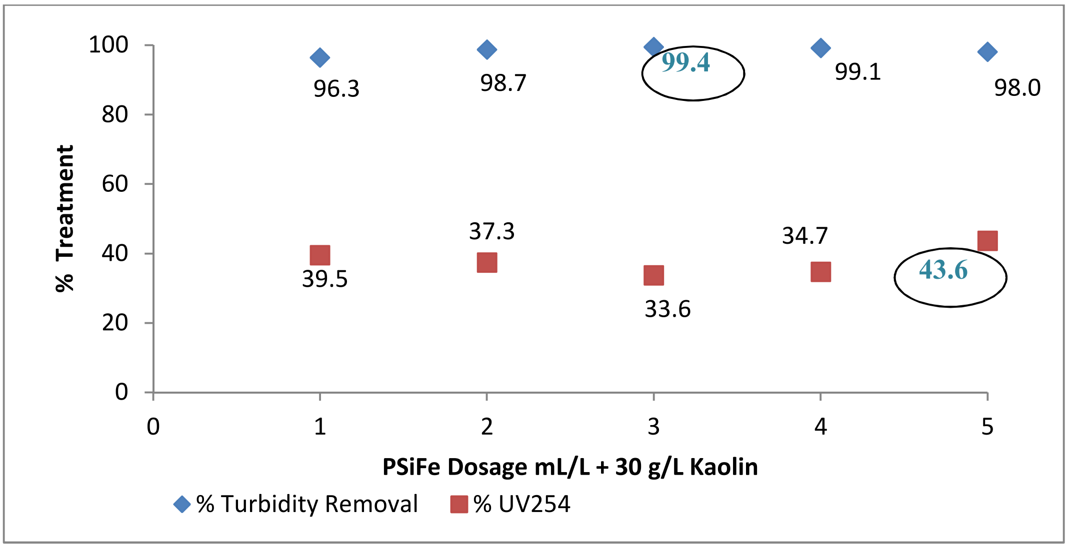


Figure 4.22 Removal of turbidity and UV 254 improvement with different PSiFe dosage

4.6 Bench Scale Coagulation-Membrane System

In this experiment the following bench scale arrangement (Figure 4.23) was prepared to evaluate the effect of pre-coagulation on the efficiency and performance of the membrane. Three coagulants were used, $FeCl_3$, PSiFe-β (traditional preparation method), and PSiFe-γ (ion exchange preparation method).

In this process, all three main wastewater pumps were adjusted for a steady state flow rate of 30 mL/min and the inline coagulation pump was adjusted according to the jar test data for an optimum dose (30 mg Fe^{3+} /L). Accordingly, by considering the area of the hollow fibre membrane, the flux was set to 20 L/m^2.hr.

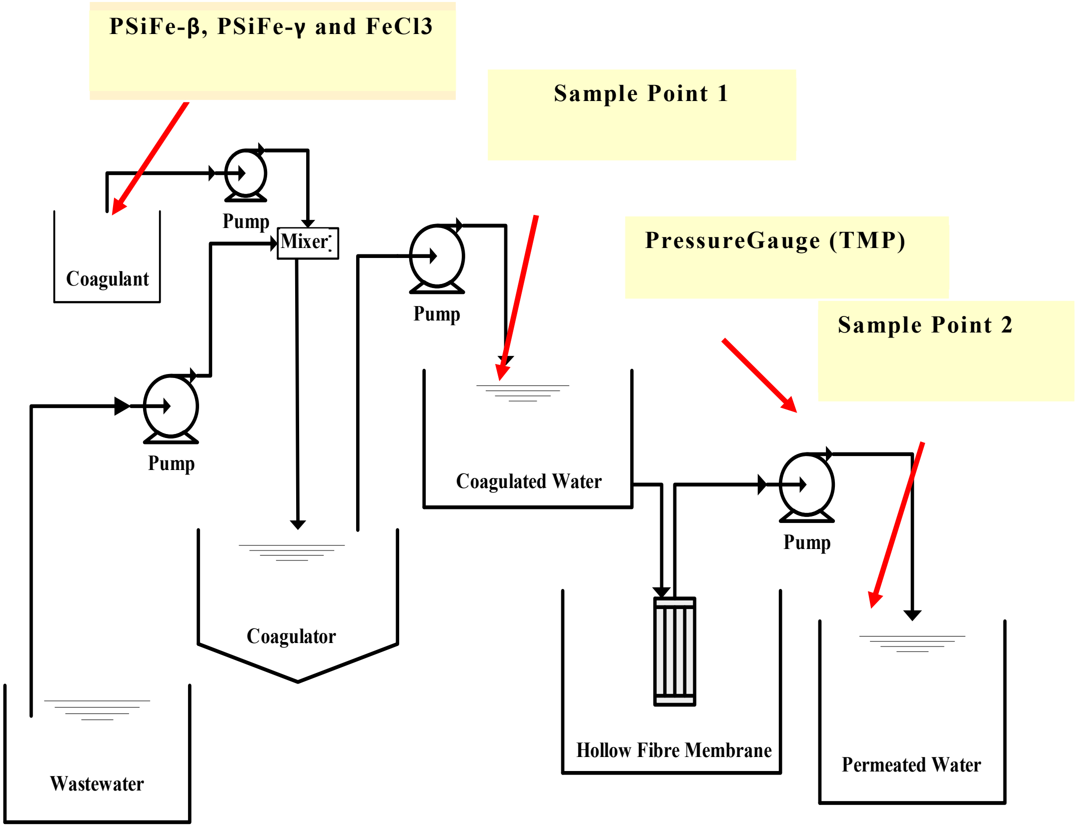


Figure 4.23 Bench scale of coagulation-membrane filtration hybrid system

Three different measurements were performed with the schematic hybrid system experiment shown above, and the results are illustrated in Figure 4.24 to 4.27. They are:

- The critical flow through the membrane was measured by measuring the commutative volumetric flow versus trans-membrane pressure (TMP), by reading the pressure gauge and measuring the filtrated water (L)
- TOC was measured at the end point of the treated water after coagulating with three chemicals and the filtrate, followed by hollow fiber membrane filtration (last sample point)

- TOC and turbidity were measured from two different sample points. The first sample was removed from the coagulated water (sample point 1 in Figure 4.22) and another one was removed from the filtrated water (sample point 2, Figure 4.22)

Figure 4.23 depicts the flow passing through the membrane at trans-membrane pressure (TMP), and since the inlet pressure of the membrane is atmospheric, the pressure at the outlet of the membrane indicates the trans-membrane pressure.

The pretreatment of wastewater before entering the membrane was carried out by an inline injection of the three different coagulants. As Figure 4.24 shows, pretreating with modified PSiFe-γ means more flow through the membrane with a lower outlet pressure than the two other coagulants ($FeCl_3$ and PSiFe-β). A lower pressure drop with a higher flow means better pretreatment and lower fouling on the surface of the membrane.

As Figure 4.24 shows, all three coagulants ($FeCl_3$, PSiFe-β, and PSiFe-γ) had a gradual increase in the rate of TMP up to their critical point, which is a sudden increase with a sharp sole of TMP versus volumetric flow rate. It can be noted that the critical point for PSiFe-γ occurred at a higher volumetric flow with a lower slope than the two other coagulants, and fouling for treated water by pre-coagulation with PSiFe-γ is possibly less than the two other coagulants.

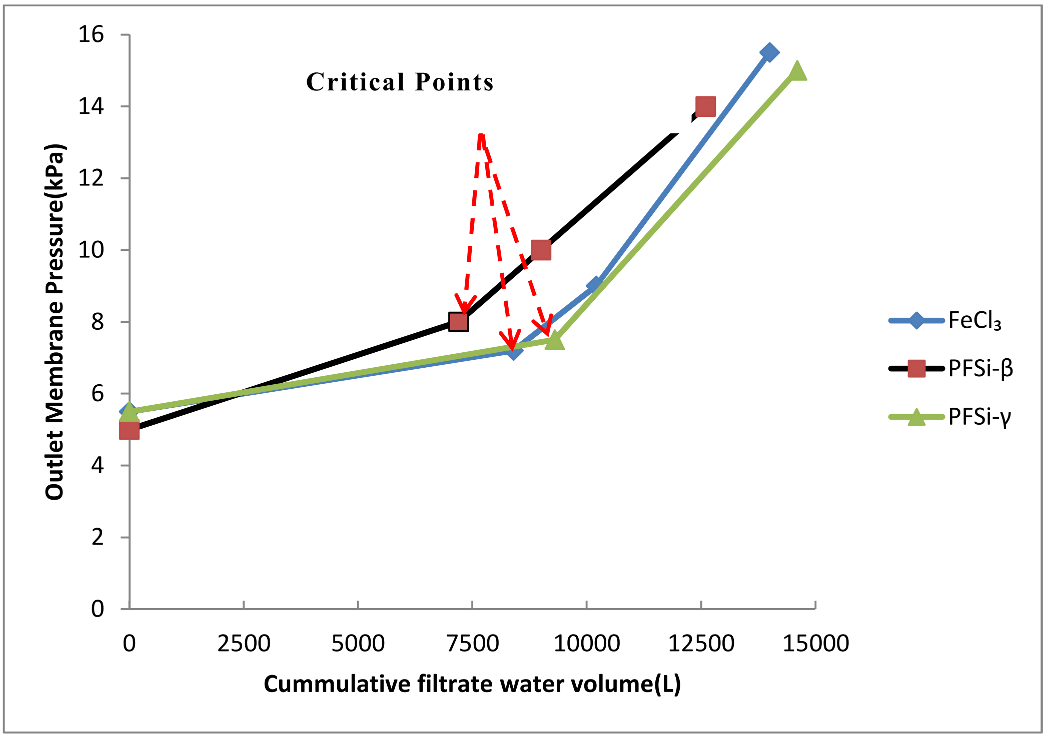


Figure 4.24 Relationship of cumulative treated wastewater with TMP

Figure 4.25 compares the efficiency of UV_{254} removal after membrane treatment. Based on the data presented in Figure 4.24, PSiFe-γ has a higher TOC removal up to a specific volume of 12400 L, but after reaching this point, PSiFe-β and $FeCl_3$ showed better TOC removal than the target coagulant, PSiFe-γ.

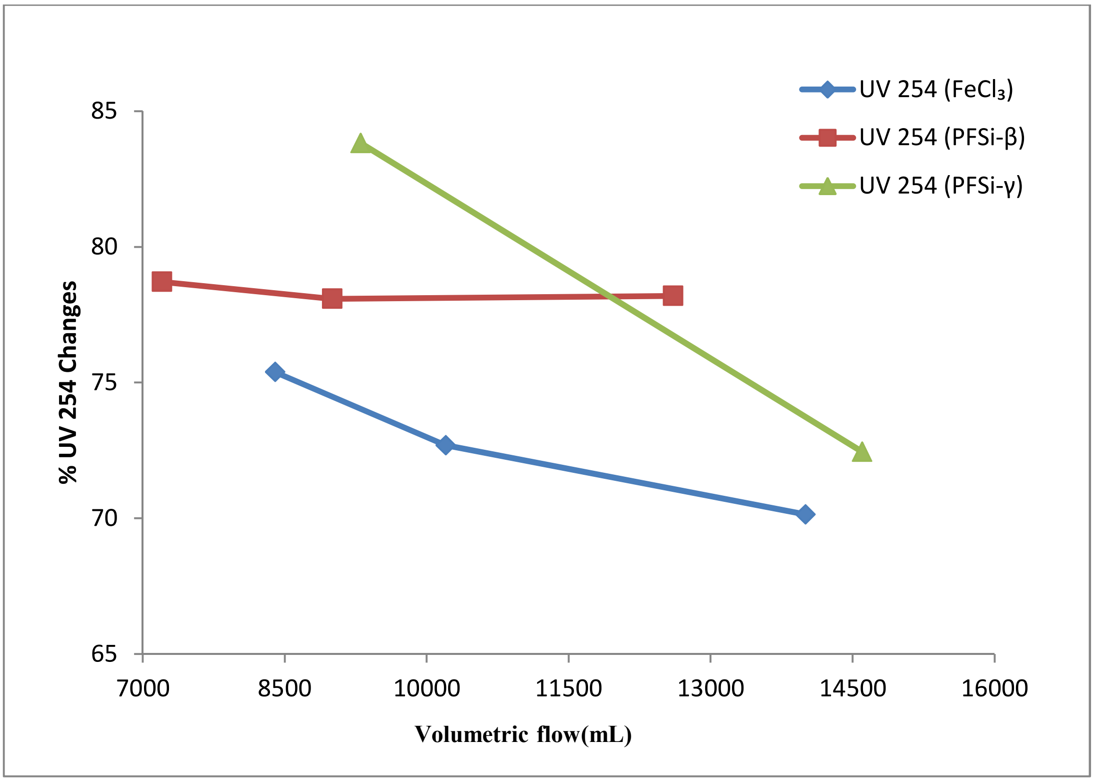


Figure 4.25 UV 254 Changes during the membrane treatment

Figure 4.26 shows the effect of pre-coagulation with two types of PSiFe on the membrane turbidity load. Two series of column charts represent the measurement of turbidity t before and after a membrane process was used. As Figure 4.26 shows, PSiFe-γ removed more turbidity before the membrane process than PSiFe-β, and better treatment of the coagulant before the membrane process resulted in less turbidity load on the membrane. The improvement in turbidity for PSiFe-γ through the membrane was 5.41% (77.49%-74.08%), and 14.65% (79.49%-64.84%) for PSiFe-β.

It can be concluded that this load direct affects the durability and performance of the membrane and consequently the quality of the water.

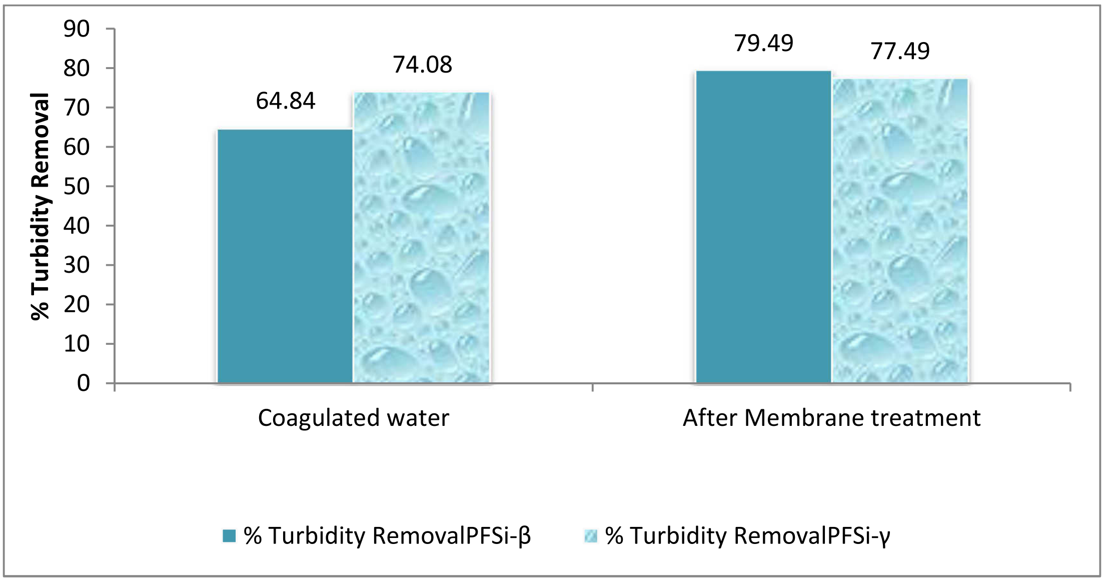


Figure 4.26 Effect of PSiFe pre-coagulation on membrane turbidity load

The same interpretation can be applied for Figure 4.27. The TOC treatment load on the membrane by PSiFe-β pre-coagulation was 19.4%, whereas this figure was 11.98% for PSiFe-γ, and hence more TOC load means the membrane process is not as efficient or durable.

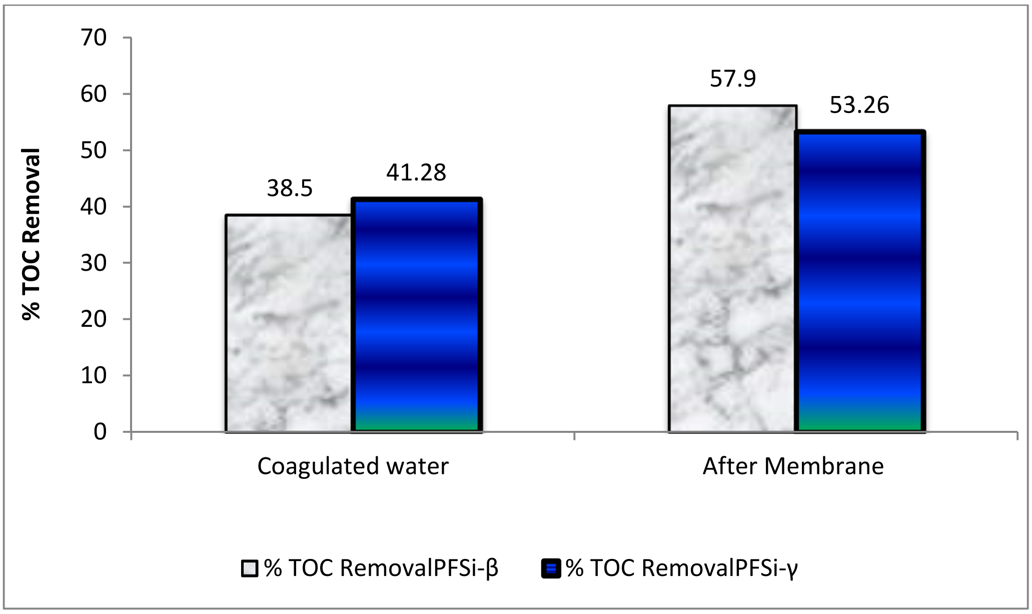


Figure 4.27 Effect of different types of PSiFe pre-coagulation on membrane TOC load

4.7 Phosphate Treatment in Raw Water

This study was performed based on jar tests using raw water in order to determine how effectively PSiFe coagulant (old and new methods) and $FeCl_3$ could remove phosphate in raw water.

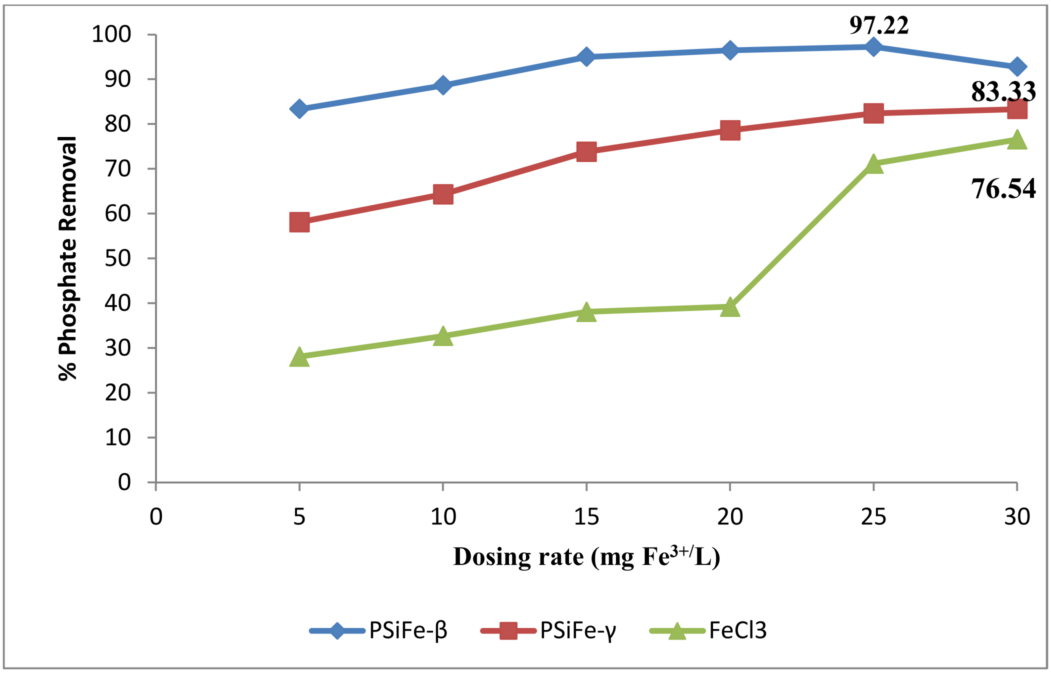
Five different doses of coagulant (5-30 mg Fe^{3+}) were injected into 1 L of raw water in each jar and then the phosphate content of the treated water was compared with raw water.

The results revealed that PSiFe-β had a higher phosphate treatment in raw water than PSiFe-γ with 83.33% and $FeCl_3$ with 76.54%, as shown in Figure 4.28.

According to Yang et al. (2009), there are two reasons for these results; first, phosphates carrying negative charges can be removed by adsorption charge neutralisation in the coagulation process, and second, PSiFe has a relatively large specific surface area, high surface free energy, and an extremely strong adsorption activity. Apart from the charge adsorption of PSiFe for phosphorus, there is another exclusive adsorption which does not regard its surface charges and whose adsorption activity is much stronger than the electrostatic attraction of $FeCl_3$. This is why completely dissolved phosphorus can be removed by coagulation with only a specific dose of PSiFe.

FeO is one of the component components of PSiFe, which contains rich hydroxyl, and provides a suitable surface area and an extremely strong adsorption activity.

According to Yan-Ling et al. (2009), the structure is suitable for adsorption bridging where under a neutral condition the surface of a particle carries positive electric charges, which is advantageous when removing the phosphates that carry negative charges in the water. The mechanism of effective coagulation for removing phosphorus is the combined results of adsorption, electric neutralisation, and adsorption bridging. Because PSiFe-γ has higher positive charge on the surface than PSiFe-β it was expected to remove more phosphate, but the results in Figure 4.28 show there was 14% more phosphate removed by PSiFeβ than PSiFe-γ.



4.28 Phosphate removal in raw water with different coagulant

4.8 Modified Fouling Index (MFI) Test

The MFI was established by Schippers and Verdouw (1980) to evaluate the membrane fouling mechanism and it has become the most widely applied method.

Equation 4.1 shows the definition and calculation of MFI. The experiment with MFI was similar to the silt density index (SDI). In the filtration period the volume of filtrate was monitored and recorded every 20 s. By proposing a linear relationship between the inverse of flow and the volume of filtrate, the MFI can be solved (Hsing Chuang et al., 2007).

$$\frac{1}{Q} = a + MFI * V$$

(Equation 4.1)

Where Q denotes the flow rate (L/s); the parameter “a” is a dimensional constant (s/L) and V is the filtrate volume (L). Therefore, if we sketch the diagram of volume (L) and time /volume (s/L), the slope of this linear diagram will represent the MFI.

This diagram was initiated by the computerised work station, as shown in Chapter 3, Section 3.3.7. The phenomena of the fouling potential of synthetic water before and after coagulation with three different coagulants (PSiFe-γ, PsiFe-β, and $FeCl_3$) are shown in Figures 4.29 to 4.32.

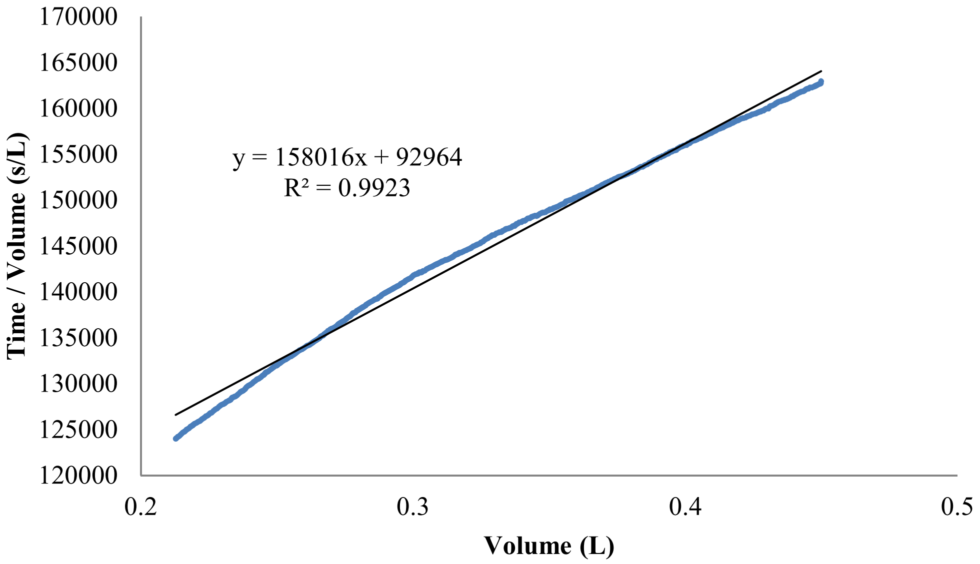


Figure 4.29 MFI diagram for wastewater before coagulation

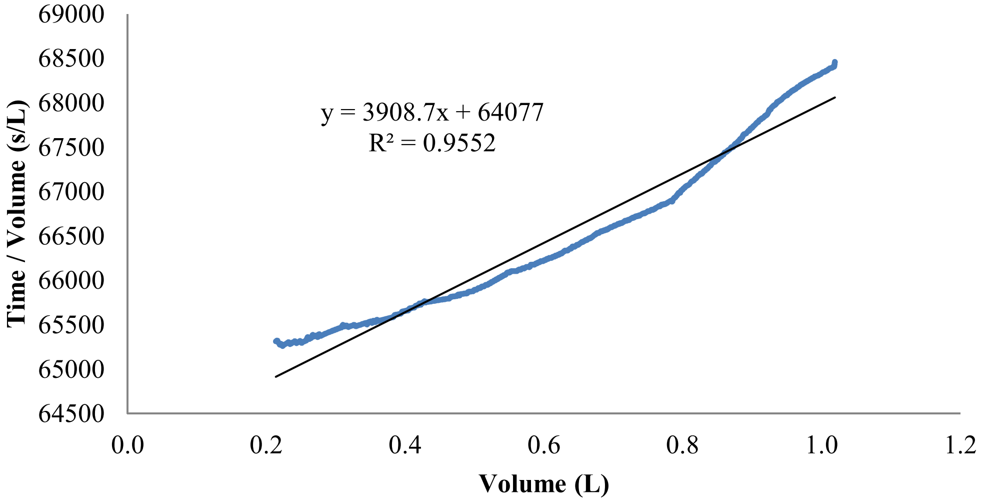


Figure 4.30 MFI diagram of coagulated wastewater with PSiFe-γ

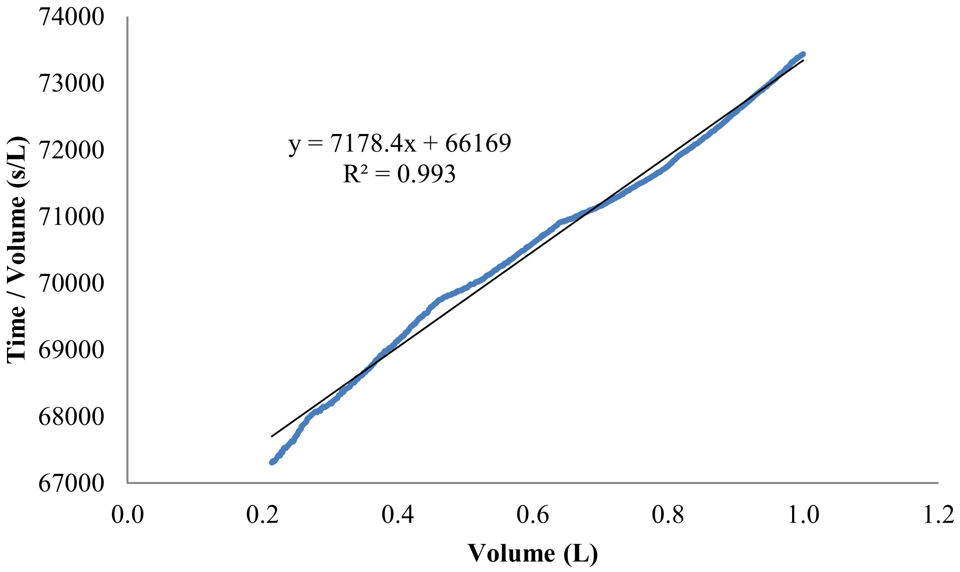


Figure 4.31 MFI diagram of coagulated wastewater with PSiFe-β

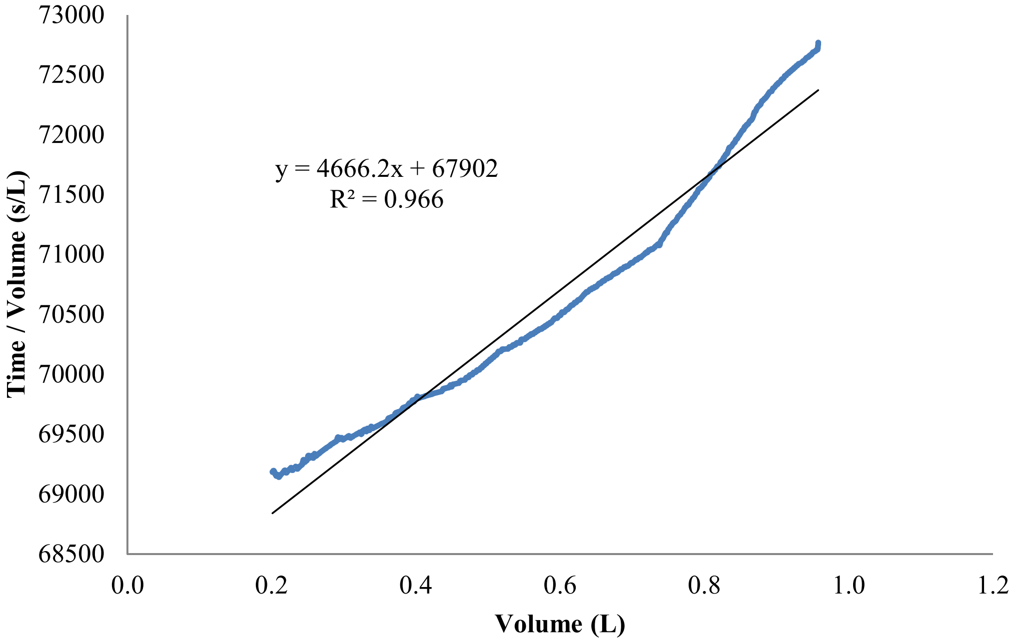


Figure 4.32 MFI diagram of coagulated wastewater with $FeCl_3$

The results showed that coagulation led to a significant decrease of UF-MFI. According to the comparison chart (Figure 4.33), the MFI was reduced about five times from 15,8016 s/L^2 in wastewater to 3908.7 s/L^2 of coagulated water with PSiFe-γ, This index was 7178.7 s/L^2 for PSiFe-β and 4666 s/L^2 for $FeCl_3$.

Ferric chloride had a better MFI than PSiFe-β, but the modified polysilicate ferric presented the best results of all of the coagulants.

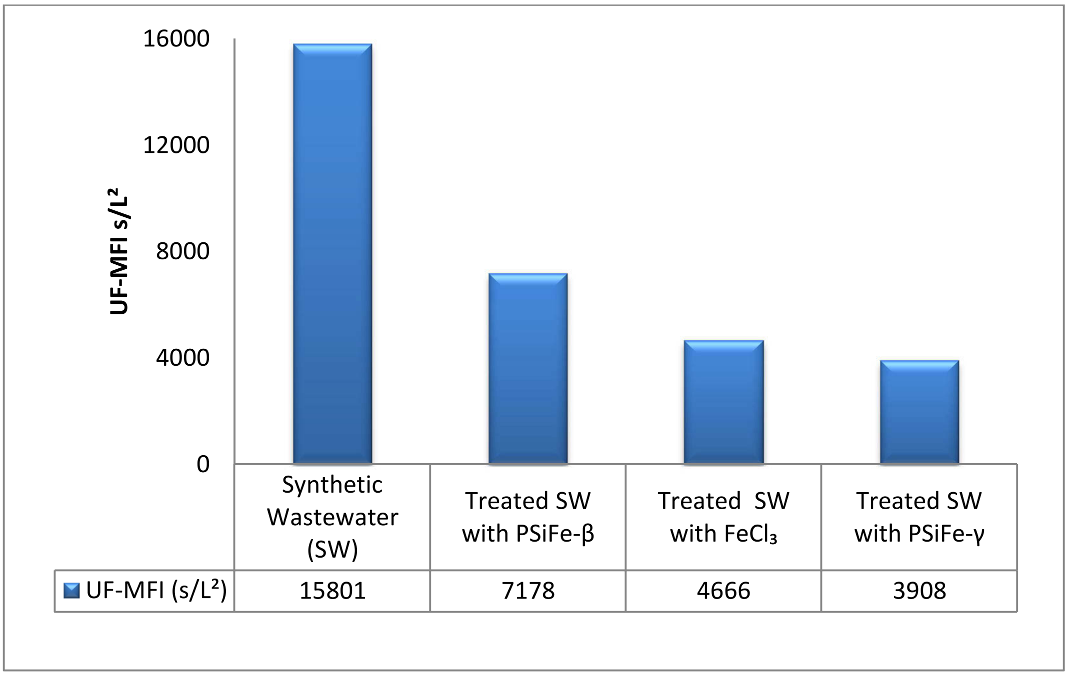


Figure 4.33 MFI comparison charts of wastewater and different coagulated wastewater

4.9 Further Evidence for the Effectiveness of the PSiFe-γ Coagulant

The newly improved coagulation reagent PSiFe-γ developed in this study was used by Jeong (2013) in laboratory scale experiments at the University of Technology, Sydney. He conducted jar test experiments for the coagulation of seawater, followed by a submerged membrane hybrid system (SMCHS) treatment. He reported that both PSiFe-γ and $FeCl_3$ were effective in removing dissolved organic compounds in seawater. However higher removal of turbidity and DOC were obtained with lower doses of PSiFe-γ (1.2 mg/L as Fe^{3+}) compared to $FeCl_3$ (3 mg/L as Fe^{3+}).

In particular, hydrophilic compounds were removed more effectively by PSiFe-γ. It emerged that approximately 55% of hydrophilic compounds in seawater was removed by PSiFe-γ (1.2 mg Fe^{+3}/L). It was observed that polysilicate based coagulant (PSiFe-γ) produced smaller size but larger amounts of flocs than FeCl3. The results reported by Jeong (2013) indicated there was more fouling on the surface of the MF membrane with a lower critical flux when PSiFe-γ was used as a flocculant.

4.10 Summary:

From the experimental program of this study the following concluding remarks can be drawn:

- When sodium metasilicate solution passed through an ion exchange resin, polymerisation occurred without the presence of sodium ion and it will improve polymer aggregation. Before adding Iron (III), increasing the temperature of the solution, controlling the pH, and ageing the solution for a certain number of hours, increased the molecular weight of the final polymer. The evidence shows that soon after polymerisation, adding iron (III) to the interaction of positive iron with negative and a large surface area of poly salicic acid caused aggregation under a hyroxy-ferric polymeric bridge
- Although the chemistry and moleculare size of aluminum is more suitable for further aggregation, the high risk factor of ammonia in some specific diseases meant that iron was the preferred choice, because it is a more environmentally friendly metal than aluminum
- Of the different Si/Fe molar ratios of PSiFe, a ratio equal to one had the optimum effect on the coagulation in wastewater and raw water, i.e. turbidity, TOC, and phosphate removal

- According to the kaolin clay experiment, PSiFe-γ could induce an effective flocculation region in a slightly acidic environment with doses comparable to the conventionally used coagulant. This coagulant could be an alternative coagulant in low alkaline water and wastewater treatment
- In the bench scale membrane hybrid system, using PSiFe-γ for pre coagulation process can improve the removal of turbidity by up to 77.5%, TOC up to 41.28%, and consequently we can experience higher critical trans-membrane pressure. Lower turbidity and TOC at the inlet water to the membrane and higher critical trans-membrane pressure at the outlet of the membrane, directly affect the performance of the membrane and consequently the quality of the final treated water
- Poly silicate ferric coagulants (β and γ) had a significant effect on the removal of phosphate in raw water (97.22% and 83.33%, respectively), compared to $FeCl_3$, which was 76.52%.
- In modified fouling tests (MFI) the results showed that PSiFe-γ had fewer tendencies towards fouling in coagulated water, and $FeCl_3$ and PSiFe-β were in the next steps of potential fouling
- Based on jar test experiments with seawater, followed by a submerged membrane hybrid system using PSiFe-γ, Jinog

(2013) provided further evidence for the effectiveness of the coagulant agent developed in this study. He found that more turbidity can be removed and DOC could be more efficient with lower doses of PSiFe-γ (1.2 mg/L as Fe^{3+}) than with $FeCl_3$ (3 mg/L as Fe^{3+}).

.

Chapter 5

Conclusions and Recommendations

5. Conclusions and Recommendations

5.1 Summary

The ever increasing demand for expanding water supplies has driven the need for more technologically cost effective wastewater treatment process to reuse treated water. Low pressure membrane technologies to remove particulates, organic matters and other contaminants from wastewater sources continue to be a widely used technology. Indeed membrane systems to treat water and wastewater have already performed extremely well against conventional systems, even though membrane fouling remains one of its most serious challenges.

Since the fixed and operating cost of membrane technology is higher than the common treatment practice, pre-treatment of wastewater is considered to be one of the most effective means of reducing membrane fouling and the cost of operating the membrane process. Of all the pre-treatment processes, coagulation is a suitable technology to remove most of the membrane foulants.

Relevant research is currently focused on the development of new and inexpensive coagulants, but the tendency in this field nowadays is to produce modified composite coagulants, which are becoming more complicated.

A characteristic example is poly silicate ferric (PSiFe), a relatively new pre polymerised inorganic coagulant. In this research, PSiFe was prepared under different Si/Fe molar ratios using two approaches: (a) acidification of sodium silicate by hydrochloric acid and the addition of iron as a common procedure for this polymer (PSiFe-β), and (b) acidification by strong acidic ion exchange resin (PSiFe-γ). The pH control, ageing, and heating procedure were used to improve the coagulation property, which can be changed in terms of its surface charge, polymer area, and molecular weight.

The coagulants prepared were characterised in terms of impurity and polymer morphology. Furthermore, the effects of different Si/Fe molar ratios have been investigated in regard to the destabilisation of colloids, the removal of organic matters (particulate and dissolved), and turbidity.

Different Si/Fe ratios were analysed based on jar tests in order to find the optimum ratio and dose. The outcomes of these series of experiments revealed that Si/Fe=1 was the best ratio and 30 mg/L Fe^{3+} was the best dose of the target coagulant (PSiFe-γ). Furthermore, the coagulation of PSiFe-γ (Si/Fe=1) was assessed by studying the reduction in the turbidity of kaolin clay model suspensions and removal of phosphorous in water.

The performance of the modified PSiFe-γ was investigated on a bench scale in line with the coagulation-membrane; and its performance was compared with other common coagulants including PSiFe-β and $FeCl_3$. The findings of this study suggest that PSiFe-γ removed more turbidity and significantly reduced the tendency of the membrane towards fouling.

Based on the detailed results presented in Chapter 4, the main outcomes and suggestions of this research are outlined in the following section.

5.2 Conclusions

5.2.1 Preparation methodology and coagulation efficiency of PSiFe-γ

The preparation of poly-silicate ferric with ion exchange resins instead of acidification by acid, and other factors such as the concentration of silica, pH control, and heating, can help to improve the specification of PSiFe-γ as a modified coagulant.

Silica has a complex structure. The degree of polymerisation, surface and molecular weight of silica can be varied by several factors such as the dilution of silicate, heating, ageing, and control of the pH.

Using an ion exchange resin for polymerisation by diluted sodium silicate, besides heating, ageing, and control of the pH was the preferred procedure to have an efficient coagulant with high molecular weight, high charge, and great absorption capacity in order to reduce the level of some impurities in wastewater.

Monomer can be removed from a solution by strong ion-exchange resin. Another indication is that polysilicic acid by ion exchange has more silanol grouped (Si-O-H) on the surface than the acidification method (Iler, 1979). The ionisation constants of acid on the polysilicic acid surface were at least two or three orders of magnitude higher than the constant of monomeric Si (OH).

Having a smooth flow and clear solution as water, free of soluble salts, and manifesting the mean particle diameters and specific surface area of the silica could be achieved by removing the sodium through ion exchange resins. The substitution of H^+ by a three valiant ion metal such as Fe^{3+} at the next step permitted the attainment of sols with larger particles (Bechtold, 1951).

Other factors such as dilution, ageing, and heating to a temperature greater than 60ºC, caused the diameters of the dispersed phase to increase, which was followed by the addition of iron to the solution at a rate slow enough to increase the surface area. The possibility of controlling the growth of the silica colloidal particles when preparing the stabilised silica solution is reachable by regulating the pH.

5.2.2 Effect of Si/Fe in the Efficiency of the Treatment

It was found that the modified PSiFe-γ at a higher Si/Fe ratio in higher doses has better turbidity and TOC removal performance. This coagulant improved the turbidity and TOC removal through an enhanced adsorption bridging mechanism. The treatment process at Si/Fe=1 had a high turbidity and a TOC removal of 93.62% and 74.06%, respectively. The results for Si/Fe=0.2 and Si/Fe=0.5 were not at a satisfactory level. The correlation between the zeta potential of flocs formed by PSiFe-γ and the changing phenomena of zeta potential varied with different Si/Fe ratios. The greatest removal performance and zeta potential were achieved, when the pH was between 5.3 and 5.7.

5.2.3 Effectiveness of PSiFe-γ in Kaolin Clay Water

The performance of PSiFe-γ appeared to be suitable enough for enhanced coagulation, and for treating water contaminated with kaolin in a low acidity source. Poly silicate ferric could induce effective flocculation in a natural and slightly acidic environment. The PSiFe-γ coagulant was hydrolysed readily when the dosage exceeded 3 mL/L. This flocculation region (i.e. pH 4-7) was practiced to remove all the organic materials (up to 99.4%). In this experiment the maximum TOC removal was 43.6% at pH 5. Since the performance of flocculation depends on the quality of the water, the flocculation region of PSiFe-γ might be different for water bodies with complex impurities.

5.2.4 Pre-coagulation Process and Lower Membrane Load

Without the coagulation of impure water to remove its TOC and turbidity, the load on the membrane system was high. Hence there was a high potential for reaching the critical flow and rapid membrane fouling by organic or particulates matters. The results indicated that when using the modified PSiFe-γ the critical flux was higher than the common PSiFe-γ and ferric chloride coagulants.

A significant amount of turbidity and TOC was removed through treatment with both coagulants (PSiFe-γ and $FeCl_3$). However, the load of turbidity on membrane filtration was reduced by 74% when PSiFe-γ was applied in the coagulation process compared to 64% for $FeCl_3$ coagulant.

The modified fouling index (MFI) tests highlighted the effectiveness of coagulation using the modified PSiFe-γ as the preferred coagulant for decreasing the tendency of membrane fouling. In other words, membrane fouling was significantly higher when feed water used without any coagulation, compared to a situation where the feed ware to the system went through a pre-treatment process using either PSiFe-γ or $FeCl_3$. However, the critical flux was 10000 units using PSiFe-γ in the pre-treatment process, whereas this value was 7500 units employing ferric chloride.

5.2.5 Optimum pH Region in Wastewater Coagulation

The modified PSiFe had a suitable coagulation performance in slightly acidic pH in the optimal region for PSiFe coagulation in wastewater and other contaminated water. The PSiFe-γ coagulant had a low pH which made its TOC removal better in a moderate dose. Depending on the type of coagulant and contaminated water, regions with a different pH for optimal coagulation can be identified. The optimum pH for PSiFe-γ based coagulant was between pH 5 and pH 7.

5.2.6 Comparison of PSiFe-γ with $FeCl_3$ Coagulant in Wastewater

In the hybrid membrane treatment, both poly silicate ferric and iron chloride can be used in wastewater coagulation as a pre-treatment process. However, the experimental results indicated that PSiFe-γ performed better in removing turbidity, while iron chloride was slightly more efficient in TOC removal.

According to these results, both the PSiFe-γ and $FeCl_3$ coagulants could be applied in the pre-treatment process for membrane systems. All the coagulants tested efficiently removed turbidity and TOC. However, PSiFe-γ may have an advantage compared to ferric chloride with a 10% better removal of turbidity, while producing larger flocs at lower doses.

In contrast, iron chloride was 2.8% more efficient at TOC removal than PSiFe-γ.

5.2.7 PSiFe-γ performance in Removing Phosphorous from Water

The coagulation-flocculation process, using modified PSiFe-γ, showed its excellence at treating phosphorous in raw water. A high removal of phosphorous (99.22%) was achieved by the modified PSiFe-γ compared to common PSiFe-β (83.33%) and $FeCl_3$ (76.54%).

5.3 Recommendations

This section presents some recommendations for further studies and examinations that might emphasise the efficiency of this polymeric coagulant (PSiFe-γ) in the treatment of water and wastewater. The recommendations for future studies in this area are as follows:

5.3.1 Short Flocculation Process

The addition of coagulant before the mixer with a short flocculation (short distance to the membrane vessel) can be another alternative for conducting a similar study. The chosen flocculation time cannot be equal to the actual flocculation step, for instance, a short pipe flocculator can be an option. For this coagulant, a shorter time of flocculation may give better results.

5.3.2 Evaluating the Effect of Temperature

Most membrane systems perform better at higher temperatures, so introducing feed water at higher temperatures to the membrane system can be topic for further study. In fact, only recently, an industrial scale heat exchanger with a low duty was added before membrane treatment.

5.3.3 Employing Membrane Air Pulsation

As the flocs formed by PSiFe-γ were larger than those in the other coagulants, some of them remained on the surface of the membrane. It seems that a physical shock by compressed air to reverse the direction of flow, could improve the efficiency and durability of the membrane.

5.3.4 Extending the Pre-treatment

The coagulation-membrane hybrid system can be extended by adding a sand and active carbon filtration, as shown in Figure 5.1, in order to find the impurity load on membrane filtration after completing physical treatments. All these systems have lower operational and fixed costs than the capital membrane and operational costs.

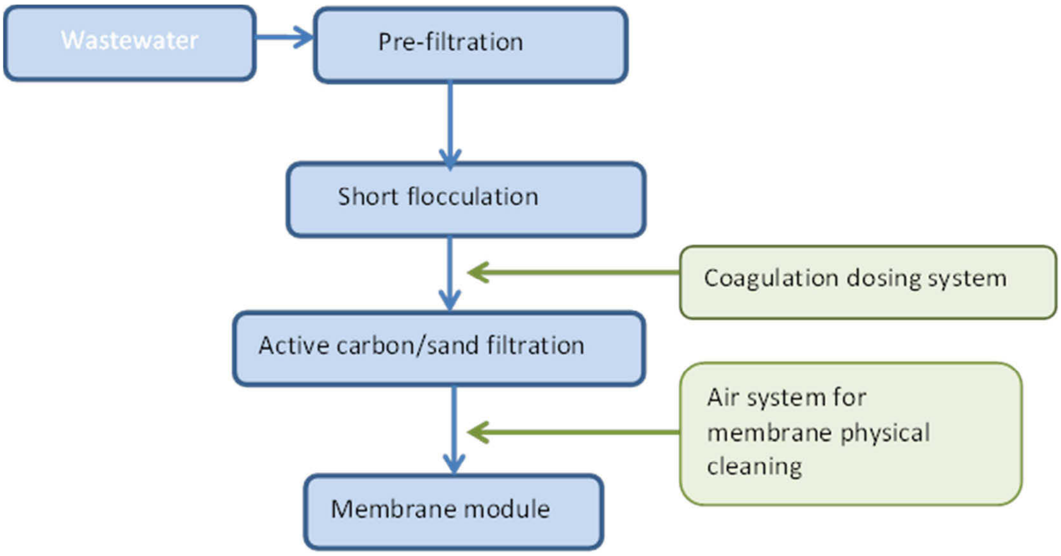


Figure 5.1 Suggested scheme for a bench scale coagulation/ membrane/ filtration hybrid system

5.3.5 Ferron Experiment for Polymerisation Rate

A Ferron experiment on prepared and dried PSiFe-γ coagulant is recommended to measure the rate of polymerisation and to investigate the hydrolysing mechanism of this type of modified coagulant. The impact of silica in the polymerisation degree and the iron species distribution can be investigated by this method.

5.3.6 Measurement of the flocs size and settling time in coagulation

Since the bigger flocs have fewer tendencies to stick on the surface of the membrane and the removing of the big flocs is easier than fine particle, it is recommended to have an investigation on this matter and find its effect on coagulation membrane system

5.3.7 Economic impact analysis

A simple economic impact analysis of the various polymeric and metal based coagulants can be a suitable to have a precise analysis among the technical factors.

REFERENCES

Adham, S. S., V. L. Snoeyink, M. M. Clark, J. -L. Bersillon. (1991). Predicting and Verifying Organics Removal by PAC in an Ultrafiltration System. Journal of American Water Works Association, 83 (12): 81.

Adham, S. S., V. L. Snoeyink, M. M. Clark, C. Anselme. (1993). Predicting and Verifying TOC Removal by PAC in Pilot-Scale UF Systems. Journal of American Water Works Association, 85 (12): 58.

Adham, S., Chiu, K. P., (2005). Development of a Microfiltration and Ultrafiltration Knowledge Base. Denver, American Water Works Association.

Adin, A. and C. Klein-Banay. (1986). Pretreatment of Seawater by Flocculation and Settling for Particulates Removal. Desalination, 58 (3): .227-242.

Adin, A., Soffer, Y. Ben Aim, R., (1998). Effluent Pretreatment by Iron Coagulation Applying Various Dose-pH Combinations for Cptimum Particle Separation. Water Science and Technology, 38: 27-34.

Akers, C.K., Parsons, D.F., (1972). Reply to Myelin Membrane Structure As Revealed by X-Ray Diffraction by David Harker. Biophysical Journal, 12 (10): 1296-1301.

Alexander G.B., (1956), Process for Producing Sols of 5-8 milimicrons silica Particles and Product, (Du Pont), US Pat. 2.750.345.

Anthlmi, D., B. Cabane, M. Meireles, P. Aimar. (2001). Cake Collapse in Pressure Filtration. Langmuir ,17: 7137–7144.

AWWA (1999). Water Quality and Treatment: A Handbook of Community Water Supplies. Fifth Edition. McGraw-Hill, Inc. Washington,D.C.

AWWA, American Water Works Association. (2005), Denver, C. Microfiltration and Ultrafiltration Membranes for Drinking Water, ISBN-10: 1583213600 1st Edition.

Bache, D.B., Gregory, R., (2007). Flocs in Water Treatment, IWA Publishing, London,UK.

Baig, M. B., Al-Kutbi. A., (1999). Design features of a 20 mgd SWRO Desalination plant, Al Jubail, Saudi Arabia. Water Supply, 17 (1), 127-134.

Baker, R.W. (2004). Membrane Technology and Applications. John Wiley and Sons Ltd. ISBN: 978-0-470-85445-7 191-196. 2nd edition.

Belfort, G., Davis, R. H. and Zydney, A. L. (1994). Behaviour of Suspensions and Macromolecular Solutions in Crossflow Microfiltration. J. Membrane Science, 96: 1-58.

Betchold M.F., Synder O.E., (1951), Chemical processes and composition, (Du Pont), US Pat 2.574.902.

Bi, S., Wang, C., Cao, Q. and Zhang, C., (2000). Studies on the Mechanism of Hydrolysis and Polymersation of Aluminium Salts in Aqueous Solution: Correlations Between the Core-links Model and Cage link Model. Coord Chem., 248: 441-445.

Bian, R., Y. Watanabe, G. Ozawa, N. Tambo. (1997). Removal of Natural Organic Matters, Iron and Manganese by Ultrafiltration with Coagulation. Journal of Japanese Water Works Association, 66 (4): 24–33.

Bian, R., Y. Watanabe, G. Ozawa, N. Tambo. (1999). Removal of Humic Substances by UF and NF Membrane Systems. Water Science and Technology, 40 (9): 121–129.

Bonnelye, V., Angel, M., Durand, S.J, Ludovic, Gueguen, Pierre, F., (2004). Reverse Osmosis on Open Intake Seawater: Pre-treatment Strategy. Desalination, 167: 191-200

Bonnélye, V., Guey, L., Castillo, J., (2008), UF/MF as RO Pre-treatment: Desalination, 222 (1-3), 59-65.

Boerlage, S.F.E., Kennedy, M.D., Aniye M.P., Abogrean E., Taraewneh, Z.S. and Schippers, J.C. (2003). The MFI-UF as a Water Quality Test and Monitor. Journal of Membrane Science, 211: 271-289.

Bottino, A., Capannelli, C., Del Borghi, A., Colombino, M., Conio, O. (2001). Water Treatment for Drinking Purpose: Ceramic Microfiltration Application. Desalination., 141 (1): 75-79.

Brauns, E., E. Van Hoof, B. Molenberghs, C. Dotremont, W. Doyen, R. Leysen. (2002). A new Method of Measuring and Presenting the Membrane Fouling Potential. Desalination, 150 (1): 31-43.

Bratby, J., (2006). Coagulation and fFocculation in Water and Wastewater Treatment, Second Edition, IWA, London.Bureau of Reclamation.

Cabane, B., M. Meireles, P. Aimar. (2002). Cake Collapse in Frontal Filtration of Colloidal Aggregates Mechanisms and Consequences. Desalination, 146: 155–161.

Carroll, T., S. King, S. R. Gray, B. A. Bolto, N. A. Booker. (2000). The Fouling of Microfiltration Membranes by NOM after Coagulation Treatment. Water Research, 34: 2861–2868.

Chan, S.H., (1989). A review on Solubility and Polymerisation of Silica. Geothermics, 18, 49-56.

Cheng, P.C., Chi, F.G., Yu, R.F., Shi, P.Z., (2005). Evaluating the Coagulants of Polyaluminium Silicate Chlorides on Turbidity Removal. Separation Science & Technology, 41, 297-309.

Chinu, K., Johir A. H., Vigneswaran S., Shon, H. K., Kandasamy, J., (2010). Assessment of Pretreatment to Microfiltration for Desalination in Terms of Fouling Index and Molecular Weight Distribution. Desalination ,250: 644-647.

Cho, M.H., Lee, C.H., Sangho Lee, Cho, M. K., C. H. Lee, S. Lee. (2006). Effect of Flocculation Conditions on Membrane Permeability in Coagulation-Microfiltration. Desalination ,191: 386-396.

Choi, K. Y. J., B. A. Dempsey. (2004). In-line Coagulation with Low Pressure Membrane Filtration. Water Research ,38 (19): 4271-4281.

Choi, H., Zhang, K., Dionysiou, D.D.,Oerther, D.B, Sorial, G.A. (2005). Effect of Permeate Flux and Tangential Flow on Membrane Fouling for Wastewater Treatment. Separation and Purification Technology, 45: 68-78.

Chua, K. T., M. N. A. Hawlader, A. Malek. (2003). Pretreatment of Seawater: Results of Pilot Trials in Singapore. Desalination, 159: 225.

Combe, C., Molis, E., Lucas, P., Riley, R., Clark, M. (1999). The Effect of CA Membrane Properties on Adsorptive Fouling by Humic Acid. J. Membrane. Science, 154: 73-87.

Crittenden, J., Trussell, R., Hand, D., Howe, K., Tchobanoglous, G., (2005). Water Treatment Principle and Design. John Willy and sons, 54 -55: 513-514.

Crozes, G.F., Jacangelo, J.G., (2001). Low Pressure membrane Filtration for Pathogen Removal: Application, Implementation, and Regulatory Issues, United States Environmental Protection Agency.

Dahm, K.G.; Guerra, K.L.; Xu, P.; Drewes, J.E., (2011). Composite Geochemical Database for Coalbed Methane Produced Water Quality in the Rocky Mountain Region. Environmental Science. Technol, 151 (1): 67-73.

DeWolfe, J., Dempsey, B., Taylor, M. and Potter, J. W., (2003). Guidance manual for coagulant changeover. American Water Works Association Press. Denver, 25-59.

Dietzel, M., (2000). Dissolution of Silicates and the Stability of Polysilicic Acid. Geochimical Acta, 64: 3275-3281.

Edzwald, J., Tobiason, J.E., (1999). Enhanced coagulation: US requirements and a broader view Original Research Articl.e, Water Science and Technology, 40 (9): 63-70.

Escobar, I.C., Sharp, M.M., (2000). Effect of Different Modes of Coagulation as Pretreatment to Membrane Filtration for Drinking Water Production in Small Systems. Department of Chemical and Environmental Engineering, University of Toledo.

Everett, D.H., (1972). IUPAC, Definitions, Terminology and Symbols on Colloid and Surface Chemistry, Journal of Pure and Applied Chemistry, 31: 579-638.

Falten. T. P., (2001). Aluminum as a Risk Factor in Azheimer's Disease, with Emphasis on Driniking Water. Brain Research Bulletin, 55: 187-196.

Fane, A.G., Schäfer, A.I., and Waite, T.D. (2005). Nanofiltration: Principles and Applications. Elsevier Ltd., NY.

Flaten, T.P., (2001). Aluminium as a risk factor in Alzheimer's disease, with emphasis on drinking water Review Articl. Brain Research Bulletin, 55 (2): 187-196.

FU, Y., YU, Z., QIU, L., HUI, B., (2007). Reaction Mode Between Si and Fe and Evaluation of Optimal Species in Poly-Silicic-Ferric Coagulant. Journal of Environmental Sciences, 19 (6): 678-688.

Gangloff, C. (2000). Membranes are on the Move. Water Technology Magazine, 35 (2): 75-79.

Gao B.Y., Wang Y., Yue Q.Y., (2005). The Chemical Species Distribution of Aluminiumin Composite Flocculants Prepared from Polyaluminum Chloride (PAC) and Polydimethyldiallyl Ammonium Chloride (PDMDAAC). Acta Hydrochimica Hydrobiologica, 33 (4): 365-371.

Gao, B.Y., Hahn, H.H., Hoffmann, E., (2002). Evaluation of Aluminum-Silicate Polymer Composite as a Coagulant for Water Treatment, Water Research, 36: 3573-3581.

Gao, B. Y., Wang, Y., Yue, Q.Y., Wei, J. C., Li, Q., (2007). Color Removal from Simulated Dye Water and Actual Textile Wastewater using a Composite Coagulant Prepared by Polyferric Chloride and Polydimethyldiallyl Ammonium Chloride. Separation and Purification Technology, 54: 157-163.

Gao, F., Lee, Y., Mandai, K., Hoveyda. A., (2010). Quaternary Carbon Stereogenic Centers through Copper-Catalyzed Enantioselective Allylic Substitutions with Readily Accessible Aryl- or Heteroaryllithium Reagents and Aluminum Chloride· Angewandte Chemie, 122 (45): 8548–8552.

Gao. B., Lio. B., Chen. T., Yue. Q., (2011). Effect of aging period on the characteristics and coagulation behaviour of poly ferric Chloride- Poly amid Composite Coagulant for Synthetic Waste water Treatment. Hazard. Materials, 187: 413-420.

Global Health and Education Foundation, (2007). Conventional Coagulation-Flocculation-Sedimentation, Safe Drinking Water is Essential. National Academy of Science, 12: 01.

Greenwood, R; Kendall, K (1999). Journal of the European Ceramic Society 19 (4): 479–488

Gregory, J. and Duan, J., (2001). Hydrolyzing Metal Salts as Coagulants. Pure Applied Chemical., 73 (12): 2017-2026.

Gregory, J., (1980). Coagulation and flocculation with an emphasis on water and wastewater treatment. Croydon, Chemical Engineering Journal, Uplands Press, 21 (1): 80.

Guigui, C., J. C. Rouch, L. Durand-Bourlier, V. Bonnelye, P. Aptel. (2002). Impact of Coagulation Conditions on the In-line Coagulation/UF Process for Drinking Water Production. Desalination, 147 (1): 95-100.

Guo, W. S., Vigneswaran, S., Ngo, H. H., Xing, W., Goteti, P, (2008). Comparison of the Performance of Submerged Membrane Bioreactor (SMBR) and Submerged Membrane Adsorption Bioreactor (SMABR). Bioresource Technology, 99 (5): 1012-1017.

Guo, W. S., Vigneswaran, S., Ngo, H. H., Chapman, H., (2004). Experimenta linvestigation of adsorption/flocculation mico filtration hybrid system in wastewater reuse. Journal of Membrane Science, 242 (1-2): 27-35.

Gurerra, K.,Pellegrino, J., 2012. Investigation of Low-Pressure Membrane Performance, Cleaning, and Economics Using a Techno-Economic Modeling Approach, U.S. Department of the Interior.

Han, S. S., T. H. Bae, G. G. Jang, T. M. Tak. (2005). Influence of Sludge Retention Time on Membrane Fouling and Bioactivies in Membrane Bioreactor System. Process Biochem, 40: 2393-2400.

Hanaor D., Sorrell C., 2011. Review of the Anatase to Rutile Phase Transformation, Journal of Materials Science, 46 (4): 855 – 874.

Hanaor, D.A.H.; Michelazzi, M.; Leonelli, C.; Sorrell, C.C. (2012). The Effects of Carboxylic Acids on the Aqueous Dispersion and Electrophoretic Deposition of ZrO_2. Journal of the European Ceramic Society, 32 (1): 235–244.

Hasegawa, T., Hashimoto, K., Onitsuka, T., Goto, K., Tambo, N., (1990). Characteristics of Metalpolysilicate coagulants, Water Science & Technology, 23: 1713-1722.

Hasegawa. T., Onitsuka.T., Ehara. Y., Hashimoto. K., Akazawa. H., (1993). Method for Production Flocculant of Water Treatment. U. S. Patent No.5, 227,089

Howe, K.J., Clark, M.M., (2002). Coagulation Pretreatment for Membrane Filtration. AWWA Research Foundation Report, Denver, CO., 264.

Hubbard, A.T., (2004). Encyclopedia of Surface and Colloid Science. CRC Press, 4230. ISBN 0824707591. Retrieved 2007-11-13.

Hunter, R.J., (2000). Foundations of Colloid Science, Vol. I, Clarendon Press, Oxford, 418.

Hwang, K. -J. and H.-C. Liu. (2002). Cross-flow Microfiltration of Aggregated Submicron Particles. Journal of Membrane Science, 201: 137–148.

Iler, R.K., (1979). The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry. Wiley, New York, ISBN 3-540-08980-2.

Iler, R.K., (1979). The Geochemistry of Colloid Systems for Earth Scientists: Journal of Colloid and Interface Science, 72(1): 177-178.

Iler, R.K., Dalton, R. L., (1956). Degree of hydration of particles of colloidal silica in aqueous solution. Gerasselli Chemical Department.

Jacangelo, J., Trussel, R., (1997). Role of Membrane Technology in Drinking Water Treatment in the United States. Desalination, 113 (2–3): 119–127.

Javeed, M.A., Chinu, K., Shon, H.K., Vigneswaran, S., 2009. Effect of Pre-treatment on Fouling Propensity of Feed as Depicted by the Modified Fouling Index (MFI) and Cross-flow Sampler Modified Fouling Index (CFS–MFI). Desalination, 238: 98-108.

Jeong, S., Nateghi,F., Nguyen, T.V., Vigneswaran, S., Tu, T.A., (2011). Pretreatment for Seawater Desalination by Flocculation: Performance of Modified poly Ferric Silicate (PFSi-δ) and Ferric Chloride as Flocculants. Desalination, 283: 106–110.

Jeong, S., G. Naidu, S. Vigneswaran, C.H. Ma, S.A. Rice. (2013)A Rapid Bioluminescence-based Test of Assimilable Organic Carbon for Seawater, Desalination, 317: 160–165.

Jiang, F., Lee, S. C. L., Wang, X., Dai, D., (2008). The application of Excitation/Emission Matrix Spectroscopy Combined with Multivariate Analysis for the Characterisation and Source Identification of Dissolved Organic Matter in Seawater of Bohai Sea, China. Marine Chemistry, 110: 109–119.

Jiang, J. (2001). Development of Coagulation Theory and Pre-Polymerized Coagulants for Water Treatment. Separation and Purification Method, 30 (1): 127-141.

Jiang, J. Q., Nigel J.D. (2003). Development of Optimal Poly-Alumino-Iron Sulphate Coagulant. J. Environmental Engineering, 129 (8): 699-708.

Jiang, J.Q., Zeng, Z., Pearce, P., (2004). Evaluation of Modified Clay Coagulant for Sewage Treatment. Chemosphere, 56 (2): 181-185.

Kim, Y.H., (1995). Coagulants and Flocculants; Theory and Practice. Tall Oaks Publishing, Littleton, USA.

Kimura, K., Hane, Y., Watanabe, Y. (2005). Effect of Pre-Coagulation on Mitigating Irrervisble Fouling During Microfiltration of a Surface Water.Water Science & Technology., 51 (6-7): 93-100.

Klijn, R. B., Van der meer, W. G. J., Vriezen, H., van Ekkendonk, F. H. J. (2000). Surface Water Treatment with Zenon Microfiltration Membranes: Minimization of Energy and Chemical use. Desal., 131: 337-343.

Koch Membrane System Manufacturing Company Website (2013)

Lee, N., G. Makdissy, G. Amy, J-P Croue, H. Buisson (2000). Effect of Coagulation Conditions on Membrane Filtration Characteristics in Coagulation-Microfiltration Process for Water treatment. Environmental Science &Technology, 34 (17): 3780–3788.

Lee, N., Amy, G., Croué, J. P., Buisson, H. (2004). Identification and Understanding of Fouling in Low-Pressure Membrane (MF/UF), Filtration by Natural Organic Matter (NOM). Water Research, 38 (6): 4511-4523.

Leparc, J., S. Rapenne, C. Courties, P. Lebaron, J. P. Croué, V. Jacquemet, G. Turner.(2007). Water Quality and Performance Evaluation at Seawater Reverse Osmosis Plants through the Use of Advanced Analytical Tools. Desalination, 203 (1): 243-255.

Letterman, R.D., Vanderbrook, S.G., (1983). Effect of Solution Chemistry on Coagulation with Hydrolysed Al(III): Significance of Sulfate Ion and pH. Water Research, 17 (2): 195-204.

Li-jun, L., Pei-Shi, Q., Yun-zhi, L., Zheng Q., (2009). Poly Ferric Silicate Sulphate(PFSiS): Charactrization, Coagulation Behavior and Applications in Oily Wastewater Treatment. IEEE, 4: 83-89.

Lin, C. -F., Y. -J. Huang, O. -J. Hao. (1999). Effect of Molecular Weight Fractions and PAC Treatment. Water Research, 33: 1252–1264.

Maartens, A., Swart, P. and Jacobs, E.P. (1999). Feed-water Pretreatment: Methods to Reduce, Membrane Fouling by Natural Organic Matter. Journal of Membrane Science, 163: 51-62.

Mahulkar. D, Wang. Y., (2006). Fumed Silica to Colloidal Silica Conversion Process. U.S patent No. 0283095 A1.

Marcel, M. (2004). Basic Principles of Membrane Technology, 2nd Edition. Kluwer Academic Publishers, UK.

Mietton, M. and R. Ben Aim. (1992). Improvement of Cross Flow Microfiltration Performances with Flocculation. Journal of Membrane Science, 68 (3): 241-248.

McNaught, A. D., Wilkinson, A., (1997). IUPAC, The Gold Book, Compendium of Chemical Terminology, 2nd edition.

Mitsubishi Ryon Co.Ltd website (www.mrc.co.jp, 2013)

Mouassas. P. A, Zouboulis.A.I, (2008). A Study on the Properties and Coagulation Behaviour of Modified Inorganic Polymeric Coagulant- Polyferric Silicate Sulphate(PFSiS). Separation and Purification Technology, 63: 475-483.

Moussas, P.A., Zouboulis, A.I., (2009). A new inorganic–organic composite coagulant, consisting of Polyferric Sulphate (PFS) and Polyacrylamide (PAA) Original Research Article. Water Research, 43 (14): 3511-3524.

Moueddeb, H., Sanchez, J., Bardot, C., Fick, M., (1996). Membrane bioreactor for lactic acid production. Original Research Article Journal of Membrane Science, 114 (1): 59-71.

MRWA Minnesota rural water association report (2013)

MWH. (2005), Water treatment Principles & Design. John Wiley and Sons, Inc, 2nd Edition.

Nakamoto, K., Infrared Spectra of Inorganic and Coordination Compounds. New York, London, John Wiley & Sons (1964)

Nassar, A.M., Mciwem, M.S. and Afifi, S. (2009). Palestinian Experience with Sewage Sludge Utilizing Reed Beds. Water Environmental Journal, 23: 75-82.

Ning, R.Y., (2003). Discussion of Silica Speciation, Fouling, Control and Maximum Reduction Original Research Article. Desalination, 151: 67-73.

Oh, H., M.Yu, S.Takizawa, S.Ohgaki. (2006). Evaluation of PAC Behavior and Fouling Formation in an Integrated PAC-UF Membrane for Surface Water Treatment. Desalination, 192: 54–62.

Orme, J., Ohanian, V., (1990). Assessing the Health Risks of Aluminium. Environmental Geochemistry and Health, 12 (1-2): 55-58.

Orme. J, Ohanian. E.V., (1993). US Environmental Protection Agency, Washington, D. C, WA (USA).

Panglisch, S., Dautzenberg, W., Kiepke, O., Gimbel, R. (2000). Ultra and Microfiltration in Drinking Water Production From Surface Water. Water Supply, 18 (1): 415-418.

Parker, D.R., Bertsch, P.M., (2002). Formation of the 'Al13' Tridecameric Polycation under Diverse Synthesis Conditions. Environmental Science & Technology, 26: 914-921.

Pearce, G., (2007). Introduction to Membranes: Fouling control, Filtration & Separation, 44 (6): 30–32.

Randtke, S.J., (1988). Organic Contaminant Removal by Coagulation and Related Process Combinations. Jour.AWWA, 80 (5): 40.

Ratajczak, M., (2007). The Use of Coagulation as a Pre-treatment to Ultra-filtration Membranes University of Waterloo, Civil Engineering Faculty, Ontario, Canada.

Richens, D.T., (1997). The Chemistry of Aqua Ions, Wiley: Chichester.

Rizzo, L., Belgiorno, V., Gallo, Meric, S. (2005). Removal of THM Precursors from High-alkaline Surface Water by Enhanced Coagulation. Desalination, 176: 177-188.

Roberts. W.O., (1998). Manufacturing and Application of Water Brone Colloidal Silica,: in Schick. M.J. (Eds.), Colloidal Silica: Fundamentals and Applications,(Eds), California, 131-147.

Sanchez M.G., (1959), Process for the Preparation of Silica Sols., (W.R. Grace & Co.), Can. Pat. 586.261.

Schippers J.C., Verdouw J. (1980). The Modified Fouling Index. A Method of determining the Fouling Characteristics of Water. Desalination, 32: 137-148.

Schock, G., Miquel, A., Birkenberger, R., (1989). Characterization of Ultrafiltration Membranes: Cut-off Determination by Gel Permeation Chromatography .Journal of Membrane Science, 41: 55-67.

Seo, G.T., Lee, T.S., Moon, B.H., Choi, K.S., Lee, H.D., (1997). Membrane Separation Activated Sludge for Residual Organic Removal in Oil Wastewater Original Research Article. Water Science and Technology, 36 (12): 275-282.

Sethi, S. and Wiesner, M.R.,(2000). Simulated Cost Comparisons of Hollow Fiber and Integrated Nanofiltraton Configurations. Water Research, 34 (9): 2589-2597.

Sethi, S., Wiesner, M.R., (1997). Modeling of Transient Permeate Flux in Cross-Flow Membrane Filtration in Corporating Multiple Particle Transport Mechanisms. Journal of Membrane Science, 136 (1-2): 191-205.

Sharp, E.L., Parson, S.A. and Jefferson, B. (2006). Coagulation of NOM: Linking Character to Treatment. Water Science & Technology, 53 (7): 67-76.

Shon, H. K., Vigneswaran, S., Ben, R., Ngo, H. H., (2005). Influence of Flocculation and Adsorption as Pretreatment on the Fouling of Ultrafiltration and Nanofiltration Membranes: Application with Biologically Treated Sewage Effluent. Environmental Science & Technology, 39: 3864–3871.

Sinha, S., Yoon, Y., Amy, G., Yoon. J., (2004). Determining the Effectiveness of Conventional and Alternative Coagulants through Effective Characterisation Schemes Original Research Article. Chemosphere, 57 (9): 1115-1122.

Siobhan, F., Boerlage, E., Maria D. Kennedy, Schippers, C., (2003). The MFI-UF as a Water Quality Test and Monitor Original Research Article. Journal of Membrane Science, 211 (2): 271-289.

Song, Y.H., Luan, Z.K., Tang, H.X., (2003). Preparation and Characterisation of Polyaluminium Silicate Chloride Coagulant. Environmental Technology, 24: 319-327.

Stauber, J., Franklin, N., Adams, M., (2005). Microalgal Toxicity Test Using Flow Cytometry, Small-scale Fresh Water Toxicity Investigations., Toxicity Test Methods. Amsterdam , 1: 203-241.

Stumm, C., (1967). Aggregation of Silica Dispersions by Iron (III) Original Research Article. Journal of Colloid and Interface Science, 23 (3): 437-447.

Stumm, W., Huper, H., Champlin, L., (1967). Formation of Polysilicates as Determined by Coagulation effects, Environmental Science & Technology, 1: 221-227.

Sutzkover-Gutman, I., Hasson, D., (2010). Feed Water Pretreatment for Desalination Plants. Desalination, 264(3): 289-296.

Suzuki, T, Watanabe Y, Ozawa G, Ikeda S. (1998). Removal of Soluble Organics and Manganese by a Hybrid MF Hollow Fiber Membrane System. Desalination, 117: 119–130.

Tang, H., Shi, B., (2002). The Characteristics of Composite Flocculants Synthesized with Inorganic Polyaluminum and Organic Polymers, Chemical Water and Wastewater Treatment VII, IWA Publishing, Gothenburg, Sweden, 17-28.

Teng, C. K., M. N. A. Hawlader, A. Malek. (2003). An Experiment with Different Pretreatment Methods. Desalination, 156: 51–58.

Tate, C.H., Armold, K.F., (1990). Health and Aesthetic Aspects of Water Quality. Water Quality and Treatment. McGraw-Hill, Toronto.

Tomaszewska, M., S. Mozia, A. W. Morawski. (2004). Removal of Organic Matter by Coagulation Enhanced with Adsorption on PAC. Desalination, 161(1): 79-87.

Tzoupanos, N.D., Zouboulis A.I., Zhao Y. C., (2008). The Application of Novel Coagulant Reagent (Polyaluminium Silicate Chloride) for the Posttreatment of Landfill Leachates. Chemosphere, 73(5): 729–736.

Van Paassen, J. A. M., Kruithof, J. C., Bakker, S. M. & Schoonenberg Kegel, F. ,(1998). Pretreatement of Nanofiltration by Riverbank Filtration and Conventional Ground Water Treatment. Desalination, 118: 239–248.

V.G. Il'In, N.V. Turutina, V.N. Solomakha., (1989) Study of Cationic (Li^+, Na^+, K^+) Specificity in Hydrated Silicate and Aluminosilicate Structure Formation Processes. Surface Science and Catalysis, 49: 345-353.

Vial, D., Doussau, G. (2002). The Use of Microfiltration Membranes for Seawater Pre-treatment Prior to Reverse Osmosis Membranes. Desalination, 153: pp. 141-147.

Vigneswaran, S., Guo, W. S., Smith, P., Ngo, H. H., (2007). Submerged Membrane Adsorption Hybrid System (SMAHS): Process Control and Optimisation of Operating Parameters. Desalination, 202 (1): 392-399.

Wang, D., Tang. H., (2001). Modified Inorganic Polymer Flocculant PFSi: its Preparation, Characterisation and Coagulation Behavior. Water. Research, 35: 3418-3428

Wang, K.Y., Teoh, M.M.; Nugroho, A.; Chung, T.-S., (2011). Integrated Forward Osmosis–Membrane Distillation (FO–MD) Hybrid System for the Concentration of Protein Solutions. Chemical Engineering Science, 66: 2421–2430.

Wang, M. and Muhammed, M., (1999). Synthesis of Al13-Cluster Based Alumina Materials. NanoStructured Materials, 11: 1219-1229.

Wei. J, Gao. B, Yue. Q, Wang. Y, Li. W, Zhu. X., (2009). Comparison of Coagulation Behaviour and Floc Structure Characteristic of Different Polyferric Cationic Polymer dual- Coagulants in Humic Acid Solution.Water Research, 43: 724-732.

WHO and UNICEF. (2004). World Health Organization and United Nations Children’s Fund. Global Water Supply and Sanitation Assessment Report.

Wu, Y., Liu, W., Gao, N., (2011). A study of Titanium Sulfate Flocculation for Water Treatment Original Research Articl. Water Research, 45 (12): 3704-3711.

Xu, X., Yu. S., Shi. W., Jiang Z., Wu C., (2009). Effect of Acid Medium on the Coagulation efficiency of polysilicate-ferric (PSF). A New Kind of Inorganic Polymer Coagulant. Separation Purification Technology, 66: 486-491.

Yang, R. and C. G. Van Den Berg. (2009). Metal complexation by humic substances in seawater, Environmental Science & Technology, 43: 7192–7197.

Ye, Y., L. N. Sim, B. Herulah, V. Chen, A. G. Fane. (2010). Effects of Operating Conditions on Submerged Hollow Fibre Membrane Systems used as Pre-Treatment for Seawater Reverse Osmosis. Journal of Membrane Science, 365: 78–88.

Yiantsos, S.G., Karabelas, A.J. (1998). The Effect of Colloid Stability on Membrane Fouling. Desalination, 118 (1-3): 143-152.

Ying, F., Shuili, Y., Chunwei, H., (2009). Morphplogy and Coagulation Performance During Preparation of Poly Silicate Ferric (PSF) Coagulant. Chemical Engineering Journal, 149 (1-3): 1-10.

Yokoyama, T., Nakazato, T., Tarutani, T., (1980). Polymerization of Silicic Acid Adsorbed on Iron (III) Hydroxide. Bull. Chemical Society, 53: 850-853.

Zhiwei. S., Nanqi. R., (2008). Properties and Coagulation Mechanism of Polyferric Silicate Sulphate with High Concentration. Environmental Science, 20: 129-134.

Zouboulis, A.I., and Moussas, P.A., (2008). Polyferric Silicate Sulphate (PFSiS): Preparation, Characterisation and Coagulation Behaviour. Desalination, 224 (1–3): 307-316.

Zouboulis, A.I., Traskas, G., (2005). Comparable Evaluation of Various Commercially Available Aluminum-Based Coagulants for the Treatment of Surface Water and for the Post-treatment of Urban Wastewater, Journal of Chemical Technology & Biotechnology, 80: 1136-1147