Electrocoagulation and Microfiltration Hybrid System for Water Treatment

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CERTIFICATE OF AUTHORSHIP

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

I also certify that the thesis has been written by me. And 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 Candidature

(Ganesh Sharma)

Sydney, July 2011

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NOMENCLATURE

DOC = dissolved organic carbon

EC = electrocoagulation

F = faraday's constant (mol^{-1})

i = current density (A cm^{-2})

J = filtrate flux at a given time (l m^{-2} hr)

J_0 = pure water flux (l m^{-2} hr)

K_1 = cake filtration constant (l^{2}min^{-1})

k_1 = filtration constant

M = relative molar mass of the electrode

MF = microfiltration

PV = photovoltaic

Q_0 = initial flux (ml min^{-1})

SPEC = solar powered electrocoagulation

T = electrocoagulation time (s)

t = filtration time (min)

V = permeate volume (ml)

V_f = volume of permeate producing hydraulic resistance equal to membrane (l)

w = quantity of electrode material dissolved (g of M cm^{-2})

Z = number of electrons transferred in the reaction

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ABSTRACT

Membrane technology for water and wastewater treatment offers many advantages over other conventional treatment systems. However, membrane process is usually hampered by the problem of membrane fouling which restricts its widespread application. Membrane fouling decreases permeate flux and plant productivity, increases hydraulic resistances thereby increasing energy consumption and increases the operational and maintenance costs ultimately affecting the overall plant economy. Pretreatment of feed water is considered one of the most effective means to reduce membrane fouling. Pretreatment increases the membrane lifetime and reduces membrane deterioration. Although several pretreatment options are available, only few studies have been reported so far for electrocoagulation (EC) as an attractive pretreatment method for membrane filtration.

The main objectives of this study are i) to evaluate water treatment by EC using aluminium and iron electrodes, ii) to evaluate the performance of microfiltration (MF) with EC as pretreatment, iii) to determine the EC operating conditions favouring removal of organic matter and turbidity, iv) to optimise EC-MF hybrid system for water treatment, v) to investigate the feasibility of solar powered electrocoagulation (SPEC) for applications in remote communities of Australia, vi) to access the feasibility of SPEC as a sustainable pretreament option for MF and finally vii) to identify the fouling mechanisms involved in the crossflow MF system when EC is used as pretreatment for the feed water.

EC pretreatment of synthetic water using iron electrodes did not reduce MF fouling due to the release of soluble ferrous ions (Fe^{2+}) as it was not capable of colloidal destabilisation and Fe^{2+} -organic matter complexation prevents $Fe(OH)_3$ precipitation and floc formation. However, EC pretreatment with aluminium electrodes significantly improved the performance of MF. The permeate flux for pretreated feed water was more than 55% higher than the feed water without pretreatment under optimum EC operating conditions. The isoelectric point for EC with aluminium electrodes occurred at pH 8. The highest removal efficiency (dissolved organic carbon (DOC) by 78%, UV abs by 85% and turbidity by 88%) occurred at the isoelectric point, where charge neutralisation occurred. Similarly, the highest organics and turbidity removal by chemical coagulation using aluminium sulphate also occurred at the isoelectric point (pH 6.5).

The potential for using solar powered electrocoagulation (SPEC) as an attractive technology for small and decentralised water purification system was explored. SPEC offered a suitable candidate for applications in the remote communities where renewable solar energy such as solar power is abundant. SPEC reactor was designed by connecting to photovoltaic panel (PV) either directly or through a set of batteries and charge control system. SPEC process system was observed sensitive to variation of solar irradiation when connected directly with PV panels and without any charge control system. SPEC reactor operated for five different times in a day (4 April 2010), yielded the highest organics removal at around midday i.e. between 10:00 AM-2:00 PM (DOC by 75%, UV abs by 85% and turbidity by 87%) under optimum EC operating conditions. However, when SPEC process was supported by batteries and charge control system, the process removal efficiency improved and also became more consistent. The variation in organic and turbidity removal was within the range of 10% for experiments conducted on three different times in a day (9 April 2010) with the highest removals at 10:30 AM in the morning.

The feasibility for SPEC as a sustainable pretreatment option, SPEC-MF hybrid system was evaluated. SPEC pretreatment using PV panel only without the charge control system improved the flux however the flux performance fluctuated due to the variation in the solar irradiation. The connection to batteries and charge control system improved the performance of MF permeate flux and also became more stable.

The fouling mechanism of crossflow MF was studied comparatively with feed water containing kaolin suspension with and without EC pretreatment. When the feed water was pretreated by EC, the fouling was found to follow both standard law of filtration and classical cake filtration model.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Water scarcity is becoming a significant problem throughout the world. The lack of water resources and safe drinking water has been recognised and analysed by different international organisations such as the World Health Organisation or the World Bank (Thomas and Durham, 2003). Water shortages affect 88 developing countries that are home to half of the world's population. In this scenario, membrane technology has emerged as a reliable technology for water treatment and wastewater reuse. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) can remove the majority of the pollutants.

MF with the largest pore size of 0.1-10 microns is commonly used to separate suspended particulates, large colloids and bacteria. MF has been increasingly applied to drinking water and wastewater treatment due to the small carbon footprint, superior treated water quality, and high level of automation compared to conventional treatment processes. However, the operating costs are generally high for membrane process because of severe membrane fouling. Fouling is one of the major challenges for the operation of MF membrane or any other membrane process and thus requires an appropriate pretreatment prior to membrane filtration. Pretreatment is emerging as a most promising solution to control the fouling since the pretreated feed water can be simply introduced to the MF directly. Various types of pretreatments such as physical, chemical, biological and electrical pretreatments are available to reduce the membrane fouling and increase membrane flux.

During the recent decades, researches have revealed electrocoagulation (EC) as an attractive and suitable method for the treatment of various kinds of water and wastewater, by virtue of various benefits including environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation, and cost effectiveness (Chen, 2000). The process is characterised by simple equipment, easy operation, a shortened reactive retention period, a reduction or absence of equipment for adding chemicals and decreased amount of precipitate or sludge which sediments rapidly. Therefore EC is one of the promising electrochemical technologies for water treatment. Due to its ability in removing wide range of pollutants and simplicity in design and operation, it is gaining enormous popularity. While EC has already been established as a highly efficient method for removing a large variety of pollutants from water and established as a promising technology especially for decentralised water treatment applications, only a few studies investigated for EC as a pretreatment method for MF. EC as a pretreatment for MF could remove wide range of pollutants, increase the membrane flux and minimise the energy requirements.

In the remote and rural areas, it is rather difficult to operate and maintain conventional treatment technology. Most conventional treatment systems are often limited by the availability of electricity, with many rural areas having no access to national electricity grid. Hence it is widely recognised that water treatment methods powered by renewable energy sources are needed in Australia and around the world. EC with its simplicity and efficiency is an attractive technology especially for small and decentralised water and wastewater purification system. With the potential of EC to be driven by solar power, EC offers a suitable candidate for applications in the remote communities of Australia where the abundant renewable energy such as solar power can gives rise to the new sustainable solar powered electrocoagulation (SPEC) technology. There is also an enormous potential of using SPEC as a pretreatment for membrane filtration.

1.2 Objectives of the study

The main objectives of this study are:

- Evaluation of water treatment by EC using aluminium and iron electrodes.
- Determination of the operating conditions favouring the removal of organic matter and turbidity by EC.
- Performance evaluation of MF with EC as pretreatment using iron and aluminium electrodes.
- Optimisation of the EC and MF hybrid system for water treatment.
- Investigate the feasibility of SPEC for applications in remote communities.
- Feasibility assessment of SPEC as a sustainable pretreament option for MF.
- Identify the fouling mechanism of crossflow MF after pretreatment of water with EC using aluminium electrodes.

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CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Filtration

2.1.1 Historical Development of Membranes

Systematic studies of membrane phenomena can be traced to the eighteenth century. For example, Abb´e Nolet coined the word 'osmosis' to describe permeation of water through a diaphragm in 1748. Through the nineteenth and early twentieth centuries, membranes had no industrial or commercial uses, but were used as laboratory tools to develop physical/chemical theories.

Early membrane investigators experimented with every type of diaphragm available to them, such as bladders of pigs, cattle or fish and sausage casings made of animal gut. Later, collodion (nitrocellulose) membranes were preferred, because they could be made reproducibly. In 1907, Bechhold devised a technique to prepare nitrocellulose membranes of graded pore size, which he determined by a bubble test. Other early workers, improved on Bechhold's technique, and by the early 1930s microporous collodion membranes were commercially available. During the next 20 years, this early microfiltration (MF) membrane technology was expanded to other polymers, notably cellulose acetate. Membranes found their first significant application in the testing of drinking water at the end of World War II.

By 1960, the elements of modern membrane science had been developed, but membranes were used in only a few laboratories and small, specialised industrial applications. No significant membrane industry existed. Membranes suffered from four problems that prohibited their widespread use as a separation process: They were too unreliable, too slow, too unselective, and too expensive. Solutions to each of these problems have been developed during the last 30 years, and membrane-based separation processes have now become popular.

Methods of packaging membranes into large-membrane-area spiral-wound, hollow-fine-fiber, capillary, and plate-and-frame modules were also developed and advances were made in improving membrane stability. By 1980, MF, ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and electrodialysis were all established processes with large plants installed worldwide. Membrane systems have now been used in specialised applications for more than 30 years, largely for water treatment, including desalination of seawater and brackish water. With technical advances and corresponding cost reductions, membrane systems are now capable of decontaminating nonsaline waters (including treated wastewaters) in single step processes at competitive costs.

2.1.2 Overview of Membrane Technology

Membrane technologies are receiving special recognition as alternatives to conventional water treatment and as a means of polishing treated wastewater effluent for reuse applications. Membranes are commonly used for the removal of dissolved solids, color, and hardness in drinking water. Membrane filtration involves separation of dissolved, colloidal and particulate constituents from a pressurised fluid using microporous materials. In general, membranes are categorised into four main groups based on the size of its pores, the applied pressure and molecular weight cut-off (MWCO), namely RO, NF, UF and MF.

MF with the largest pore size of 0.1-10 microns is commonly used to separate suspended particulates, large colloids and bacteria; hence it is suitable for the treatment of water having high turbidity and low colour or organic content (Schafer, 2001). The first large-scale application of MF membranes was to culture microorganisms in drinking water which remains a significant application. The test was developed in Germany during World War II, as a rapid method to monitor the water supply for contamination. Similarly, UF (0.001-0.1 microns) can exclude macro-molecules and fine colloidal suspensions such as proteins, dyes and bacteria but removal of dissolved organics are limited. MF and UF can also be used as pre-treatment for NF and RO processes (Schafer, 2001).

NF with smaller pore sizes between 15-30 angstroms is employed for water softening and the removal of disinfection by-products (DBPs). NF can reduce 60-80% of hardness and more than 90% of colour causing substances (Cheryan, 1998). RO with the smallest pore size (5-15 Å) is widely used as a polishing treatment to remove salts and low molecular weight (MW) pollutants from water and wastewater. In general, the selection of a suitable membrane is dependent on the targeted materials to be removed and the quality of treated effluent.

In the membrane filtration process, the removal efficiency is significantly influenced by the nature of the solution including MW distribution, charge groups and polarity (e.g. hydrophobicity or hydrophilicity) and roughness of the compounds. The interactions between organic matter and the membranes are either adsorption which easily leads to membrane fouling or rejection due to electrostatic and/or steric exclusion (Millis, 2000). Other factors that can affect removal efficiency are pH, ionic strength and foulant concentration in the solution (Amy and Cho, 1999). Combined membrane processes have also been studied for instance; an MF and UF system was able to reduce 75% of DOC while a MF and NF system was able to remove in excess of 90% (Jarusutthirak and Amy, 2001).

Low pressure membrane filtration, such as MF and UF has many advantages over conventional water treatment processes including superior and consistent product water, less chemical use, smaller spatial requirements and easier siting and expansion (Adham et al., 1995). Therefore, MF and UF have attracted more attention than NF and RO as they require relatively lower cost and lower pressure for operation. In fact, UF and MF coupled with physico-chemical and/or biological processes can achieve superior pollutant removal in an economical manner.

2.1.3 Membrane Filtration Mechanisms

In the filtration process, the membrane functions as a thin semi-permeable barrier that allows certain components in the feed stream to permeate freely while retaining the passage of other components. The transport of the permeable components through the membrane is mostly driven by the pressure. As a result, the two components are completely separated and the product stream is relatively free of unwanted impermeable constituents. The characteristics and comparison of different membranes are presented in Table 2.1.

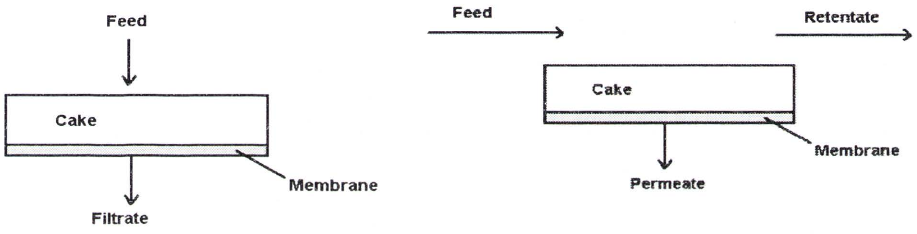
Table 2.1 Characteristics of membranes (Adapted from Stephenson et al., 2000)

Membrane operation	Mechanism or Separation	Molecular Weight Cut off range (Da)	Pore size, range, (µm)	Operating pressure, kPa
MF	Sieve	>100,000	0.1-10	20-640
UF	Sieve	>2,000-100,000	0.01-0.1	60-4700
NF	Sieve + solution/ diffusion + exclusion	300-1,000	0.001-0.01	1490-4680
RO	Solution/diffusion + exclusion	100-200	<0.001	17000-25500

2.1.4 Membrane Filtration Modes

Membrane filtration is operated in two main modes known as dead-end and crossflow (Figure 2.1). In dead-end filtration, the entire fluid flow is forced through the membrane under pressure. As particles accumulate on the membrane surface or in its interior, the pressure required to maintain the required flow increases, until at some point the membrane must be replaced.

In the crossflow operation, the feed solution is circulated across the surface of the filter, producing two streams: a clean particle free permeates and a concentrated retentate containing the particles. The accumulation of the contaminants on the membrane surface is substantially reduced in crossflow filtration as the flow sweeps a part of the deposits over the surface. Therefore, the permeate flux can be maintained at a higher level than in dead-end filtration. However, cross-flow filtration requires higher pressure and energy to maintain the flow at a relatively high speed. The reduction of the flux during the filtration caused by the build-up of filter cake is also referred to as membrane fouling. Once fouling occurs, the membrane needs to be cleaned by means of physical and chemical cleaning or backward flushing to remove contaminants attached to the surface or trapped inside the pores of the membrane. After cleaning, the membrane can be operated for another filtration period. In comparison, cross-flow mode can attain a more stable flux and longer filtration time while requiring less cleaning time than in the dead-end mode.



Dead-end filtration

Crossflow filtration

Figure 2.1 Membrane filtration modes

2.1.5 *Submerged Membrane System*

In the submerged membrane system, MF membrane module is mounted and immersed in a reactor. The solid-liquid separation is governed by a suction pump which is connected to withdraw permeate out of the membrane. Air scour is also supplied from the bottom of the reactor to provide oxygen as well as generate turbulence along the surface of the membrane. In fact, aeration is an important factor used to control concentration polarisation and membrane fouling of the MF submerged membranes (Chang and Judd, 2002; Cui et al., 2003).

Compared with the external membrane system, the submerged (internal) system involves more membrane area per unit volume and a lower transmembrane pressure (TMP). Moreover, the submerged system reduces space requirements and minimises installation and operating costs (Fane and chang, 2005). The submerged membrane concept was initially developed for membrane bioreactors (MBRs). However, it is now widely applied in water and wastewater treatment and other hybrid membrane processes.

2.2 Membrane Fouling

2.2.1 Definitions and causes of membrane fouling

Membrane fouling is an extremely complex phenomenon which occurs by the formation of undesirable deposition of particulate/colloidal or organic matter to the membrane surfaces (Amoudi, 2010). Membrane fouling decreases the water flux and increases the energy consumption ultimately affecting plant economy. The membrane fouling has a significant impact on the operational cost, design and operation of membrane application. Therefore it has been the major challenge in the operation of the membrane processes. It usually involves adsorption and deposition of foulant species on the membrane surface or internal pore that directly affects the water transport efficiency of the membrane. Membrane fouling involves complex mechanisms which are influenced by many factors such as feed water composition (foulant concentration, pH, ionic strength), hydrodynamic conditions (flux, crossflow velocity) and membrane properties (roughness, charge hydrophobicity). As membrane filtration proceeds, the foulants may transform into different structures, types and layers on the membrane surface depending on the parameters (aeration, flux, cross flow) applied, the water chemistry, and the progress of biofouling (Bellona et al., 2004). In addition, membrane foulant significantly vary depending on the types of membranes and the characteristics of water used. All these complexities make it difficult to understand the correct mechanisms of membrane fouling. MF has more fouling problem as compared with other membrane processes due to large pore size (Le et al., 1984; Scott, 1995).

2.2.2 Types of membrane fouling

2.2.2.1 Membrane foulants

The different types of membrane foulants which are commonly found in membrane filtration are presented in Table 2.2. Organic fouling caused by the deposition and adsorption of organic substances is one of the major membrane foulants. Scaling generated by inorganic compounds is defined as the formation of mineral deposits precipitating from the feed stream to the membrane surface (Durancear, 2001). Biofouling originates from the growth of biological species on the membrane surface. Colloidal fouling also results in a loss of permeate flux due to deposition on the membrane surface. While biofouling is important in the long term it is the most likely to occur after organic, inorganic or colloidal fouling which are related to the nutrients and microbial communities. Since interactions between solutes and the membranes are poorly understood, it is possible that the effects like charge interactions, bridging, and hydrophobic interactions may play an important role on membrane fouling. In general, membranes with larger pores exhibit a greater flux decline as filtration proceeds due to internal clogging. However, flux decline is not necessarily only due to membrane fouling. Other factors such as concentration polarisation, osmotic pressure of the feed, membrane compaction, etc. can appear as fouling, whereas it is difficult to control, characterize and interpret in detail.

Table 2.2 Membrane foulant types

Inorganic fouling	Organic fouling	Biofouling
- Ca^{2+}, residual Cl^-	- Polyacrylic polymers	- Bacteria
- Calcium alumino silica	-Protein and Polysaccharides	-Anaerobic sulfate reducing
- Mg^{2+}/Ca^{2+} phosponate	- Humic and fulvic acid	- Aerobic heterotrophic
- CO_3^{2-}, SO_4^{2-} -> $CaCO_3$, $CaSO_4$, $MgCO_3$, silica	- Carboxylic acid	- Fungi
- Al^{3+}	- Extracellular polymeric substances (EPS)	- Yeast
- Fe^{2+}		- Algae
		-Direct attack of membrane surface

2.2.2.2 *Particulate/colloidal fouling*

Colloids or particulate matters dominate the membrane fouling (Potts, 1981). Particulate matters in the size range of nanometres to micrometer are defined as colloids. Inorganic (clays, silica salt, metal oxides), organic (aggregated natural and synthetic organic) and biological (bacteria, microorganism) are the examples of common colloidal foulants. Champlin (2000) reported that removal of the particles size of down to 1 μm may not be sufficient to avoid fouling in many cases. The high concentration of the rejected ions in the membrane surface could promote the aggregation of dissolved matter into colloidal sized particles. Moreover, the influence of salt retention and concentration polarisation in the membrane surface area electrostatic particle-membrane and particle-particle interaction allow colloids to foul the membrane.

2.2.2.3 Organic fouling

Organic fouling is one of the major causes of membrane fouling which is related to the molecular size, shape and chemical characteristics (steric, polar, functional group and stability to form hydrogen bond) of organic matter. The organic fouling occurs mainly due to adsorption on the membrane, precipitation, and the interactions with cations present in the feed water. Depending on the characteristics of the organics, the membrane type and its operating condition need to be carefully considered and selected. Organic fouling cannot be fully reversed by physical cleaning and therefore needs proper chemical treatment. Membrane fouling with respect to the size of organic matter shows different behaviour for porous membrane (MF, UF) and non-porous membrane (NF and RO). The porous membranes are significantly affected by larger foulant species such as suspended solids, particulate organic matter and large organic matter, while the non-porous membranes such as NF and RO are influenced by smaller size colloidal and dissolved organic matter. Kaiya et al. (1996) reported that organic compounds with MW larger than 100 kDa are major foulants in MF operation.

Membrane fouling has been observed to be severe with a positively charged membrane which can easily attract the negatively charged organics (Mulder, 1996) and therefore positively charged membranes are not usually manufactured commercially. Many researchers have suggested that the humic substances fraction of organic matter is a major foulant which controls the rate and extent of fouling in many water treatment plants (Combe et al., 1999; Jones and O'Melia, 2000; Yuan and Zydney, 1999). However, recent studies have reported that hydrophilic (non-humic) organic matters are more significant in fouling.

2.2.2.4 Inorganic fouling

Inorganic fouling or scale formation is a serious problem which occurs from the increased concentration of inorganic matter present in the feed beyond their solubility limits and their ultimate precipitation onto the membranes (Wiesner and Mallevialle, 1989). Scaling usually refers to the formation of deposits of inverse-solubility salts such as $CaCO_3$, $CaSO_4 \cdot xH_2O$, silica, and calcium phosphate. It occurs most often on nonporous membranes (NF and RO).

2.2.2.5 Biofouling

Lappin and Costerton (1989) reported biofouling as the fouling where biologically active organisms are involved. The unwanted accumulation of microbial communities on membrane surface is part of the biofouling process. Membrane biofouling is caused by bacteria, fungi and other eukaryote microorganisms (Flemming et al., 1997). Even though biofouling on membrane surface is one of the most undesirable phenomena in pressure-driven membrane technology, little is known about the fundamental nature of the process due to its very complex generation and prediction. Biofouling often occurs with NF and RO due to the abundant nutrients on the membrane surface compared to MF and UF.

2.3 Fouling Prevention

Membrane fouling is the major challenge and one of the major drawbacks for successful application in membrane technology. It can be controlled by altering the operating conditions (i.e. operating under critical flux and pressure), adding anti-foulant chemicals (especially for membrane scaling) and pretreating the targeted water (Mulder, 1996). The brief summary on the membrane fouling control is presented in Table 2.3. Modification of membrane properties, transformation of module processes, effective cleaning procedures, compaction and pretreatment are used. Among the different methods, pretreatment is one of the most effective ways to reduce membrane fouling. Feed pre-treatment is a key factor determining the success or failure of MF system for water/wastewater treatment and reuse.

Table 2.3 Methods to reduce membrane fouling (Adapted from Mulder, 1996)

Pretreatment	Membrane properties	Module process	Cleaning	Compaction
1.Heat treatment 2.pH adjustment 3.Addition of complexing 4. Chlorination 5. Adsorption 6. Flocculation 7. Pre-MF 8. Pre-UF	1. Narrow pore size distribution 2. Hydrophobic/ hydrophilic charge 3.Pre-adsorption of the membrane	1. Decrease of concentration of polarisation 2. Increase of mass transfer coefficient (high flow velocities) 3. Turbulence promoters	1. Hydraulic 2. Mechanical 3. Chemical 4. Electric	1. Irreversible 2. Mechanical deformation of polymeric membrane matrix 3.Low pressure

2.4 Pretreatment

Pretreatment is considered the most effective alternative to reduce membrane fouling, increase membrane lifetime and reduce membrane deterioration as it can simply be added to the existing membrane application. As such, pretreatment is the first choice to reduce fouling at membrane installations. When pretreatment is applied, membrane material, module type, feed-water quality, recovery ratio, and final water quality must be carefully incorporated to select an appropriate pretreatment. Pretreatment can be selected depending on feed water quality, membrane performance and permeate water quality. The conventional pretreatment such as filters (sand, anthracite) does not provide sufficient pretreatment to the membrane process. Thus a combination of biological and physico-chemical processes such as coagulation-flocculation, sedimentation, oxidation, and adsorption processes is necessary to control the membrane fouling.

2.4.1 Adsorption

Adsorption is predominantly a physical phenomenon where organic matter is attracted to the surface of adsorbent namely activated carbon by intermolecular forces of attraction. Small size (less than 10 nm) organic foulant can be removed by adsorption. Adsorption of activated carbon is mainly caused by van der Waals force and electrostatic force between organic matter and activated carbon. In principle, any porous solid can be an adsorbent, however for an efficient and economical adsorption process, the adsorbent must have a large surface, long life, and a well-defined microcrystalline structure to possess high adsorption selectivity and capacity. The main factors that affect the adsorption of organics are: i) the characteristics of adsorbent: surface area, particle size, and pore structure, ii) the characteristics of adsorbate: solubility, molecular structure, ionic or neutral nature, and iii) the characteristics of the solution: pH, temperature, presence of competing organic and inorganic substances.

2.4.2 Media Filter

A media filter which is applied to remove colloids and particulate solids is one of the most widely used pretreatment processes. A bed of sand, crushed granite, granular activated carbon or other material is used to filter the contaminated water. The removal of membrane organic foulant occurs at the initial filtration stage. Once microbial communities become established on the filter, the media filter functions as a biofilter. As such, a physical filter is always associated with biofiltration.

2.4.3 Cartridge filter

Cartridge filter is a simple option to pretreat water before membrane filtration. A cartridge filter can remove large particulate organic matter (more than 5 μm). Generally string-wound polypropylene filters that remove between 1-5 μm sized particles are used. It is applied when contaminations in the influent are lower than 100 ppm. Surface or depth-type filter can be utilised. Surface filters that are made of thin materials such as papers, woven wire and cloths remove particles at the surface of the cartridge filter. On the other hand, depth-type filters remove particles by the thickness of the medium. Cartridge filters can be easily disposable and replaced.

2.4.4 UV irradiation

Pretreatment of UV irradiation can be used to disinfect the feed water to membrane application. While germicidal UV wavelengths range from 200 to 300 nm, the 260 nm is the most effective wavelength for disinfection (Bolton and Hooper, 2004). UV light can be absorbed into the DNA of a microorganism to rupture the cross bonds between the two strands of DNA, or RNA in the case of virus. Details on the removal of various microorganisms can be found elsewhere (Cleancy and Hargy, 2004). They reported that UV is now considered as the most effective disinfectant for the control of *Cryptosporidium*, which cannot be removed by chlorine at practical dosages. Further, disinfection by Cl_2 produces disinfectant-by products (DBP). The advantages of UV pretreatment compared to the other chemical disinfectants such as chlorine, chloramine, chlorine dioxide, and ozone are i) no chemical requirement, ii) lower cost, iii) reduced hazards compared to chlorine gas, iv) minimal space requirement, v) short residence time, vi) no DBP formation and vii) no residual disinfection which is good for membrane preservation. The disadvantage is that periodic lamp cleaning is required.

2.4.5 Flocculation/Coagulation

Flocculation removes most colloids which carry a negative charge in water and wastewater, but a colloidal dispersion does not have a net electrical charge. The primary charges on the particles are counterbalanced by charges in the aqueous phase, resulting in an electrical double layer at every interface between the solid and water. The forces of diffusion and electrostatic attraction spread the charge around each particle in a diffuse layer. Repulsive electrical forces and attractive van der Walls forces interact between particles in the solution, producing a potential barrier that prevents aggregation. The process of overcoming the repulsive barrier and allowing aggregation to occur is called flocculation.

2.4.6 pH adjustment

Pretreatment of pH adjustment is used when the feed water has a high salt concentration. Hardness and alkalinity in the feed water lead to scaling. As such, acid is added to maintain carbonates in their soluble carbonic acid form. Carbonic acid is not associated with calcium to form calcium carbonate scale.

2.4.7 Ion Exchange

Pretreatment of ion exchange is used to remove small size of organic matter as it is more economical than activated carbon, carbonaceous resins or metal oxides if on-site regeneration of ion exchanger is performed. Waters containing small organic matter are difficult to treat by the flocculation processes, as the smaller molecules and uncharged species are less effectively removed by flocculation. Since organic foulant has negative charge at neutral pH, basic anion exchanger is commonly used.

2.4.8 Lime ($Ca(OH)_2$) Softening

Pretreatment of lime ($Ca(OH)_2$) softening converts the Ca^{2+} and Mg^{2+} compounds in water into calcium carbonate ($CaCO_3$) and magnesium hydroxide ($Mg(OH)_2$). To generate $CaCO_3$ and $Mg(OH)_2$, the pH of the water needs to be increased by dosage with lime. Ca^{2+} and Mg^{2+} compounds can be removed at pH 9.0-9.5 and pH 10.0-0.5, respectively. Silica concentration is also reduced during a lime-soda softening process.

2.4.9 Chlorination

Chlorination pretreatment is used to reduce membrane biofouling which is the most problematic foulant in membrane operation. Chlorine is added as a disinfectant to remove microorganisms that generate membrane biofouling. Chlorine is a strong oxidiser. It kills bacteria by stripping electrons off of the structures in bacteria cell walls, entering into the cells and then breaking down enzymes and other molecules once inside the cell. Chlorine reacts to form a pH dependent equilibrium mixture of chlorine, hypochlorous acid and hydrochloric acid.

2.4.10 Dechlorination

Dechlorination treatment is the process of removing residual chlorine after a pretreatment of chlorination. This needs to be done before the membrane filtration stage as the chlorine used as a pretreatment will irreversibly damage the thin film composite membranes. Sulfur dioxide (SO_2) and sodium (meta) bisulfate ($Na_2S_2O_5$) are most commonly used. When sulfur dioxide or sulfite salts are added in chlorinated water, aqueous sulfur compounds in the +4 oxidation (S (IV)) state are generated. The S (IV) species, such as the sulfite ion (SO_3^{-2}), react with both free and combined forms of chlorine (WEF, 2005).

2.4.11 Biofiltration

Biofiltration pretreatment is most commonly used in membrane filtration. In addition to providing filtration, it is a pollution control technology using microorganisms to degrade biodegradable inorganic and organic compounds. A physical filtration at the initial stage of sand filtration, dual-media filter and granular activated carbon (GAC) filter converts to biofiltration with time. Any type of filter with attached biomass on the filter-media may be defined as a biofilter. It can be the trickling filter in the water treatment plant, or horizontal rock filter in a polluted stream, or GAC or sand filter in a water treatment plant. Biofilters have been successfully used for pretreatment to membrane filtration.

2.4.12 Electrical pretreatment

Electrical and electromagnetic pretreatment utilises electrical charging and electromagnetic force. Electrical power uses water forces with oppositely-charged ions to move in the opposite directions. This results in the formation of microscopic nuclei which cause calcium carbonate to precipitate within the water. Then, electromagnetic power can be applied and water is passed through a magnetic field. This leads to a change of the electrical properties of the water. This also separates agglomerations or clusters of water molecules. The electric and electromagnetic water pretreatment can improve the dissolution capacity of water. Electric and electromagnetic pretreatment removes sparingly soluble salts, colloidal particles and suspended solids. Electrocoagulation (EC) is the most widely used electrical pretreatment for membrane filtration.

2.5 Microfiltration Hybrid System

Fouling is considered as the major technical problem when operating a membrane system in water and wastewater treatment. Fouling is due to the deposition and accumulation of primarily organic and particulate matter on the surface and inside pore entrances of the membrane resulting in flux loss and higher energy requirements. Experience has shown that pretreatment of the feed water can significantly enhance the performance of membrane systems. Various processes are available for pretreatment including coagulation/flocculation, ion exchange, UV/ozone and adsorption by activated carbon. The employment of these methods aims to reduce particulates and dissolved organic matter, increase rejection and minimise fouling of the membrane. Although pretreatment leads to an increase in additional cost, it will be recovered over the life of the plants on terms of extending the life of the membrane and improving the performance of the system.

2.5.1 Coagulation – Microfiltration Hybrid system

MF with a large pore size can only remove a very small amount of dissolved organic compounds especially trace organic compounds, taste and odor-causing materials and synthetic organic chemicals. In order to increase their rejection by the membrane, the dissolved organics need to be aggregated into particulates. This can be done by adding coagulants and/or flocculants such as alum, aluminum sulfate and ferric chloride. Consequently, coagulation has been widely employed as a pre-treatment option for MF/UF.

A combined system of coagulation and MF was studied in treating secondary wastewater for reuse (Vickers and Kelkar (1995), Al-Malack and Anderson (1996), Mo and Huanga (2003)). Their results showed that pretreatment with coagulation helped reduce suspended solids, phosphorus and arsenic; optimising backwash efficiency and preventing fouling (Mo and Huanga, 2003; Shon et al., 2004). Further studies by Kim et al. (2005) and Jung et al. (2006) confirmed the positive effect of coagulation on membrane filtration. By increasing the particle sizes, coagulation reduces the potential of internal blocking while increasing cake porosity (Kim et al., 2005; Jung et al., 2006).

Coagulation pre-treatment was also found to improve the removal of hydrophobic compounds, resulting in the increase of permeate flux (Oh and Lee, 2005; Chen et al., 2007). According to Chen et al. (2007), organic removal by the membrane after coagulation increased by 20%, with 14.3% for the hydrophobic fraction and 2.5% for hydrophilic fraction, respectively. Correspondingly, the flux was reported to recover completely after backwash for each filtration cycle compared with gradual 20% flux drop when membrane was used alone (Chen et al., 2007). However, the performance of coagulation/membrane combined system is significantly dependent on the nature of the organic matters, coagulant dosage and floc characteristics leading to a process which is difficult to control (Schafer, 2001; Shon et al., 2005).

2.5.2 Adsorption – Microfiltration Hybrid system

Combining activated carbon adsorption with membrane filtration MF is another promising option to improve organic removal efficiency. In the hybrid system, the small molecular species not usually rejected by the membrane alone are adsorbed onto the AC particles which subsequently can be separated easily by the MF process. As a result, organic compounds are retained from the treated water. There are two types of activated carbon available namely powdered activated carbon (PAC) and granular activated carbon (GAC). Between the two, PAC is preferable due to its large surface area per unit volume and its affinity for a wide range of dissolved organics (Guo et al., 2005).

In the combined system, PAC can be continuously dosed to the membrane reactor or dosed at the beginning of the membrane filtration cycle. Previous studies showed that PAC pre-adsorption contributed to higher dissolved organic carbon (DOC) and disinfection by-products (DBPs) removal, flux enhancement and fouling reduction; thus prolonging the continuous filtration time (Lebegue and Grasmick, 2007); Kim et al., 2005; Chang et al., 2005). One of the hybrid system known as submerged membrane adsorption hybrid system integrate the entire treatment activity including adsorption/biodegradation, liquid-solid separation and sludge accumulation into one single unit, which can offset the disadvantage of the large equipment size and space requirement (Mozia, et al., 2005; Guo et al., 2006).

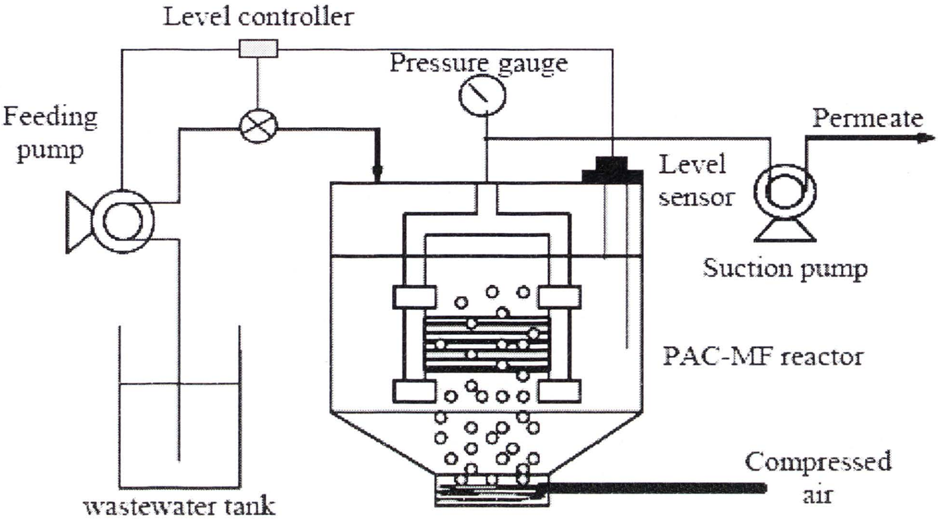


Figure 2.2 Experimental set-up of submerged membrane adsorption hybrid system (Adapted from Guo et al., 2006)

Submerged membrane adsorption hybrid system has several advantages. The system can be consistently operated for a long period with a very low energy (0.2 kWh/m^3) and without any major sludge problems (Seo et al., 1996). The studies conducted by Kim et al. (2008) showed a relatively high removal efficiency of 85% of total organic carbon (TOC) with 40 g/l of PAC for 40 days. Using a lower dose of 10 g/L of PAC added at the beginning of the experiment, Guo et al. (2005) obtained approximately 84% of TOC removal for a 15-day operation. A long term study conducted showed that 10 g/l of one off addition of PAC at the beginning of the operation and replacement of 1% of PAC on a daily basis led to a consistent TOC removal of more than 90%. The PAC dose was found to be less than 20 mg/l when one considers an operation period of 50 days.

In fact, PAC can provide better physical removal of organic pollutants; yet, the addition of high PAC concentration may lead to the accumulation of carbon on the membrane surface, resulting in membrane fouling (Fabris et al., 2007). Furthermore, previous researchers suggested that the dependence of the removal efficiency and membrane fouling on several parameters including the pre-adsorption, PAC dose, aeration rate, filtration flux and backwash duration (Guo et al., 2005).

PAC adsorption was found to remove 60–75% of DOC from biologically treated wastewater effluent (Shon et al., 2004; Arana et al., 2002). Lin and Hao (1999) studied the use of PAC adsorption at a dose of up to 400 mg/L as pretreatment to remove humic substances of 20 mg/L in concentration. The PAC was ineffective in removing the MW fractions of less than 300 Da or greater than 17000 Da. The flux decline in UF for the PAC-treated streams was worse than that without pre-adsorption. Thus, the operation of the hybrid system is considered to be relatively complicated.

2.6 Electrocoagulation Membrane Hybrid System

While EC has already been established as a highly efficient method for removing a large variety of pollutants from water and as a promising technology for decentralised water treatment applications, only a few studies have investigated for EC as a pretreatment method for MF.

A new hybrid process of EC with iron electrodes and MF was proposed and experimentally proved by Mavrov et al. (2006). At a continuous regime with treatment time of 20 min and a current density of the anode of 4.8 $mAcm^{-2}$, a reduction of 98.7% was achieved for selenium with a parallel reduction of more than 99.9% for As, more than 98.0% for Cu and Pb, and more than 99.9% for Zn and Cd, satisfying all the requirements for direct discharge of treated water. The addition of iron-based EC before MF significantly increased the removal rates of viruses (Zhu et al., 2005). Bagga et al. (2008) showed that unlike conventional coagulation, iron-based electrofloatation before dead-end MF of lake water with pH 6.4-8.3 did not reduce the fouling. They attributed this to the low flocculation capabilities of Fe^{2+} dissolved from the anode.

Al-Malack et al. (2004) studied the effect of iron-based EC on crossflow MF. After 60 min of operation, EC appeared to have only a marginal effect. Nevertheless, they concluded that EC alters the dominant fouling mechanism from standard filtration (i.e. internal fouling) to cake filtration. Overall, these works showed only marginal effects, if any, of iron-based EC on mitigation of colloidal fouling. Unlike iron, when MF was pretreated by aluminium-based EC, dramatic fouling mitigation was observed in both crossflow (Pouet and Grasmick, 1994) and dead-end (Ben-Sasson and Adin, 2010) operation modes. Harif et al. (2006) observed 20% higher fluxes at pH 5 and 6.5 as a result of pretreatment by aluminium-based EC before UF of kaolin suspension. The observed high fouling mitigation when aluminium based EC, as well as conventional iron flocculation, was used as pretreatment for MF suggesting that iron-based EC should have a pronounced positive effect on colloidal fouling. It was suspected that the chemistry of the specific solutions and the tendency of Fe^{2+} to complex with natural organic matter (NOM) were the reasons for the observed marginal effect on fouling mitigation. Thus, unlike those works which used tap or lake water contaminated with organic matter, it was suggested that the process be investigated using solutions of highly pure water contaminated with chemical mechanical polishing silica colloids which do not tend to complex with Fe^{2+} ions.

Recently EC has also been investigated for removal of silica to prevent fouling of RO membrane (Den and Wang, 2008). The investigation demonstrated severe flux declines over the first 3 h, yielding only 70% of its initial flux for brackish water containing 100 mg/l silica, and progressively lower with higher silica concentrations. For the pretreated water by EC, the extent of flux decline was markedly improved, suggesting that the EC pretreatment presents a feasible alternative in dealing with brackish water containing high silica concentrations. EC was also studied as a pretreatment of seawater prior to UF for military water purifications systems (Thomas and Brian, 2009). The bench scale experiments indicated EC as a feasible and competitive pretreatment strategy.

It is important to understand not only that a fouling-reduction method such as EC can improve membrane filter performance (e.g. increase the flux), but also energy can actually be saved. In addition to fouling mitigation, applying EC before MF may lead to other benefits. Zhu et al. (2005) and Mavrov et al. (2006) showed that it can increase the removal rate or membrane pore size needed to achieve satisfactory filtration of viruses and selenium. Thus EC-MF hybrid system renders an enormous potential for future research and applications.

2.7 Electrocoagulation

2.7.1 Historical Background

EC has a long history as a water treatment technology having been employed to remove a wide range of pollutants. The concept of electrochemically treating water for purification using electrodes is thought to have been first proposed in 1889 in England (Strokach, 1975). In the United States, a patent for the purification of wastewater by electrolysis using aluminium and iron corroding electrodes was received in 1909 (Vik et al., 1984). The literature indicates that it has been regularly discovered over the last hundred years or so, both in batch and continuous applications.

During the late 19th century several large-scale water treatment plants were commissioned in London (Matteson et al., 1995), while electrolytic sludge treatment plants were operating as early as 1911 in various parts of the USA (Vik et al., 1984) with similar plants being commissioned to treat municipal wastewater in the following decades. On a larger scale, a method for the purification of drinking water by EC was first applied in the U.S. in 1946 (Vik et al., 1984). This method utilised aluminium anodes to produce aluminium hydroxide flocs by reaction at the electrode followed by hydrolysis. The electrogenerated flocs sedimented rapidly, removing color from the drinking water. In 1956, Holden treated (Vik et al., 1984) river water in Britain using iron electrodes with a similar type of system. Both investigations in 1946 and in 1956 showed promising results, e.g. high water quality as measured by turbidity and color removal, but the methods were not widely accepted because of some expectations of high initial capital costs as compared to chemical dosing. In 1972, EC was studied in the treatment of wastewater from a food industry (Kuhn, 1972). This report compared EC to chemical dosing followed by dissolved air flotation. Floc formation was rapid in both cases, with the flocs formed from EC being compacted more quickly. The concept of EC has also been applied to microorganism harvesting from cultures (Contreas et al. 1981; Contreas and Toha, 1981) and the removal of protein and other soluble substances from wastewater (Matveenko et al., 1981). In the 1980s, there was a great deal of work performed by Russian scientists employing EC in a variety of ways in the treatment of wastewater

(Kornilov and Smirnov, 1980) and in the removal of oil from oil-in-water emulsions (Pazenko et al., 1985).

In more recent times, there has been interest in continuously fed water treatment plants based on EC technology (some with sizeable throughputs) for specialised industrial applications, such as the removal of fine material from coal wash water. However because of its proven ability to effectively remove an extremely wide range of pollutants, together with its inherent simplicity of design and operation, EC is being re-examined as a localised low-cost treatment technology.

2.7.2 Electrocoagulation theory and fundamentals

EC is a complex and interdependent process. A sacrificial metal anode is used to produce coagulating agent to dose the polluted water and electrolytic gases (mainly hydrogen at the cathode) are generated. Electrochemistry, coagulation and hydrodynamics form the basis of EC (Chen and Yeu, 2000). In an EC process the coagulating ions are produced 'in situ' and it involves three successive stages: (i) formation of coagulants by electrolytic oxidation of the sacrificial electrode, (ii) destabilisation of the contaminants, particulate suspension, and breaking of emulsions and (iii) aggregation of the destabilised phases to form flocs. The destabilisation mechanism of the contaminants, particulate suspension, and breaking of emulsions have been described in broad steps and may be summarised as follows (Mohammad et al., 2004):

- Compression of the diffuse double layer around the charged species by the interactions of ions generated by oxidation of the sacrificial anode.
- Charge neutralisation of the ionic species present in the solution by counter ions produced by the electrochemical dissolution of the sacrificial anode. These counter ions reduce the electrostatic interparticle repulsion to the extent that the van der Waals attraction predominates, thus causing coagulation. A zero net charge results in the process.
- Floc formation: the floc formed as a result of coagulation creates a sludge blanket that entraps and bridges colloidal particles still remaining in the aqueous medium.

- Fe/Al is dissolved from the anode generating corresponding metal ions, which almost immediately hydrolyse to polymeric iron or aluminum hydroxide. These polymeric hydroxides are excellent coagulating agents. The consumable (sacrificial) metal anodes are used to continuously produce polymeric hydroxides in the vicinity of the anode. Coagulation occurs when these metal cations combine with the negative particles carried toward the anode by electrophoretic motion. Contaminants present in the solution stream are treated either by chemical reactions and precipitation or physical and chemical attachment to colloidal materials being generated by the electrode erosion. They are then removed by electroflotation, or sedimentation and filtration. Thus, rather than adding coagulating chemicals as in conventional coagulation process, these coagulating agents are generated in situ.
- Water is also electrolysed in a parallel reaction, producing small bubbles of oxygen at the anode and hydrogen at the cathode. These bubbles attract the flocculated particles and, through natural buoyancy; float the flocculated pollutants to the surface.

In addition, the following physiochemical reactions may also take place in the EC cell (Paul, 1996):

- Cathodic reduction of impurities present in solution
- Discharge and coagulation of colloidal particles.
- Electrophoretic migration of the ions in solution.
- Electroflotation of the coagulated particles by O_2 and H_2 bubbles produced at the electrodes.
- Reduction of metal ions at the cathode.

The most widely used electrode materials in EC process are aluminium and iron, sometimes steel. The electrode or electrode assembly is usually connected to an external direct current source. The amount of metal dissolved or deposited depends on the quantity of electricity passed through the electrolytic solution. A simple relationship between current density (A cm^{-2}) and the amount of substances (M) dissolved can be derived from Faraday's law:

$$w = \frac{itM}{nF} \qquad \text{(Eq. 2.1)}$$

where w is the quantity of electrode material dissolved (g of M cm^{-2}), i is the current density (A cm^{-2}), t the time in s; M the relative molar mass of the electrode concerned, n the number of electrons in oxidation/reduction reaction, F the Faraday's constant, 96,500 $Cmol^{-1}$.

2.7.2.1 Reactions at the electrodes

A simple electro coagulating reactor made up of one anode and one cathode is shown in Figure 2.3. When a potential is applied from an external power source, the anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals. In the case of aluminium, the main reactions are as:

Anode: $Al \rightarrow Al^{3+} + 3e^-$ (Eq. 2.2)

Cathode: $3H_2O + 3e^- \rightarrow 3/2H_2 + 3OH^-$ (Eq. 2.3)

The generated Al^{3+} and OH^- react with each other to form $Al(OH)_3$:

$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$ (Eq. 2.4)

In the case of iron, the main reactions are as (Bagga and Clifford, 2007):

Anode: $Fe(0)(s) = Fe^{2+} + 2e^-$ (Eq. 2.5)

Oxidation: $4Fe^{2+} + O_2 + 4H+ = 4Fe^{3+} + 2H_2O$ (Eq. 2.6)

Hydrolysis: $Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$ (Eq. 2.7)

Cathode: $2H_2O + 2e^- = 2OH^- + H_2$ (Eq. 2.8)

Overall: $4Fe(0)(s) + 10H_2O + O_2 = 4Fe(OH)_3(s) + 4H_2$ (Eq. 2.9)

For aluminium or iron electrodes, the generated Fe^{3+}(aq) or Al^{3+}(aq) ions will immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. For example, Al^{3+} ions on hydrolysis may generate $Al(H_2O)_6^{3+}$, $Al(H_2O)_5OH^{2+}$, $Al(H_2O)_4(OH)^{2+}$ and the hydrolysis products may form many monomeric and polymeric species such as, $Al(OH)^{2+}$, $Al(OH)_2{}^{+}$, $Al2\ (OH)_2{}^{4+}$, $Al(OH)_4{}^{-}$, $Al_6\,(OH)_{15}{}^{3+}$, $Al_7\,(OH)_{17}{}^{4+}$, $Al_8(OH)_{20}{}^{4+}$, $Al_{13}O_4(OH)_{24}{}^{7+}$, $Al_{13}(OH)_{34}{}^{5+}$ (Rebhum and Lurie, 1993) over a wide pH range. Similarly, ferric ions generated by electrochemical oxidation of iron electrode may form monomeric ions, $Fe(OH)_3$ and polymeric hydroxy complexes, namely: $Fe(H_2O)_6{}^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)^{2+}$, $Fe_2(H_2O)_8(OH)_2{}^{4+}$ and $Fe_2(H_2O)_6(OH)_4{}^{4+}$ depending on pH of the aqueous medium (Johnson and Amirtharajah, 1983).These hydroxides/ polyhydroxides/polyhydroxymetallic compounds have strong affinity for dispersed particles as well as counter ions to cause coagulation. The gases evolved at the electrodes may impinge on and cause floatation of the coagulated materials.

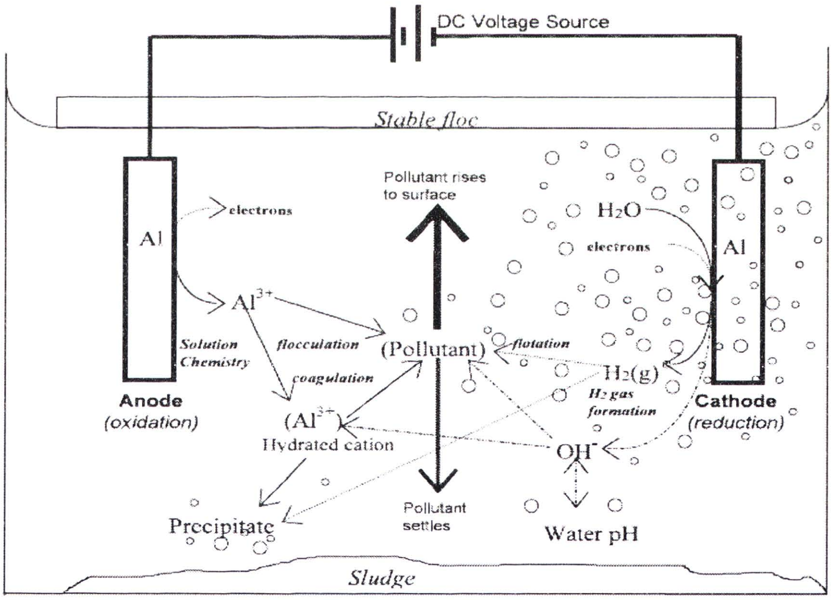


Figure 2.3 Schematic of a bench-scale two-electrode electrocoagulation cell (Holt et al.2002)

2.7.2.2 Advantages of EC over conventional chemical coagulation:

- Alkalinity is not consumed.
- There is no change in bulk pH.
- The direct handling of corrosive chemicals is nearly eliminated.

- It can be easily adapted for use in portable water treatment units especially during emergencies.
- Requires less space.
- Simple in design and operation.
- Environmentally compatible.
- Less space is needed.
- Effectiveness for removal of wide range of pollutants.
- Enormous potential for decentralised treatment applications.
- Can be used with renewable energy source such as solar power.
- The use of renewable solar energy can be one of the major merits in terms of energy savings.

2.7.3 Applications of electrocoagulation

With the growing need for small-scale decentralised water treatment facilities and for its simplicity in design, ease of operation and automation and high separation efficiency (Chen 2004) EC is considered as one of the promising and evolving technology for water and wastewater treatment.

EC has been applied successfully to treat potable water (Vik et al, 1984) and various wastewaters such as oil–water emulsions (Utverew and Koparal, 1997), dye-containing solutions (Do and Chen, 1994; Gurses and Dogar, 2002), urban wastewater (Pouet and Grasmick, 1995) and restaurant wastewater (Chen and Yue, 2000). Further, EC process has been proposed in the last decades as an effective method to remove soluble ionic species from solutions, particularly heavy metals (Parga et al., 2005; Kumar et al., 2004; Adhoum et al., 2004)

EC was found to be effective to arsenic containing wastewater (Kim et al., 2002), phosphate containing wastewater (Bektas et al., 2004), electroplating wastewater (Mills and Am, 2000), metal finishing effluents (Khelifa and Naceur, 2005) and textile wastewater (Kobya and Bayramoglu, 2003). Recently, it has also been used in the removal of turbidity, color, algae and microorganisms in water treatment (Xueming and Po, 2002).

EC also has the potential to replace sophisticated processes that require large volumes and number of chemicals, massive containers that are present in a typical wastewater treatment plant as shown in Figure 2.4. As a consequence, a very simple replacement will prevent economically unfeasible capital cost.

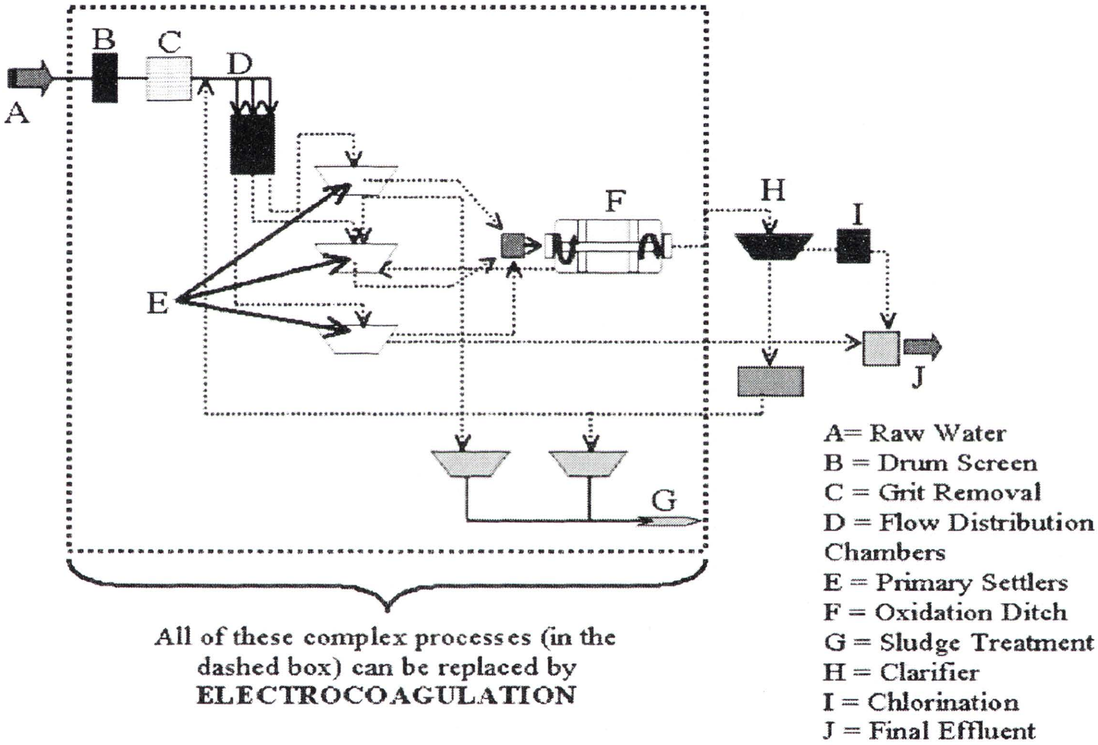


Figure 2.4 Schematic flow-diagram of a typical wastewater treatment plant and complex processes that can be replaced by EC (section with dashed box) - Adapted from Mohammad et al. (2004).

Thus EC has enormous and wide applications. It is an emerging and promising technology. Furthermore EC is also effective as a pretreatment for membrane filtration and possess the potential to be used with solar power for applications as a decentralised treatment in remote communities of Australia.

2.8 Solar Powered Electrocoagulation

The lack of water resources and safe drinking water scarcity has been recognised and analysed by different international organisations such as the World Health

Organisation or the World Bank (Thomas and Burham, 2003). The problem is being further deteriorated by the pollution of the rivers and lakes from industrial waste and sewage discharge. On a global scale, man-made pollution of natural resources of water is becoming the single largest cause for the fresh water shortage (Malik et al., 1985). Further, the lack of adequate treatment facilities leads to adverse health effects for local community members especially in rural and remote areas. While the remote conditions make it rather difficult to operate and maintain conventional treatment technology, its application is often limited by the availability of electricity, with many rural areas having no access to a national electricity grid. Furthermore, the social concern about the environment has led to the research and development of new forms of renewable energy. One of the most widespread and studied is the photovoltaic (PV) power (Sen, 2004; Markvart, 1994). Therefore, it is widely recognised that water filtration methods powered by renewable energy sources are needed in Australia and around the world (Joyce et al., 2001).

Water in many areas of Australia is scarce and of poor quality. In some areas high levels of treatment are required either due to contamination of waters or due to high salinity. In remote communities the operation of such facilities may be limited by the availability of electricity. Therefore, these communities often drink water of substandard quality, as they do not possess the electrical power or appropriate technology to purify the water. Solar or PV energy is the ideal source of energy in Australia to overcome this problem. Most areas in Australia possess an excellent solar radiation resource, as depicted in Figure 2.5 and more than two-thirds of the country receives an average of at least 6.1 hour of full sunshine each day (Lee and Williamson, 1995; Richards and Schafer, 2002) albeit the regions with lower population density.

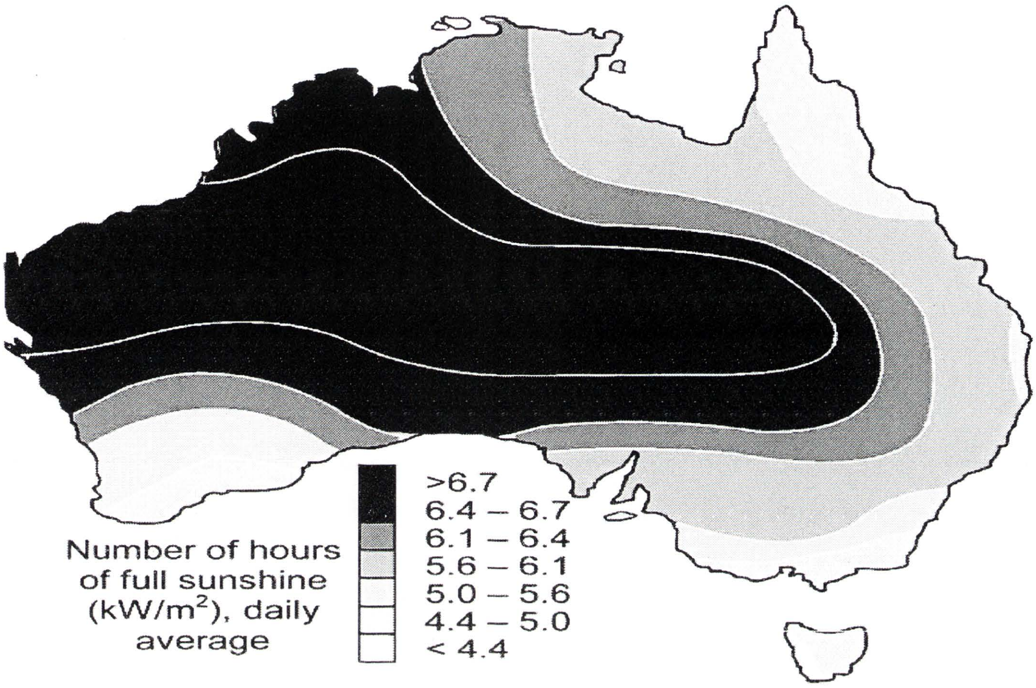


Figure 2.5 Solar radiation resource possessed by Australia (Adapted from Richards and Schafer, 2002).

The environmental impact induced by the use of solar energy is minimal and this renders the solar powered electrocoagulation (SPEC) process environmentally attractive. The application of SPEC system to treat water contaminated with organic pollutants holds promise for regions receiving strong sunlight throughout the year. Solar or PV, panels are an excellent choice for remote water treatment applications (Bryce and Schafer, 2002) due to:

i. Long life: solar panels have a warranty of up to 20 years, contain no moving parts, and withstand harsh environments;
ii. Modularity: More solar panels can be added at a later stage to meet increased demand;
iii. Low maintenance: solar systems that do not include batteries, an inverter (to convert from DC to AC electricity), the panels follow the path of the sun across the sky, rarely break down and require very little maintenance;

iv. Low noise level: the only noise would be from the pump. Without batteries, the system would only run in the daytime and would not disturb people at night;

v. Well-matched to load: solar panels produce more power in areas that receive more sunshine, where people are likely to consume more drinking water;

vi. Storage: it is possible to store energy in batteries.

Generally, a PV system consists of PV modules, batteries, a regulator or controller, an inverter (DC–AC) and loads (charges). The PV modules can be connected in series and/or parallel and the solar radiation incident on the surface of the PV array is transformed into electric energy (direct current) by the PV modules. The generated electricity is passed to the regulator, which protects the batteries from overcharging or an excessive discharge. The batteries store energy that can be used as electrical back up during periods of low solar radiation—for example, during cloudy weather or at night. The inverter transforms the direct current into alternating current (AC) for those devices that work with the latter. These systems can be used in remote sites for the self-sufficiency of electrical power in a reliable and autonomous way (Irfan 1997).

There had been several renewable solar energy-powered desalination systems designed to produce 100–3000 l of clean drinking water per day using RO membranes (Mathew et al., 2000; Keefer and Schrack, 1985). Studies were done and implemented for PV powered desalination system for remote Australian communities (Bryce and Andrea, 2003) where results showed successful removal of particulates, bacteria and viruses with an UF module and NF and RO membrane for removing salts.

The use of PV modules as a power supply for electrochemical systems has been previously reported for electrodialysis of brackish water (Ortiz et al., 2007). However, until now, only one study was done using PV technology for supplying the power needed for an EC system which successfully demonstrated the application of a synthetic textile effluent powered by PV energy without batteries (Valero et al., 2008). It is interesting to note that PV modules produce DC, which can be directly used by the EC system. This is an important fact, because the EC system can be directly supplied and there is no need of an inverter module.

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CHAPTER 3

EXPERIMENTAL

3.1 Introduction

This chapter describes in detail all the experimental materials and methods used in this study. All the analytical equipment and their principles are also presented in this chapter.

3.2 Experimental Materials

3.2.1 Wastewater

Two kinds of synthetic water were used in this study. The first was representative of biologically treated sewage effluent and the other represented surface water with humic acid and kaolin clay as organic and particulate foulants. The details of both of these wastewaters are described as follows:

3.2.1.1 Synthetic Surface water

The majority of experiments using synthetic surface water were conducted in the laboratories of the University of Technology, Sydney (UTS), Australia. The synthetic water was prepared using kaolin and humic acid. Stock solution was prepared using 2 g humic acid sodium salt and 40 g kaolin which were then diluted with normal tap water to give a fairly constant turbidity between 80 to 85 NTU. The characteristic of synthetic water is presented in Table 3.1.

Table 3.1 Properties of synthetic water

Turbidity	Total Organic Carbon (TOC)	UV Abs (254 nm)	Conductivity
80 NTU	5.5 mg/l	0.150	0.0805 mS/cm

3.2.1.2 Synthetic Wastewater

The first synthetic wastewater used in this study was representative of the biologically treated sewage effluent (Seo et al.; 1996). The constituents of this synthetic wastewater are presented in Table 3.2. It consists of both organic and inorganic compounds including easily biodegradable matter as well as some persistent organics such as humic acid, tannic acid, lignin and polysaccharides. 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 Daltons with the highest fraction at 940-1200 Daltons.

Table 3.2 Constituents and characteristics of the synthetic wastewater

Compounds	**Concentration (mg/l)**	**Molecular Weight (Daltons)**	**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 sulfonate	2.4	12,120	0.067
Sodium lauryle sulfate	0.94	34,265	0.042
Arabic gum powder	4.70	925,256	0.213
Arabic acid (polysaccharide)	5.0	38,935	0.156
$(NH_4)_2SO_4$	7.10	-	-
K_2HPO_4	7.00	-	-
NH_4HCO_3	18.80	-	-
$MgSO_4.7H_2O$	0.71	-	-

*DOC: Dissolved organic carbon

3.2.2 Membrane

The membrane used in this study was a flat sheet microfiltration (MF) porous hydrophilic membrane (Pure Envitech. South Korea). The detailed characteristics of the membrane provided by the manufacturer is given in Table 3.3.

Figure 3.1 shows the scanning electron microscope image of the microfiltration membrane used in this study.

Table 3.3 Properties of flat sheet microfiltration membrane module

Nesting materials	Polymer of hydrophile property
Pore size	0.4 μm
Material	Acrylonitrile butadiene styrene (ABS)
pH resistance range	2~11
Temperature range	2~38 °C
Pressure range	0~ 80 kPa

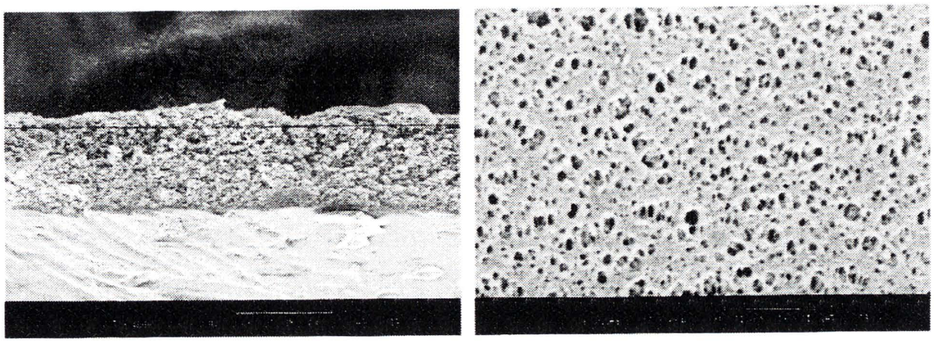

Figure 3.1 Scanning electron microscope image of MF membrane used in this study.

3.3 Experimental Methods

3.3.1 Chemical Coagulation

Conventional chemical coagulation tests were conducted as a pretreatment process for membrane filtration using a standard jar tester (Figure 3.2). Chemical coagulation was carried out with both ferric chloride ($FeCl_3$) and aluminium sulphate ($Al_2(SO_4)_3$) to study coagulation-microfiltration hybrid system. Aluminium sulphate and ferric chloride were added to the wastewater at room temperature. The sample was stirred rapidly for 3 mins at 130 rpm, followed by 20 min of slow mixing at 30 rpm, and 60 min of settling. Jar tests were performed at different dosing of aluminium sulphate (10-60 mg/l) and ferric chloride under wide pH range (2-11) to determine the optimum conditions. The pH of the solution was adjusted with 0.1 N HCl and 0.1 N NaOH.

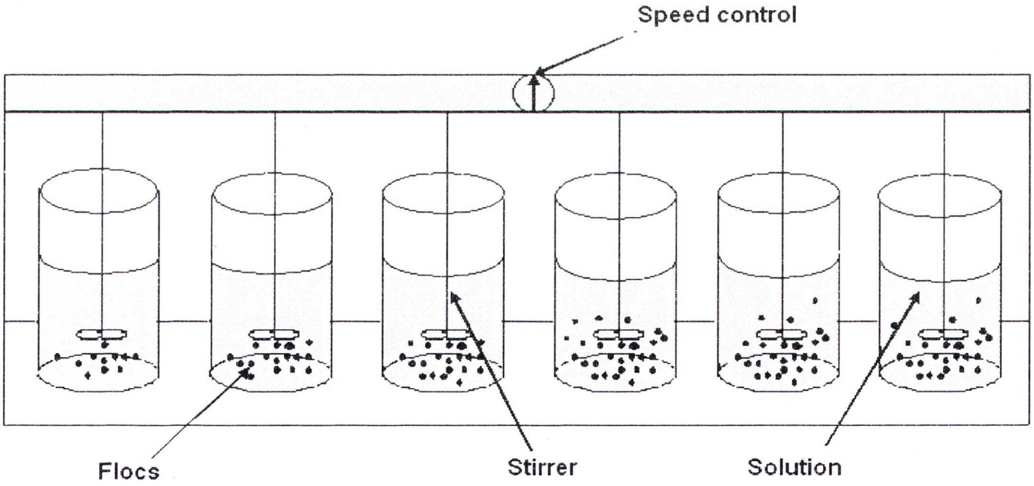

Figure 3.2 Schematic for the experimental setup of chemical coagulation.

3.3.2 Electrocoagulation

The electrocoagulation (EC) reactor used in this study consisted of a 5 L pyrex glass beaker with two aluminium or iron electrodes (17 cm high, 9 cm wide and 0.2 cm thick) in a monopolar configuration and the spacing between the electrodes was 2 cm (Figure 3.3). The source of power supply included DC power converter (Q1770, Dick Smith Electronics, Australia). Suspensions were stirred using a magnetic stirrer adjusted to an optimal rate (250 rpm) so as to obtain the highest efficiency of turbidity removal. Experiments were performed at different generation times (5-30 mins) and at wide pH range (3-11) for determining the optimum conditions. Prior to each test, 5 L of synthetic wastewater was used in the EC cell which was carried out by varying the process operating parameters. The current was adjusted by varying the voltage. When not in use, the aluminium electrodes were immersed in acid bath (4% HCl) and prior to each experiment, they were carefully cleaned using steel wool to remove any aluminium oxide that may have formed on the surface. The desired aluminium concentration can be achieved by operating the unit under variable generation time (t) mode in accordance with Faraday's law:

$$M = \frac{27It}{ZF} \qquad \text{(Eq. 3.1)}$$

Where M is the mass of Al generated (g of Mcm^{-2}), I is the current density (Acm^{-2}), t the time (seconds), Z the number of electrons transferred per Al atom (3) and F is the Faraday's constant (96,486 C Mol^{-1}).

Faraday's law is mostly used for calculating the amount of aluminium released as a good correlation between the theoretically calculated and the experimentally determined amount of aluminium that went into solution was found in the previous study (Al-Malack et al.; 2004).

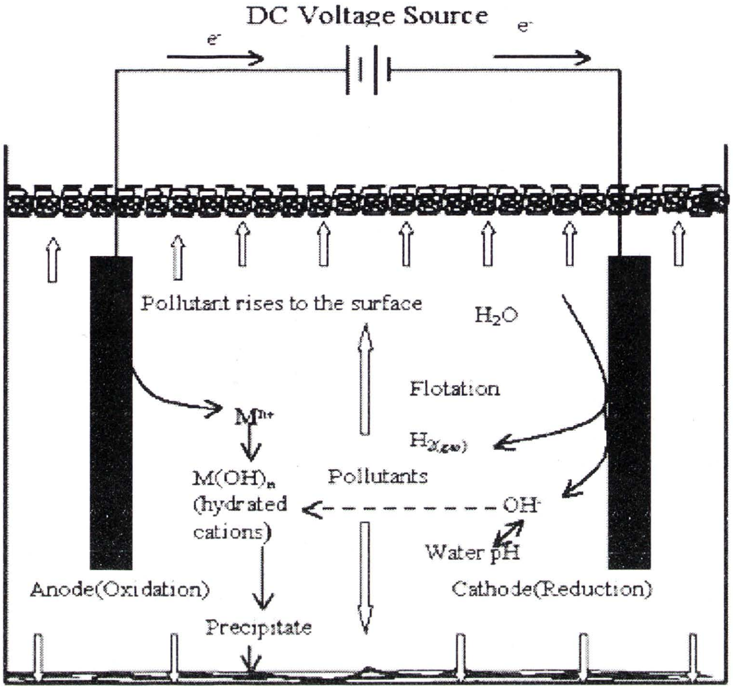

Figure 3.3 Schematic of a bench-scale two-electrode electrocoagulation cell.

3.3.3 Solar Powered Electrocoagulation

The EC reactor for solar powered electrocoagulation (SPEC) consisted of a 5 L pyrex glass beaker with two aluminum electrodes (17 cm X 9 cm X 0.2 cm) in a monopolar configuration. The source of power supply included a photovoltaic panel (PV) with or without charge controller to study solar powered electrocoagulation for water treatment and as a sustainable pretreatment option for membrane filtration. Monocrystalline silicon PV panel (Powertech, Australia) with maximum power of 65 W was used with or without charge controller. The dimension of panel was 1210 X 540 X 28 mm and weight 8 kg. Sealed rechargeable batteries were used in conjunction with panel (6 V and 12 V combinations) for power storage system. The SPEC setup is shown is Figure 3.4. The basic chemical process occurring for electrocoagulation using PV panel is the same as with the electrical DC power supply. Experiments with the photovoltaic panel were carried out at latitude of 33° 52' 58" and longitude of 151° 12' 41". Charge controller with battery system voltage of 12 V was used. Dimension of the charge controller was 97 x 46 x 26 mm and weight of 108 g. Charge controller was installed for the following two reasons:

- To prevent overcharging the battery. It stops the battery from charging when the battery voltage reaches more than 12 V
- To prevent backward discharge from the battery to the PV panel when the voltage of the battery is higher than the voltage of the PV panel.

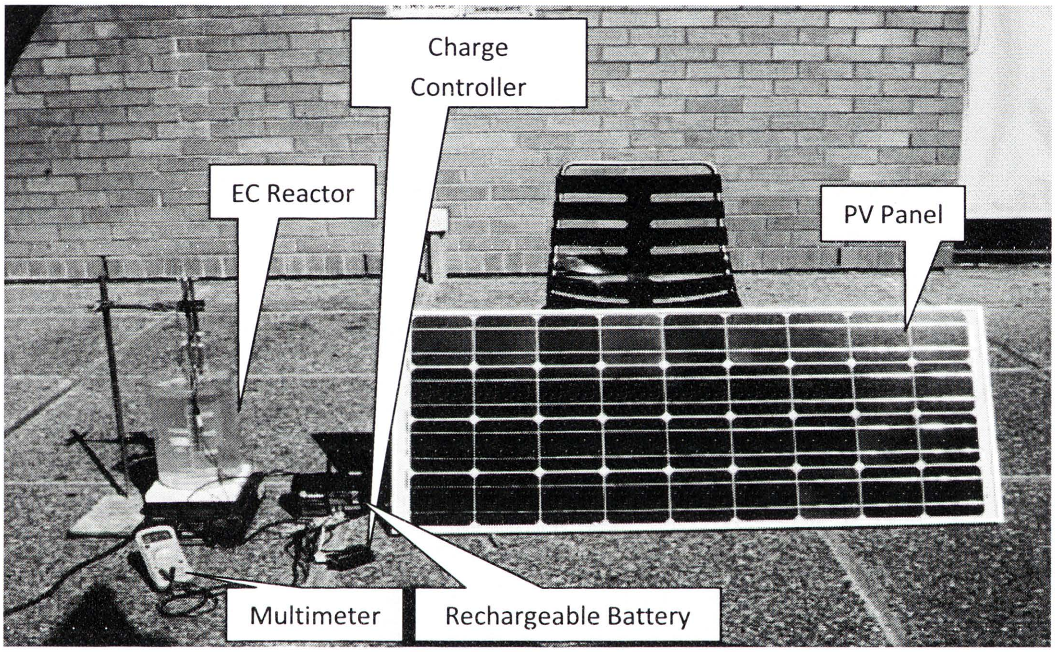

Figure 3.4 Experimental setup for solar powered electrocoagulation

3.3.4 Crossflow Microfiltration Setup

A crossflow MF unit (Nitto Denko Corp., Japan) was used to study the effect of pretreatment on membrane performance and to investigate the membrane fouling mechanism on EC-membrane hybrid system. The schematic diagram of the crossflow MF experimental setup is shown in Figure 3.5. Feed solution with and without pretreatment, was pumped into a flat sheet membrane module (effective membrane area of 0.007 m^2). The operating transmembrane pressure and cross-flow velocity were controlled at 10 kPa and 0.5 $l\ min^{-1}$ by means of bypass and regulating valves. The filtrate was accumulated. The mass of filtrate was determined by using an electronic balance and transferred to a computer. New membranes were used in each experiment to avoid the effect of residual fouling and to compare the results obtained under different conditions.

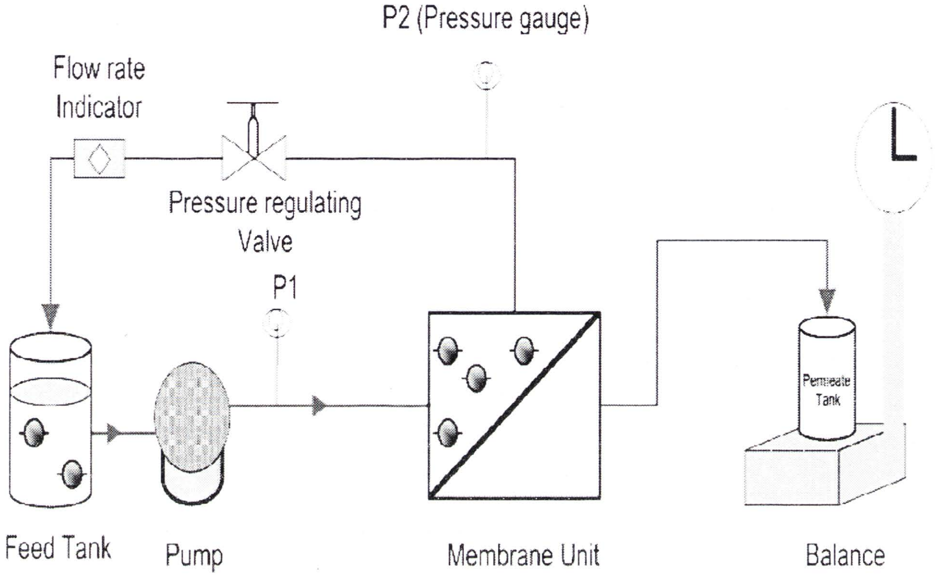

Figure 3.5 Schematic of the cross flow MF unit.

3.4 Analytical Methods

3.4.1Turbidity and pH

Turbidity was measured in terms of NTU (Nephelometric Turbidity Units). A turbidimeter (HACH 2100P, USA) was used to measure the turbidity for all samples. 25 ml of the sample was taken for turbidity measurement. Measurements for the turbidity were taken three times and the mean value was recorded. The pH was measured using potable pH measurement meter (Model-920A, Orion).

3.4.2 Dissolved Organic Carbon (DOC) and UV Absorbance

A dissolved organic carbon (DOC) concentration measured by a Multi N/C 2000 analyser (Analytik Jena AG) equipped with an auto sampler. Virtually the total organic carbon (TOC) analyser measures the gaseous carbon dioxide (CO_2) formed as the organic carbon is oxidised and inorganic carbon is acidified. Once the CO_2 is formed, it is measured by a detector which is a non-dispersive infrared (NDIR) cell. All samples were filtered through a 0.45 μm filter prior to the TOC measurement. Thus, the TOC values obtained are, in fact, DOC values.

UV absorbance was measured with a UV-vis spectrophotometer (Shimadzu, N 595, Kyoto, Japan) in a 1 cm quartz cell. Here too, the samples were filtered through a 0.45 μm filter prior to measurement.

3.4.3 Zeta Potential

The zeta potential of the supernatants was measured with Zetasizer Nano Series-Zs (Malvern, UK) as shown in Figure 3.6. The particles in a colloidal suspension or emulsion usually carry an electrical charge. The charge is more often negative than positive and it may arise in a number of ways. The zeta potential is the overall charge 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 the particles have a large negative or positive zeta potential they will repel each other and there is dispersion stability. If the particles have low zeta potential values then there is no force to prevent the particles coming together and there is dispersion instability. A dividing line between stable and unstable aqueous dispersions is generally taken at either + 30 or - 30 mV.

Zeta potentials of samples after EC and chemical coagulation were measured in this study at different pH to find the isoelectric point where the net charge is zero i.e. zeta potential value is zero. The zetasizer nano series calculates the zeta potential by determining the electrophoretic mobility and then applying the Henry equation. The electrophoretic mobility is obtained by performing an electrophoresis experiment on the sample and measuring the velocity of the particles using laser Doppler velocimetry.

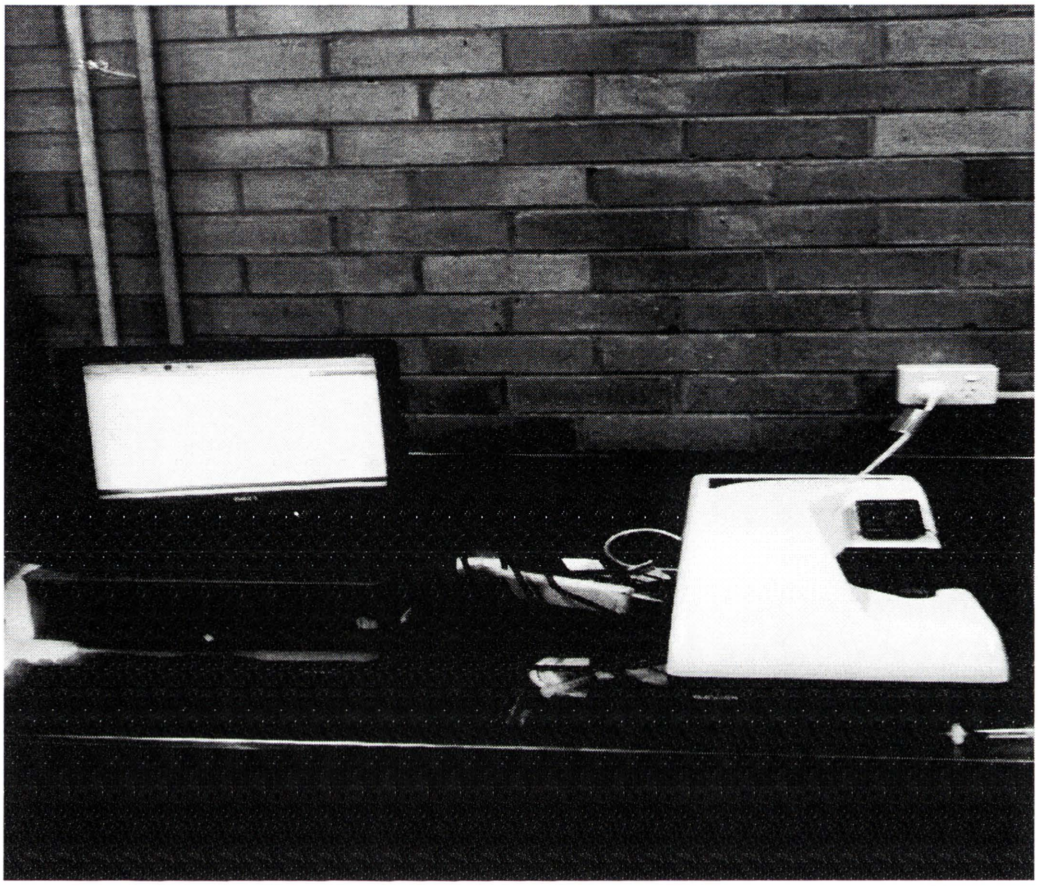

Figure 3.6 Zetasizer Nano Series-Zs (Malvern, UK)

University of Technology, Sydney

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Electrocoagulation with sacrificial iron electrodes for water treatment

Electrocoagulation (EC) is an electrochemical method of treating polluted water whereby sacrificial anodes corrode to release active coagulant precursors (usually aluminium or iron cations) into solution. The electrolytic reactions evolve gas (usually as hydrogen bubbles) at the cathode. It has a wide application field and it can also be effective for complicated wastewater which contains heavy metals, oils, and bacteria (Shin and Lee, 2006). It was found to be effective to treat dye wastewater (Kim *et al.*, 2002; Gurses *et al.*, 2002; Kobya *et al.*, 2006a), arsenic containing wastewater (Kumar *et al.*, 2004), phosphate containing wastewater (Bektas *et al.*, 2004), electroplating wastewater (Adhoum *et al.*, 2004), metal finishing effluents (Khelifa *et al.*, 2005), poultry slaughterhouse wastewater (Kobya *et al.*, 2006b) and textile wastewater (Kobya *et al.*, 2003). Recently, it has also been used in the removal of turbidity, colour, algae and microorganisms in water treatment (Xueming and Po, 2002). Thus EC is an attractive and promising technology for water and wastewater purification and has recently attracted great attention. EC reactor of a 5 L pyrex glass beaker with two iron electrodes were used in a monopolar configuration. Experiments were performed at different generation times (5-30 min) and at wide pH range (3-11) using synthetic water. The objective of this section of study is to evaluate the feasibility of EC using iron electrodes as pretreatment for microfiltration (MF) for water treatment.

4.1.1 Turbidity removal with electrocoagulation using iron electrodes

In all of our experiments, iron electrodes were noted to introduce a green colour into the treated synthetic water which then turns yellow and turbid. This effect is due to the release of soluble ferrous ions (Fe^{2+}) which oxidise to Fe^{3+} in acidic or neutral conditions. The formation of $Fe(OH)_3$ as a result of the reaction of Fe^{3+} with OH^- ions gives yellow colour to the water and increases turbidity. Similar results were obtained in previous study (Bagga and Clifford, 2008). Therefore in all of our experiments, the EC using iron electrodes is followed by fast and slow mixing using the flocculator i.e. coagulant is added into the water through iron electrodes which is followed by mixing and settlement using the jar test.

The effectiveness of the EC process using iron plates and its performance for pretreatment of MF was measured in terms of turbidity and organic removal. Figure 4.1 presents turbidity removal for synthetic water as function of different EC generation time. pH adjustment was not required as EC did not consume alkalinity and alter the bulk pH significantly. Little or no turbidity change was observed with lower EC time. The highest turbidity removal of 93% was achieved at EC generation time of 20 min which is also equivalent to 62.5 mg l^{-1} of iron dosing. Less turbidity removal at lower EC time suggests insufficient coagulant dose to cause destabilisation and floc formation. With increase in EC time up to 20 min, the turbidity removal gradually increased due to the destabilisation of colloidal particles and the formation of ferric hydroxide precipitate. Organics and particles were removed by settling and floatation. After 20 min, it was found that the turbidity started to increase due to excess hydrolysed iron compounds which could not settle down.

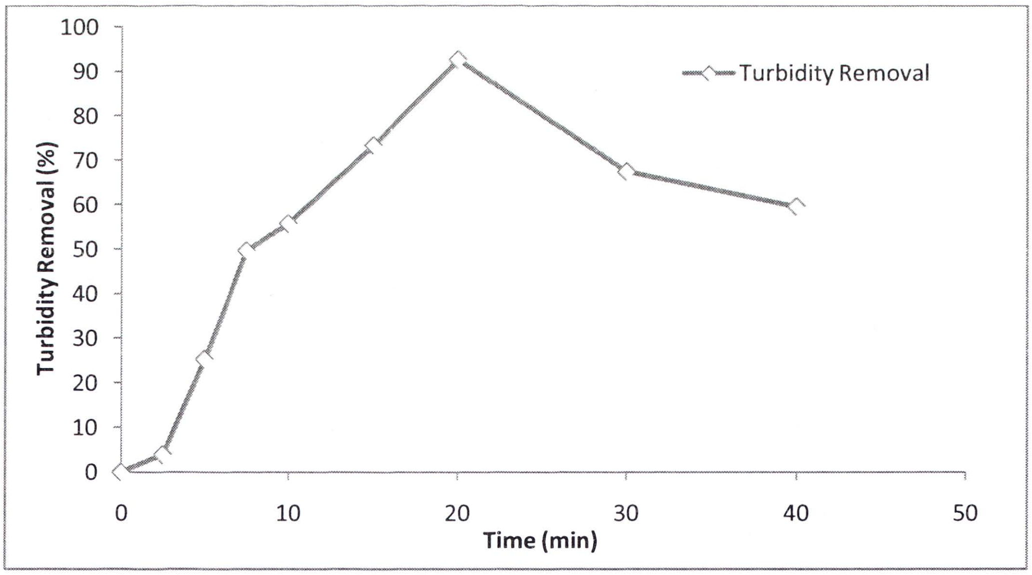

Figure 4.1 Turbidity removal efficiency at different EC generation time (current density: 12 A m^{-2}, pH 8, iron electrodes).

4.1.2 Organic removal with electrocoagulation using iron electrodes

Organic matter in synthetic water was quantified in terms of dissolved organic carbon (DOC) and UV absorbance at 254 nm wavelength. The removal for DOC and UV abs as a function of different EC generation time is shown in Figure 4.2. The organic removal efficiency was promoted by increased ferric chloride addition. The highest DOC and UV abs removals were found to be 78% and 95% respectively at optimum EC time of 20 min. The decrease in organic removal after 20 min is due to the presence of excess ferric ions which could not hydrolyse and precipitate as a result the organics could not be removed by sweep flocculation. More details on organic removal is provided in section 4.1.4.2.

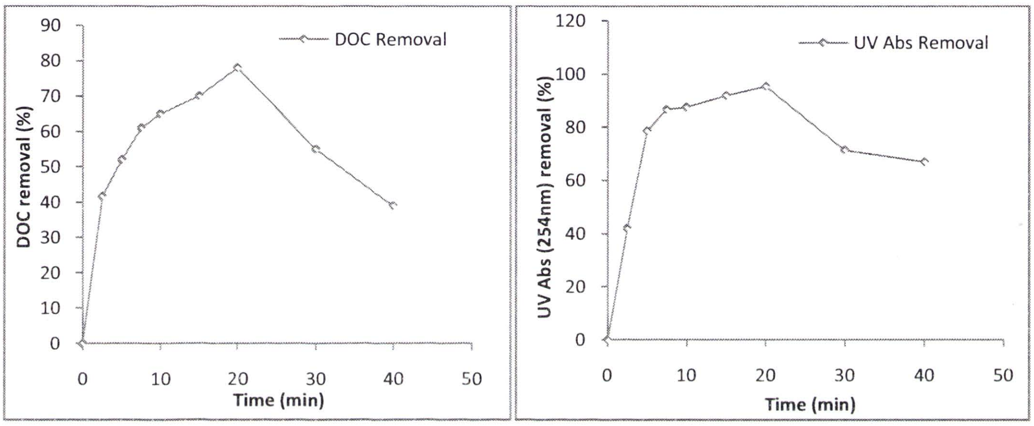

Figure 4.2 DOC (left) and UV Abs (right) removal at different EC generation time followed by fast mixing, slow mixing and sedimentation using flocculator (current density: 12 A m^{-2}, pH 8, iron electrodes).

4.1.3 Performance of microfiltration with electrocoagulation using iron electrodes as pretretment

EC was followed by slow and fast mixing using flocculator before performing crossflow MF. Ferrous ions (rather than ferric ions) were produced at the anode during EC of synthetic water. When iron is used as an anode, upon oxidation in an electrolytic system, it produces iron hydroxide, $Fe(OH)_n$ where n = 2 or 3. Two mechanisms for the production of the metal hydroxide have been proposed (Kim et al., 2007). Similarly, ferric ions generated by electrochemical oxidation of iron electrode may form monomeric ions, and polymeric hydroxy complexes, namely: $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)^{2+}$, $Fe_2(H_2O)_8(OH)_2^{4+}$ and $Fe_2(H_2O)_6(OH)_4^{4+}$ depending on the pH of the aqueous medium. The presence of organic matter in synthetic water is highly detrimental to iron EC because, even with increasing pH and long coagulation time, the Fe^{2+}- organic matter complexation prevents $Fe(OH)_3$ precipitation and floc formation. It is highly disadvantageous to generate Fe^{2+} since it is highly soluble and therefore, is not capable of colloid destabilisation by sweep flocculation thereby causing poor EC performance (Bagga and Clifford, 2008).

The variation of filtration flux after pretreatment with different generation time of iron EC is presented in Figure 4.3. The variation is shown in terms of normalised permeate flux. Normalisation was done by dividing the obtained flux by pure water flux (J/J_0). Here, J_0 is the pure water flux and J is the permeate flux at a given time. The current density was kept constant at 12 A m^{-2} for all the experiments. The flux decline was rapid at an initial stage (0-20 min) followed by more gradual decline. However after pretreatment, MF flux was significantly improved. Flux decline was 75% after 80 min of MF operation. After pretreatment of iron EC with optimum generation time of 20 min (equivalent coagulant dose of 62.5 mg l^{-1}), the MF did not experience any flux decline. However pre-EC with generation times below and above 20 min led to flux decline.

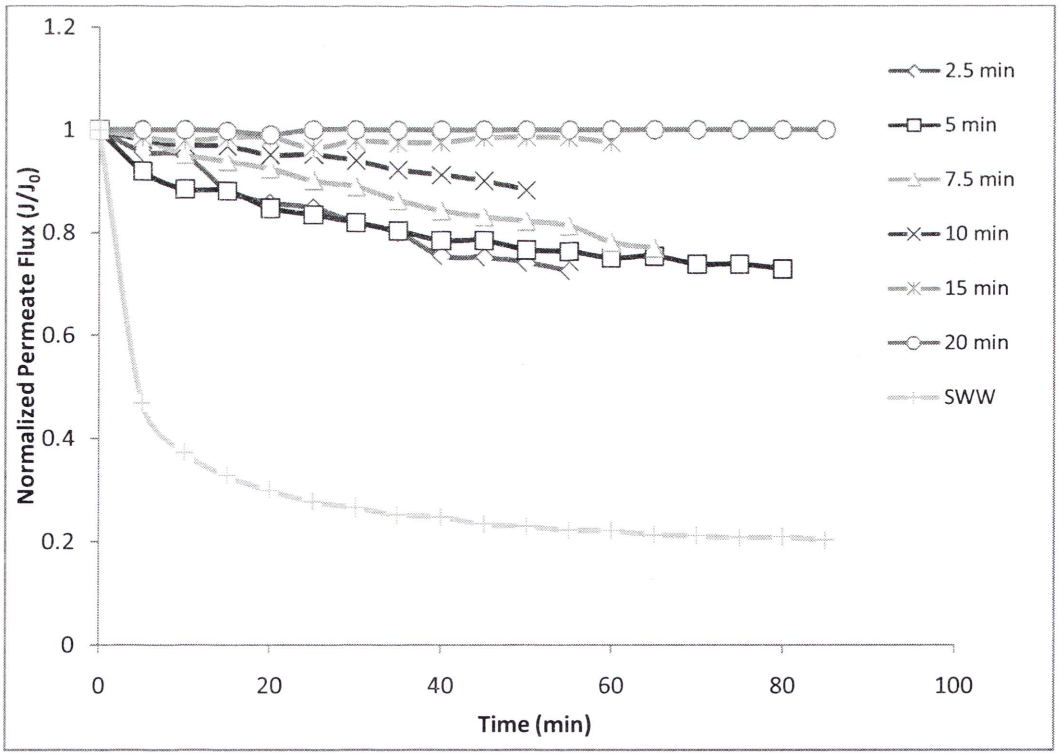

Figure 4.3 Normalised permeate flux at different generation time of EC followed by fast and slow mixing using flocculator (current density: 12 A m^{-2}, transmembrane pressure 10 kPa, cross flow velocity 0.5 l min^{-1}, pH 8).

4.1.4 Comparison of Electrocoagulation with iron electrodes with chemical coagulation

A direct comparison between electro and chemical coagulation is not practicable. The systems do not operate on an equivalent basis. In chemical coagulation, coagulant addition is a discrete (shot-fed) event with equilibrium determining coagulant speciation and pH. Pollutant separation processes are also different that settling is the only removal path for chemical coagulation while a combination of flotation and settling is employed by EC (Holt et al., 2002).

During iron EC, in situ oxidation of Fe^{2+} results in destabilisation and aggregation, whereas in chemical coagulation, it is due to hydrolysis of added Fe^{3+} and hydrolysis products that form $Fe(OH)_3$ precipitates. Oxidation of Fe^{2+} to Fe^{3+} and subsequent hydrolysis are a less efficient pretreatment process compared with hydrolysis of Fe^{3+} added directly in chemical coagulation. Fe^{2+} oxidation in solution has been shown to produce a colloidal and less precipitate (Stumm and Morgan, 1996) that is consequently also more soluble than freshly precipitated $Fe(OH)_3$ partially explaining the poor performance of iron EC.

4.1.4.1 Turbidity removal with chemical coagulation using ferric chloride

Turbidity removal as a function of different dosing and pH for the optimum dosing are presented in Figure 4.4. Under neural pH, the optimum ferric chloride dosing was 30 mg l^{-1} with turbidity removal of 98% at pH 6.5.

Chemical coagulation with ferric chloride (Figure 4.4) is induced by formation of ferric hydroxide precipitates in solution and by adsorption of ferric precipitates and dissolved species onto the surface of the clay particles. The turbidity levels of ferric chloride-precipitated effluent were markedly improved by raising the pH above 4.0. At pH 6.5 and low ferric chloride concentrations, adsorption of positively charged ferric hydroxide precipitated and dissolved species onto the clay particles reducing their negative charge and thus promoted aggregation at ferric dosages where the particles have no net charge. The turbidity removal increased continuously as the ferric chloride dose increased, and it reached maximum removal at 30 mg l^{-1} dose. It was found that even at low ferric chloride concentrations, the clay particles aggregated where the particles are negatively charged. At high ferric chloride concentrations, sweep floc coagulation is the predominant aggregation mechanism. (Ching and Elimelech, 1994). The large ferric hydroxide precipitates enmesh suspended particles and effectively removed them by settling.

At low ferric dose (<10 mg l^{-1}) and low solution pH, coagulation is induced by adsorption of ferric species and hydroxide precipitates which can form positively charged patches on the surface of the clay particles, and thus induce aggregation. In addition, formation of hydroxide precipitates can increase the solid concentration and hence, the inter particle collision rate increases (Ching and Elimelech, 1994). At low pH values, it is not expected that significant amounts of large precipitates would be formed. Therefore, because of low inter particle collision rates, aggregates did not increase in size significantly and removal of turbidity by settling was low.

At ferric chloride concentrations greater than 10 mg l^{-1}, aggregates increased in size because of the higher coagulation rate, and residual turbidity after settling reached lower values. Efficient coagulation with rapid settling of aggregates was observed over broader pH at high ferric concentrations (>10 mg l^{-1}), consistent with previous study (Stumm and Morgan, 1981).

At the highest ferric chloride dosage tested (50 mg l^{-1}), turbidity removal was less effective than at lower doses, most likely indicating some measures of colloidal destabilisation occurring. Under changing pH conditions, the turbidity removal efficiency changed. Fe^{3+} was hydrolysed and formed with different cationic complexes at acidic pH. Near neutral pH, ferric hydroxide precipitates were dominated whereas at more alkaline pH, anionic complexes were predominated. Performance of ferric chloride for turbidity removal was less at pH 3 and below it.

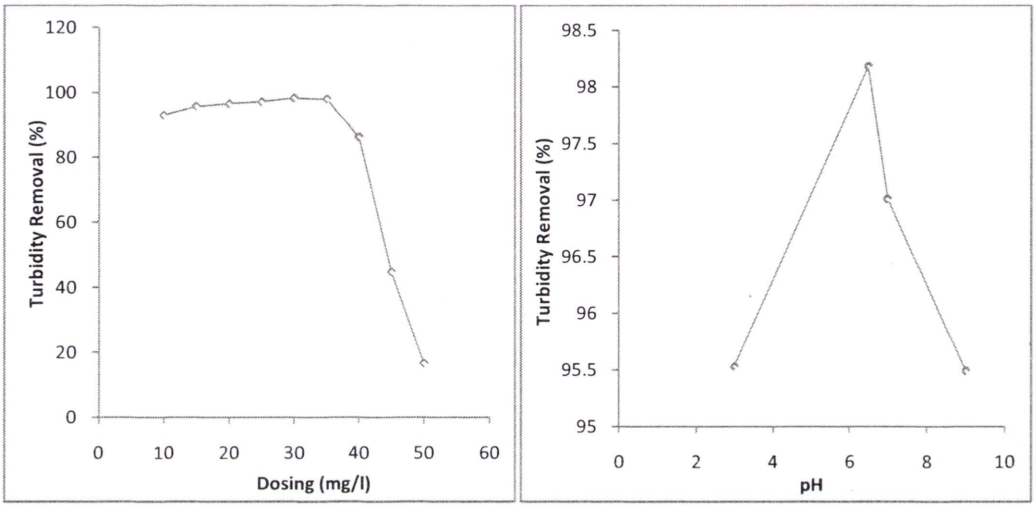

Figure 4.4 Turbidity removal at different dosing at neural condition (left) and at different pH with optimum dosing (right).

4.1.4.2 Organic removal with chemical coagulation using ferric chloride

The removal of DOC under neutral pH and at different pH under optimum dose of ferric chloride is presented in Figure 4.5. The organic removal was also measured in terms of UV absorbance. The results are presented in Figure 4.6. DOC gradually reduced from the average value of 5.5 mg l^{-1} to as low as 1.2 mg l^{-1} at dosing of 30 mg l^{-1} which corresponded to the removal efficiency of up to 74.5%. The removal efficiency varied at different pH conditions but the maximum removal of 74% was obtained at pH 6.5. UV Abs reduced from the initial value of 0.112 to 0.022 with removal efficiency of 80.5% which was the maximum removal efficiency at ferric chloride dosing of 30 mg l^{-1} and pH 6.5. Organic removal increased gradually with ferric chloride dosages. Above the optimum dosage, the removal decreased as restabilisation may occur due to charge reversal of the particulates. The pH increase above 6 did not favour organic matter removal which may be due to decrease in the zeta potential of colloidal suspension at higher pH. This decrease was more pronounced for pH > 6.5 in the study of Kaleta and Elektorowicz (2009). According to Paul (1996) for pH < 6.0, dissolved organic matter is mainly removed by precipitation with iron species whereas for pH 6.0, adsorption reactions at the surface of ferric hydroxides and coprecipitation with ferric hydroxides predominate. Increasing pH led to the deprotonation of organic matter and to the decrease of the zeta potential of hydroxide precipitates; removal of organic matter by sorption was limited and hydroxide precipitates were poorly sorbing compounds.

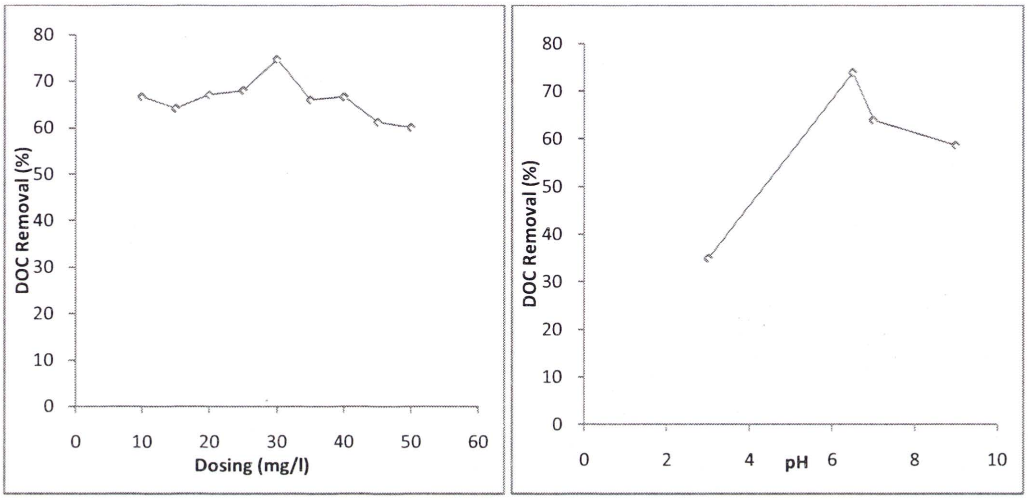

Figure 4.5 DOC removal at different dosing at neutral condition (left) and at different pH with optimum dosing (right).

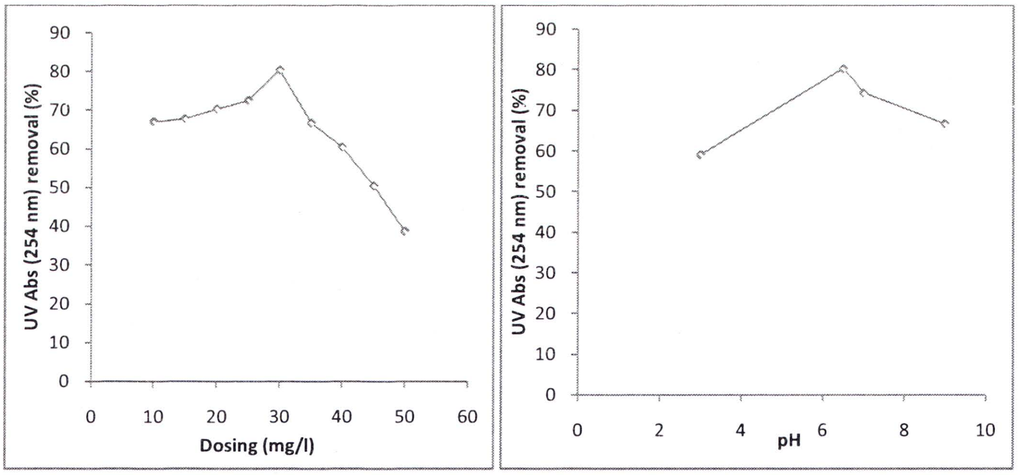

Figure 4.6 UV removal at different dosing at neutral condition (left) and at different pH with optimum dosing (right).

4.1.4.3 Performance of microfiltration flux with chemical coagulation using ferric chloride as pretreatment

The variation of filtration flux after pretreatment at different doses of ferric chloride was investigated (Figure 4.7). The variation is depicted in terms of normalised permeate flux. Fouling started reducing from iron dose ≥ 10 mg l^{-1}. Without pretreatment with ferric chloride, 80% of flux decline was observed. After the pretreatment of flocculation with the optimum dose of ferric chloride (30 mg l^{-1}), there was only 20% decline in MF flux (60% increase compared to without pretreatment). Due to the change in particle characteristic and reduction in contaminant loading the MF performance was improved. Coagulation followed by sedimentation evidently removed considerable amounts of contaminants that caused fouling, which leads to improvement in flux. Flux sharply declined at the beginning, and then decreased gradually after 30 min. Pore blocking and adsorption onto the membrane matrix are believed to cause the initial rapid decline, while cake formation caused slow decline (Ben-Sasson and Adin, 2010). Organics and colloids can penetrate and adsorb onto the membrane matrix, which causes fouling by blocking membrane pore. Contaminants sit on the membrane surface and form a cake layer, which causes fouling. Pore blocking and adsorption were found important for membrane fouling at the initial stage, while cake formation was found important at a later stage (Ben-Sasson and Adin, 2010).

Colloidal particles play a significant role in membrane fouling. The coagulation of colloidal particles reduced membrane fouling due to relatively high degree of destabilisation (Zhang et al., 2006). The improvement of filtration flux by ferric chloride pretreatment might also be attributed to the agglomeration of particles and the consequent formation of larger particles (aggregates) by pretreatment; which decreased the extent of plugging and the void of sedimentation layer on membrane surface increased (Mietten and Ben, 1992; Zhong and Wang, 2003).

The high dosing of ferric chloride (50 mg l^{-1}) led to flux decline even greater than synthetic water. High dose reduced membrane permeability due to the deposition of residual ferric chloride at the MF membrane. Thus coagulant itself may have the potential to become foulants if they are overdosed. The above results have important implications that an excessive amount of coagulant should not be added with regard to fouling control.

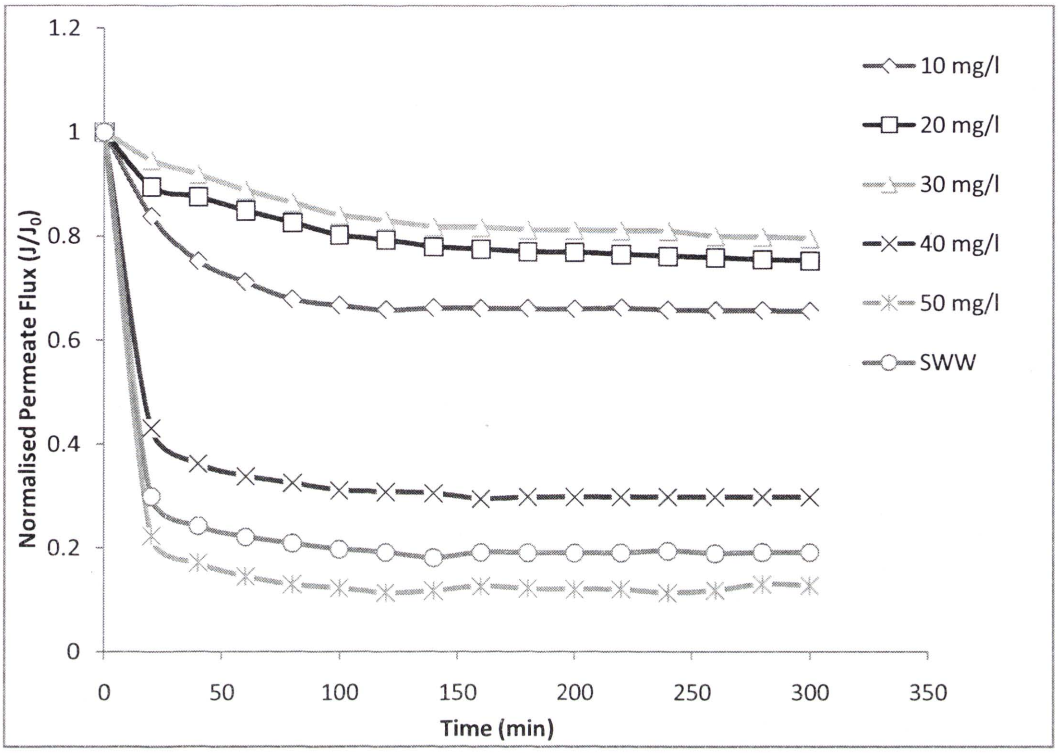

Figure 4.7 Normalised permeate flux at different dosing of ferric chloride (transmembrane pressure 10 kPa, cross flow velocity 0.5 l min^{-1}, pH 6.5).

4.2 Electrocoagulation with sacrificial aluminium electrodes for water treatment

As explained earlier, the release of soluble ferrous ions (Fe^{2+}) by iron electrodes showed green colour into the treated synthetic water which then turned yellow and turbid. The soluble ferrous ions are oxidised to Fe^{3+} in acidic or neutral conditions. The formation of $Fe(OH)_3$ as a result of the reaction of Fe^{3+} with OH^- ions gave yellow colour to the synthetic water and increased turbidity. Also it was found that EC using iron electrodes did not reduce MF fouling in the entire range of experimental conditions investigated as ferrous ions (rather than ferric ions) were produced at the anode during EC of synthetic water which is highly soluble and therefore, is not capable of colloid destabilisation by sweep flocculation thereby causing poor EC performance. Therefore in all of the further studies, iron electrodes had been replaced by aluminium electrodes.

4.2.1 Effect of pH on turbidity and zeta potential with electrocoagulation

To examine the effect of pH on EC pretreatment for MF performance, experiments were conducted in the pH range of 3–11. Figure 4.8 shows the turbidity removal efficiency and zeta potential for synthetic water in the pH range 3-11. It was observed that turbidity removal efficiency increased gradually from 52% at pH 3.0 to as high as 88% at pH 8.0 and decreased to 46% at pH 11.0.

One possible reason for getting higher turbidity removal is the formation of stable aluminium floc. At lower pH, alum dissolves itself. However, at pH 8 the alum performed well but at over pH 8, the floc became unstable and began to separate. This is supported by zeta potential result which showed isoelectric point at pH 8. The pH below 8 gave positive values of the zeta potential, whereas the pH above 8 produced negative zeta potentials. This behaviour could be explained in terms of the charge of the particles, which were positive due to the adsorption of cations such as Al^{3+}, $Al(OH)_2^+$, $Al(OH)^{2+}$ and negative due to the adsorption of anions ($Al(OH)_4^-$). The zero isoelectric potential shows that no net charge is formed at this pH. This suggests that the aluminium hydroxide is precipitated and suitable for flocculation that helps to remove maximum turbidity at pH 8.

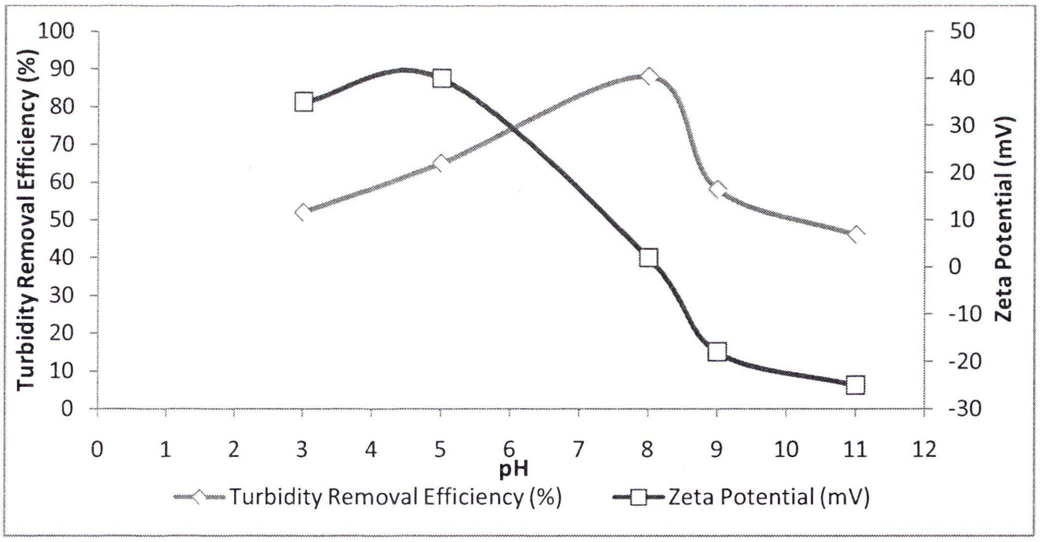

Figure 4.8 Turbidity removal efficiency and zeta potential after EC treatment at different pH (current density: 12 A m^{-2}; EC time: 30 min).

4.2.2 Effect of pH on organic matter removal with electrocoagulation

Organic matter removal in terms of DOC and UV absorbance at 254 nm at different pH was investigated (Figure 4.9). DOC removal increased from 40% at pH 3.0 to 68% at pH 8.0 and gradually decreased to 48% at pH 11.0. As can be seen from the graph, the maximum DOC removal was found to be 68% at pH 8. Normalised UV abs also followed the same trend gradually decreasing from pH 3.0 and then again increasing after pH 8. Normalised UV 254 absorbance was minimum at pH 8. The intensity corresponded to 78 % removal.

Increasing the pH from the very acidic levels to near neutral levels had a strong positive effect on removal of organics. Adsorption of organics onto preformed aluminium hydroxide flocs followed by precipitation is the more dominant mechanism at higher pH values and elevated coagulant additions (Pazenko et al., 1985). The net result is that the removal of organic compounds can occur over a wide range of pH (Pazenko et al., 1985), and that a maximal removal is observed by combining the two mechanisms through pH adjustment.

If the pH is below the isoelectric point of the metal hydroxide, positively charged polymers will prevail and adsorption of these positive polymers may occur. Above the isoelectric point, anionic polymers will predominate, where particle destabilisation may take place through adsorption and bridge formation (Kilic and Hosten, 2010).

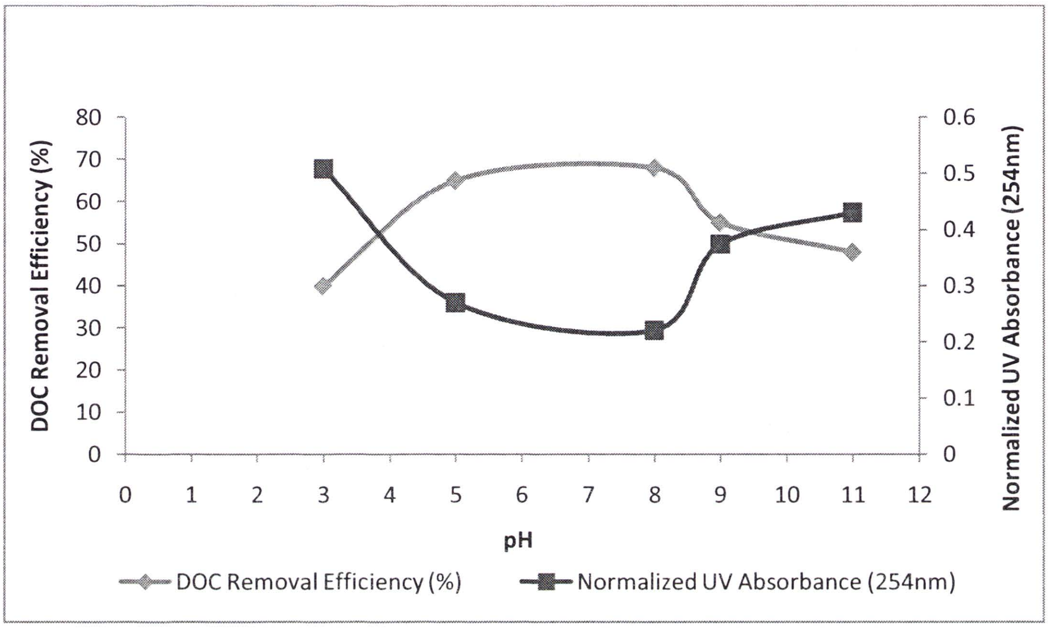

Figure 4.9 DOC removal efficiency and normalised UV absorbance after EC treatment at different pH (current density: 12 A m^{-2}; EC time: 30 min)

4.2.3 Effect of pH on turbidity and zeta potential with chemical coagulation using alum

To study the effect of pH on the MF performance by chemical coagulation pretreatment, coagulation was performed at different pH in the wide range of 3-11 using alum as coagulant. Figure 4.10 shows turbidity removal efficiency and zeta potential for synthetic water for pH range 3-11. The turbidity removal efficiency was only 52% at pH 3 and increased steadily with increasing pH up to 94% at pH 6.5 and then gradually decreased to 60% at pH 11. The zeta potential curve went through two isoelectric points at pH 3.0 and pH 6.5. The zeta potential remained at the near-zero point within the wide pH range of 5–8 where the turbidity removal efficiencies were about 90%.

As the zeta potential shows two isoelectric points, neutralisation is expected to occur at two points. At low pH, almost all aluminium compounds are in cationic monomeric species Al^{3+} and $Al(OH)_2^+$ (Kilic and Hosten, 2010). Kaolin clay contains net negative charge on its surface. So the clay surface and other particles in the solution attract the aluminium ion on its surface and are neutralised. The first point of zero charge is mainly due to adsorption of Al^{3+} ion on remaining kaolin. The first isoelectric point is not due to the aluminium itself but due to the adsorption of aluminium with the particles of the solution. As the pH increases from pH 5 to 8, hydrolysis occurred forming various monomeric species aluminium hydroxyl such as $Al(OH)_2^{+}$, $Al(OH)_2^{+2}$, and polymeric species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_{13}(OH)_{34}^{5+}$ predominate, which finally transform into $Al(OH)_3$ (Mehtap and Cetin, 2010). These hydroxyl species being positive in charge, tends to adsorb on the solution resulting in very low zeta potential. As the pH crosses the neutral pH, Al starts to form a stable hydroxide ($Al(OH)_3$) that begins to precipitate. But at higher pH the floc breaks and form $Al(OH)_4^{-}$ ions.

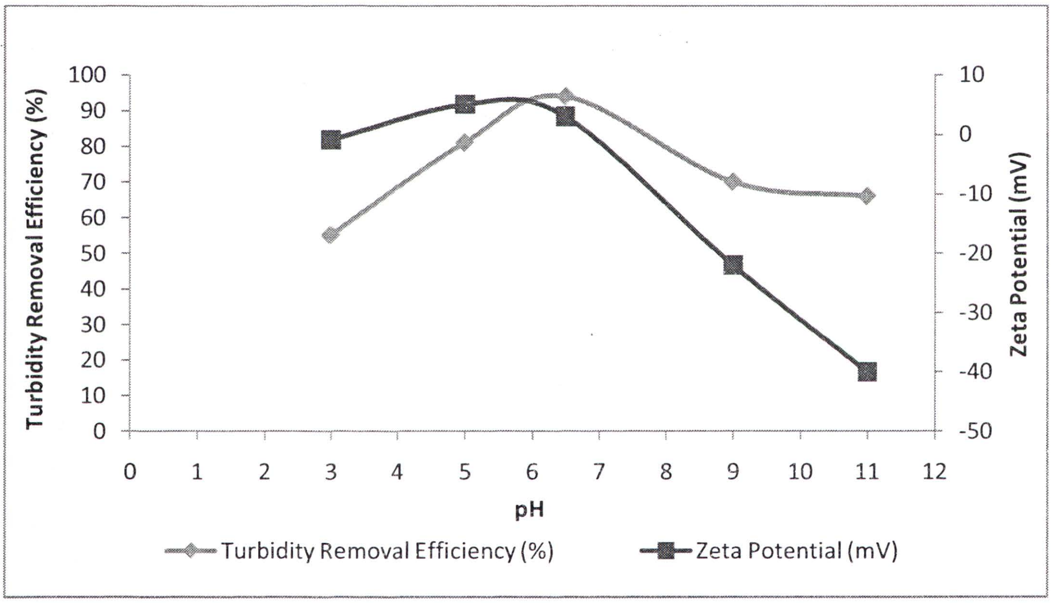

Figure 4.10 Turbidity removal efficiency and zeta potential after chemical coagulation experiments at different pH.

4.2.4 Effect of pH on organic matter removal with chemical coagulation

DOC removal efficiency and normalised UV absorbance at 254 nm in the pH range 3-11 is presented in Figure 4.11. The maximum DOC removal (78%) was observed at pH 6.5. The DOC removal was 55% at pH 3.0 and 58% at pH 11.0. UV abs (254 nm) also showed the highest removal at pH 6.5 (86%). It was observed that the MF membrane performed better under the conditions when organic matter removal was highest.

Three possible mechanisms for DOC removal in a conventional alum coagulation/sedimentation process have been proposed (Fabris et al., 2007; Ching and Elimelech, 1994). They are i) charge neutralisation, ii) adsorption and iii) entrapment. According to the equilibrium concentrations of hydroxo aluminium (III) complexes in a solution in contact with $Al(OH)_3$, aluminium from Al^{3+} at pH 4.5 converts to $Al_7(OH)_{17}{}^{4+}$ at pH 6 and becomes $Al(OH)_3$ at the isoelectric point of around pH 6.5, i.e., the positive charge of aluminium increases as pH increases from 4.5 to 6.5, whereas visible floc particles of aluminium hydroxide precipitate form after the isoelectric point. It is to say that with the increasing pH from 4.5 to 6.5, contribution of charge neutralisation to DOC removal increased, whereas after pH 6.5 contribution of charge neutralisation decreased and contributions of adsorption and entrapment predominated for DOC removal (Jung and Kang, 2006).

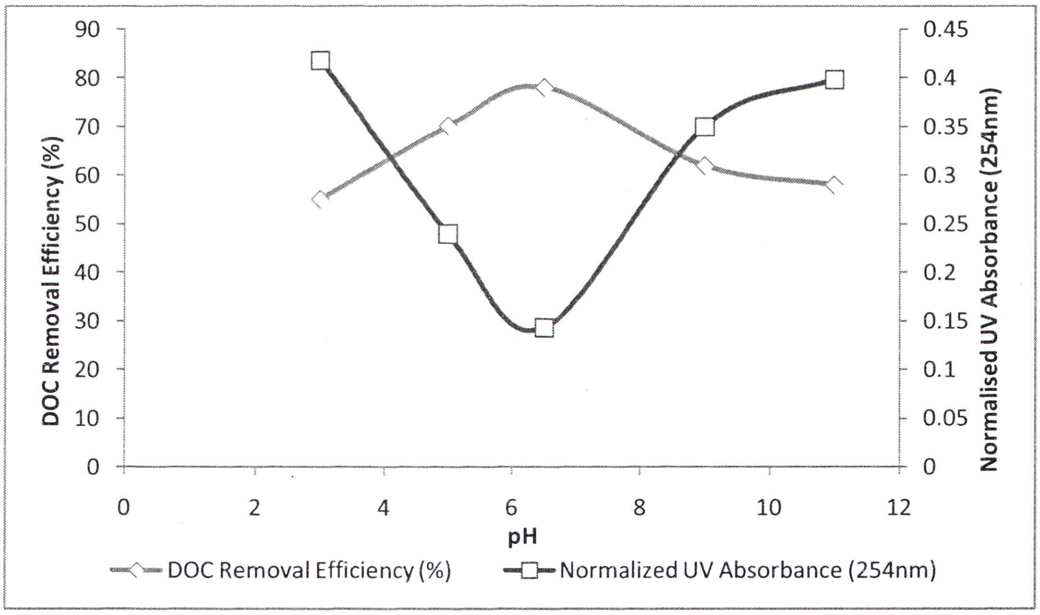

Figure 4.11 DOC removal efficiency and normalised UV absorbance after chemical coagulation experiments at different pH.

4.3 Performance of microfiltration with electrocoagulation using sacrificial aluminium electrodes and chemical coagulation as pretreatment

While EC has been shown to be highly efficient at removing a large range of pollutants from water, such as chemical oxygen demand (Linares-Hernandez et al.,2009), boron (Sayiner et al., 2008), heavy metals (Heidmann and Calmano, 2008) and colloidal silica (Hu et al., 2005), only a few studies have investigated EC as a pretreatment method for MF or UF. The only study we found on MF with an aluminium-based EC pretreatment showed dramatic fouling mitigation in cross-flow MF of wastewater (Pouet and Grasmick, 1994). In that study, there were no settling steps in the process and it was unclear what pH and electric current values had been applied. The addition of iron-based EC before MF significantly increased the removal rates of selenium and viruses (Zhu et al., 2005; Mavrov et al., 2006). Bagga and Clifford (2008) showed that unlike conventional coagulation, iron-based EC before dead-end MF does not mitigate fouling at pH 6.4–8.3. They attributed this mitigation failure to anode dissolution of Fe^{2+} rather than Fe^{3+}, which is the prevalent iron species in conventional flocculation. Al-Malack et al. (2004) studied the effect of iron-based EC on cross-flow MF. After 60 min of operation, EC appeared to have only a marginal effect. Nevertheless, those authors concluded that EC alters the dominant fouling mechanism from a standard filtration mechanism (i.e. internal fouling) to cake filtration (external fouling). Overall, these works showed only marginal effects, if any, of iron-based EC on mitigation of colloidal and organic fouling. Unlike iron, when MF was pretreated by aluminium-based EC, dramatic fouling mitigation was observed in both crossflow (Pouet and Grasmick, 1994) and dead-end (Ben-Sasson and Adin, 2010) operation modes. Harif and Adin (2006) demonstrated that the performance of aluminium based EC before UF of a kaolin suspension may reduce fouling; at pH 5 and 6.5, the flux was 20% higher than without the EC pretreatment while at pH 8, there was only marginal improvement.

The objective of this section is to evaluate the performance of crossflow MF with EC and chemical coagulation as pretreatment. This research also aims in finding out the operation conditions favouring removal of organic matter and turbidity by electro and chemical coagulation. MF performance was evaluated using flux decline and organic removal at constant transmembrane pressure and cross-flow velocity.

4.3.1 Effect of electrocoagulation generation time on performance of microfiltration

The normalised permeate flux profile for 60 min operated at different EC generation time (0-30 min) is presented in Figure 4.12. The current density was kept constant at

12 A m^{-2} for all the experiments. The flux decline was rapid at the initial stage (0-20 min) followed by more gradual decline. The flux decline trend was proportional to EC generation time. Without EC pretreatment, the flux was declined sharply by 90%. As EC time increased, the flux through MF was gradually improved. For 5 min of EC pretreatment, the flux decline was only 55% which indicated a flux increase of 35% compared to without pretreatments. EC pretreatment possibly affected the colloidal/turbidity suspension in two ways. On the one hand it caused the formation of a layer that protected the membrane pores or built a cake with lower hydraulic resistance, which, in turn, led to a reduction in fouling intensity. On the other hand, when the aluminium concentration is above solubility values, the formed aluminium-hydroxide solids increase the number of particles in the suspension. More particles imply a higher accumulation rate on the membrane surface for each filtered volume, resulting in an increase in fouling intensity. The optimum EC duration is the value at which superposition of positive and negative EC effects leads to the best improvement in filtration performance.

The flux found narrowly changed after 30 min suggesting that the optimum EC time is 30 min. At this point we also observed the highest turbidity and organic removal (DOC and UV abs). It was believed that pretreatment by EC increased the size of particles by the formation of aluminium hydroxide flocs which mitigated the fouling by: (1) reducing foulant penetration into pores, thereby lessening the extent of plugging; (2) forming a more porous cake on the membrane surface that may act as a dynamic membrane, thereby protecting the membrane from long-term fouling; and (3) increasing transport of potential foulants away from the membrane (Wiesner and Mallevialle, 1989; Hwang and Liu, 2002).

The coagulation captured and agglomerated colloids, thereby reducing the membrane fouling by colloids. The primary particles could be swept or adsorbed into the aluminium-hydroxide particles during EC process or could be trapped by the aluminium-hydroxide layer that acts as secondary membrane to filter out the small particles. The combination of these two mechanisms prevents the primary particles from reaching the membranes pores and plugging them, thus the internal fouling is reduced. Sufficient aluminium ions were released with increasing EC time. As the experiment was conducted at pH 8, it was believed that the released ion converted to

$Al(OH)_3$ floc quickly. Thus the formed floc caused the particles and organics to agglomerate, float, settle and remove from the synthetic water.

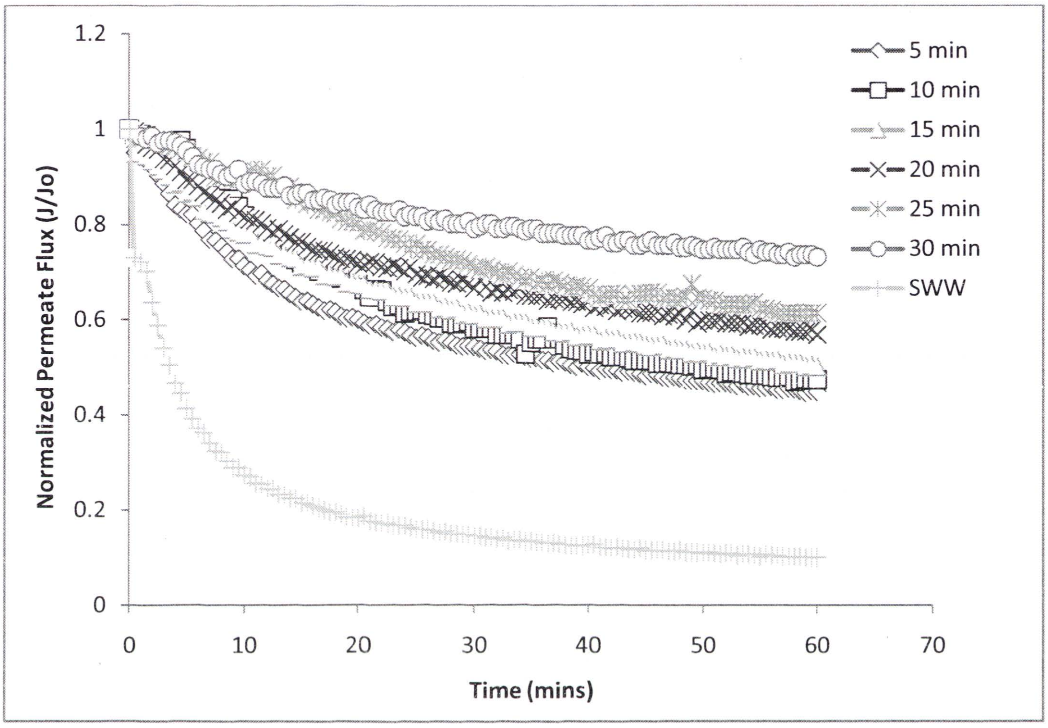

Figure 4.12 Normalised permeate flux at different generation time of EC (current density: 12 A m^{-2}, transmembrane pressure 10 kPa, cross flow velocity 0.5 l min^{-1}, pH 8).

4.3.2 Effect of chemical coagulant dose on performance of microfiltration

The effect of alum doses in the performance of MF flux variation is shown in Figure 4.13. MF flux without pretreatment decreased by 90% within 60 min of operation. A significant result was observed at 30 mg l^{-1} dose where MF did not experience any flux decline. The flux declined sharply at the beginning, then more gradually after twenty min. The flux decline was 84% and 50% at 10 and 20 mg l^{-1} doses respectively. The decrease in flux is due to fouling by colloidal and organic matters. The dose response curve shows that the optimum dose for chemical coagulation was 30 mg l^{-1}. Alum doses above and below the optimum dose reduced the MF flux. This result confirms with the optimal concentration determined by the jar-test where the maximum removal of organic matter and turbidity occurred at this dose. A possible reason for obtaining lower flux below the optimum dose is due to less availability of the aluminium coagulant. As the dose increased above optimum dose (30 mg l^{-1}), the excess floc caused alteration in the flux size that reduced the performance of colloidal removal (Peuchot and Aim, 1992).

At optimum dose, membrane flux increased due to high removal of contaminant loading. The flux improved as the coagulant destabilised negatively charged colloids by charge neutralisation. However, at higher doses of alum (>30 mg l^{-1}), the flux declined again as sufficient degree of over saturation occurred to produce a rapid precipitation of a large quantity of aluminium hydroxide, enmeshing the colloidal particles in what has been termed a sweep floc (Malack and Anderson, 1996).

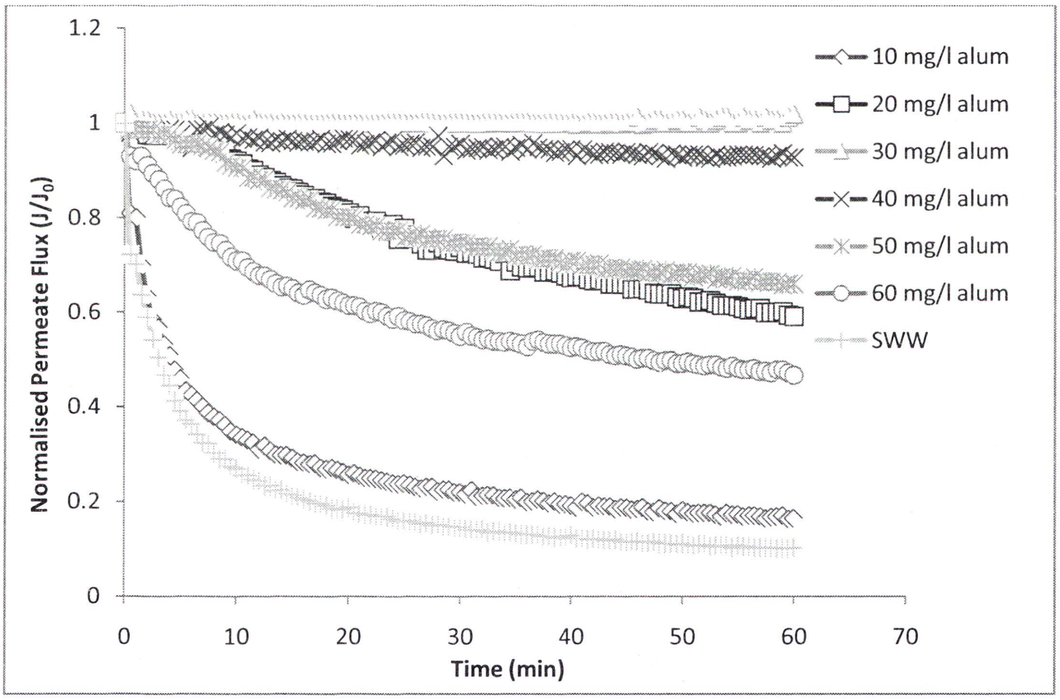

Figure 4.13 Normalised permeate flux at different generation time at different dosing of chemical coagulation (transmembrane pressure 10 kPa, cross flow velocity 0.5 l min^{-1}, pH 6.5).

4.3.3 Validation of pH on Microfiltration flux

The performance of MF was evaluated in terms of normalised permeate flux (J/Jo) at different pH. Figures 4.14 and 4.15 show the flux variation in EC and chemical coagulation. During the experiments, the operating conditions (cross flow velocity and pressure) and feed water characteristics (kaolin and humic acid) remained constant except pH. The optimum pH was found to be in the range of 5-7 (Ching and Elimelech, 1994)

Solution pH is usually an important factor in membrane fouling as it is expected that there is an increase in electrostatic attraction caused by higher negative surface charge of membranes at higher pH. Also the structure and surface charge of solid amorphous aluminium hydroxide depend on pH (Duan and Gregory, 2002). At around neutral pH, the initially formed colloidal precipitates are positively charged and hence stable. As the pH increases, the stability decreases and the particles can aggregate into large and settleable flocs (Duan and Gregory, 2002).

Figure 4.14 shows that the flux through the membrane depended on pH of the feed solution. MF performed well at pH 8.0 where flux decline was only 35% (increased by 55% compared to without pretreatment). However above pH 8, the flux decline was 80% and 88% at pH 9 and pH 11 respectively. The performance was very poor at pH 3.0 where the flux decline was 92%, which was only 2% increase in flux compared to without pretreatment. At lower pH the coagulation was very poor. As pH was increased (above 3) the flux through MF was improved. Increase of pH above 3 helped to form the floc as well as to dissolve the humic acid. The optimum flux was observed at pH 8.0 after which the flux improvement started to decline again. This result is confirmed from our previous experiments that this maximum flux occurred at isoelectric point for EC where there was optimum removal of turbidity and organic matter. Above pH 8.0, the decline in flux was again observed. As mentioned above, the decline was possibly due to breakage of floc above pH 8.

The profile of normalised flux after chemical coagulation pretreatment at different pH is shown in Figure 4.15. Chemical coagulation also followed the similar trend as with EC. At pH 6.5, the MF did not experience any flux decline. Flux decline was 15% and 35% at pH 3 and pH 5 respectively. Initially the flux decline was sharp for the first 20 min for all the experiments. After 20 min, the decline gradually increased. Compared to EC, chemical coagulation showed higher flux. Previously we observed two isoelectric points at pH 3 and pH 6.5. Between these two pH the isoelectric point was very minimal compared to EC. This shows that floc formation is relatively higher in chemical coagulation compared to EC. The enriched (higher) floc formation in chemical coagulation caused higher removal of colloidal (kaolin as well as humic acid) materials from the synthetic water. This possibly caused high flux from the beginning in chemical coagulation. Above pH 6.5, the flux declined. At pH 9 and pH 11 the flux decline was 37% and 68% respectively.

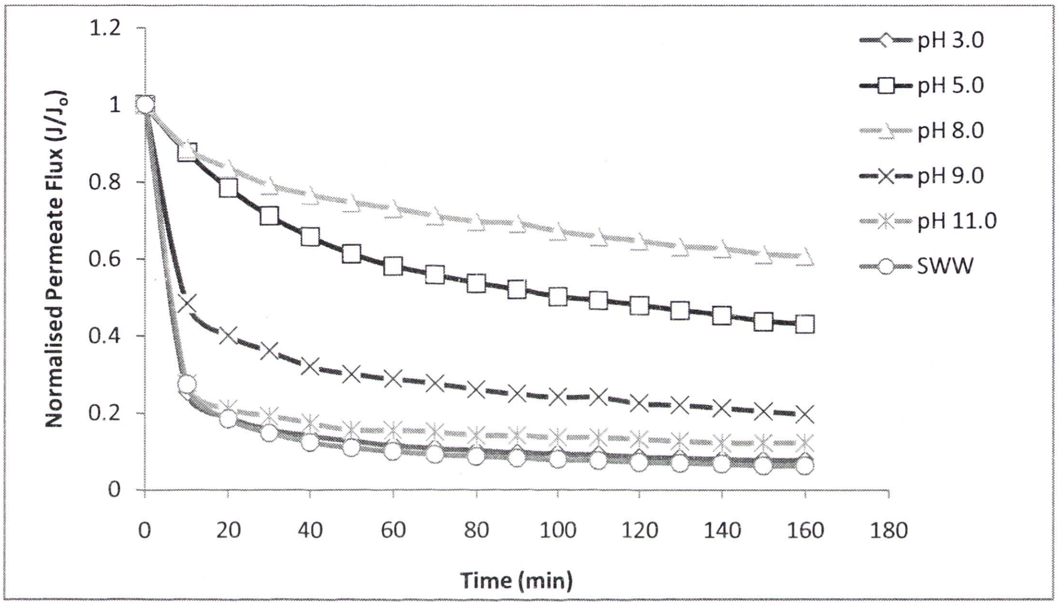

Figure 4.14 Normalised permeate flux through MF for EC using aluminium plates (transmembrane pressure 10 kPa, cross flow velocity 0.5 l min^{-1}).

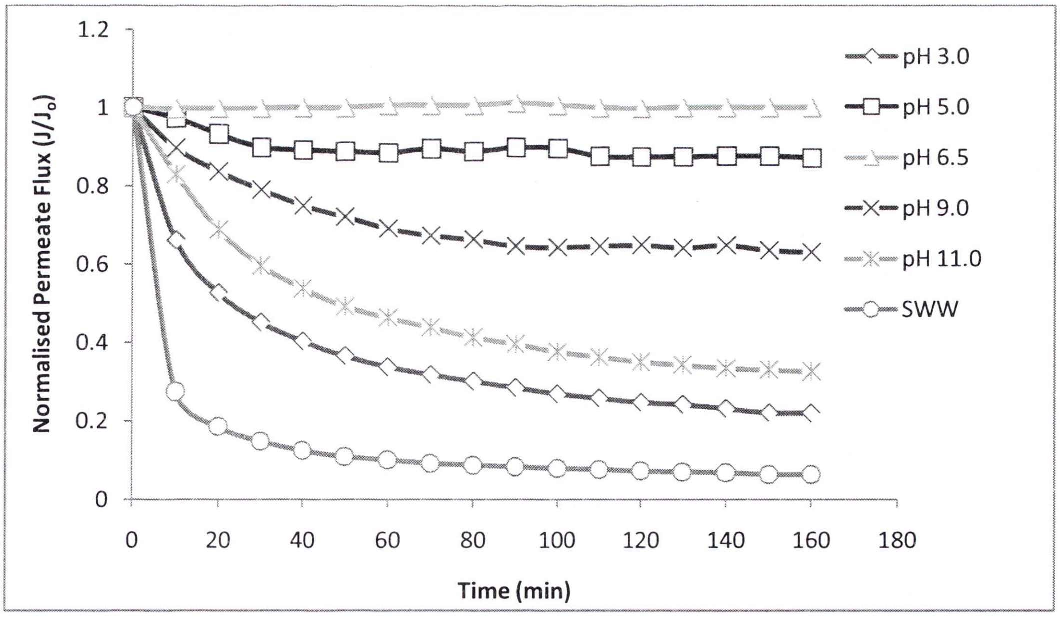

Figure 4.15 Normalised permeate flux through MF for chemical coagulation (transmembrane pressure 10 kPa, cross flow velocity 0.5 l min^{-1}).

4.4 Solar powered electrocoagulation for water treatment

EC with its simplicity and performance is an attractive technology especially for small and decentralised water and wastewater purification system. EC driven by solar panel is one of the sustainable technologies for applications in the remote communities of Australia where the renewable energy such as solar power is abundant.

There has been several renewable solar energy-powered desalination systems designed to produce 100–3000 l of clean drinking water per day using reverse osmosis (RO) membranes (Mathew et al., 2000; Keefer and Schrack, 1985). The studies conducted with photovoltaic (PV) powered desalination system for remote Australian communities (Richards and Schafer, 2003) showed successful removal of particulates, bacteria and viruses with ultrafiltration module and a nanofiltration and RO membrane for removing salts. A study to demonstrate the feasibility of the desalination of brackish water by means of an electrodialysis system powered directly by PV solar panels was investigated by Ortiz et al. (2007). However, only one study had been done for the feasibility of EC using PV energy (Valero et al., 2007) which successfully demonstrated the application of a synthetic textile effluent powered by PV energy without batteries. It was proved that PV array configuration is a factor of great influence on the use of the generated power. The optimum PV array configuration must be reshaped depending on the instantaneous solar irradiation. A useful and effective methodology to adjust the EC-PV system operation conditions depending on solar irradiation was also proposed.

The objective of this section is to demonstrate the feasibility of solar powered electrocoagulation (SPEC) for water treatment. Optimisation of various operating parameters such as pH, voltage/current, electrodes gap and initial pollutant concentration etc. was first performed using direct electrical current. SPEC was performed with PV panel connected to the aluminium electrodes with/without a set of batteries and charge control system. The model electrolyte used in this study was synthetic water.

4.4.1 Process Optimisation

The effects of specific process variables, such as initial pH, mixing, current, initial organic loading, electrodes gap were studied using electrical direct current as a source of power. The optimum values for each variables were determined based on the highest removal of HA (UV254 absorbance) and turbidity.

4.4.1.1 Effect of current

The variation of turbidity and UV absorbance (254 nm) at different current was investigated with aluminium plates (Figure 4.16). Current density directly determines both coagulant dose and bubble generation rates, as well as strongly influencing both solution mixing and mass transfer at the electrodes. A series of experiments were carried out to quantify the impact of operating current on reactor performance. The results indicate that turbidity and organics removal were directly dependent on the intensity of current (or current density) as the release of aluminium ions relies on the flow of current to the electrodes. The highest removal was achieved at a current of 1.5 A (current density of 8.82 mA $cm\text{-}^{2}$), with 91% turbidity and 90% organic removal. Initially (within 10 min of EC), turbidity and organic removal was seen to depend on the current density, with higher current achieving higher removal efficiency for both turbidity and UV removal. However, after 35 min of EC, the removal efficiency remained constant up to 85-90% for both turbidity and HA. Normalisation was done by dividing obtained turbidity, uv abs by initial value.

As the applied current increased, the turbidity and organic removal were improved. This was probably because the organic compounds present in the synthetic water that reacted with aluminium ions to form insoluble compounds were mostly removed. The required treatment time to reach over 90% organic removal efficiency was 20 min for 2 A and 2.5 A current. Turbidity removal of synthetic water reached over 80% in 10 min of EC for currents 2 A and 2.5 A. As the current increased, the length of each EC process decreased. Due to a sufficient current through the solution, the metal ions generated by the dissolution of the sacrificial electrode were hydrolysed to form a series of metallic hydroxide species. These species neutralised the electrostatic charges on the dispersed particles to reduce the electrostatic inter particle repulsion enough for the van der Waal attraction to predominate, thus facilitating agglomeration. However, it took a longer time to reach optimum turbidity and organic removal efficiency for lower current density. This was because the applied lower current density was unable to completely destabilise the pollutants in the solution.

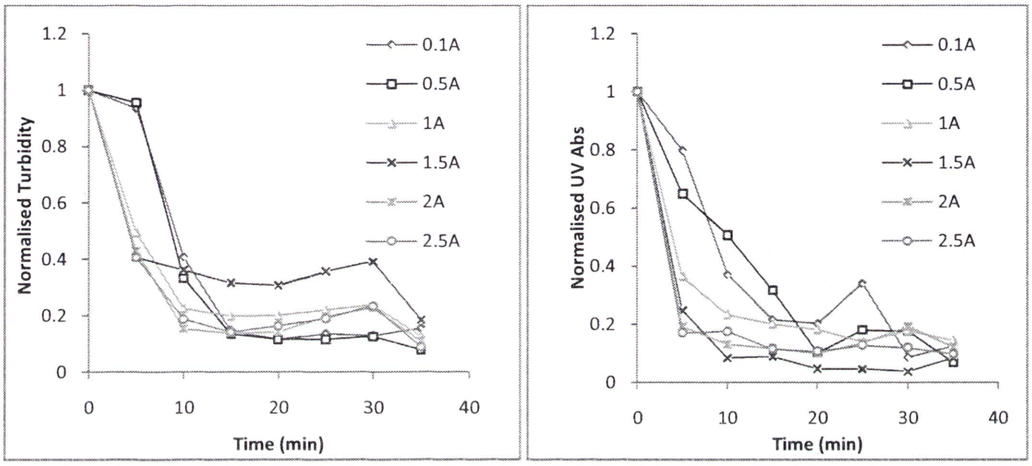

Figure 4.16 Variation of turbidity (left) and UV removal (right) under different current intensity (Initial turbidity= 80 NTU, initial UV= 0.150 cm^{-1}, pH=8.0 and electrodes gap= 2 cm).

4.4.1.2 Effect of pH

The variation of turbidity and UV absorbance at different pH for EC is shown in Figure 4.17. The results indicate that turbidity and HA removals were significantly influenced by the initial pH of the synthetic water. It was found that the optimum pH for the operation of EC was 8.0 where 87% of turbidity removal and 88% of UV removal were obtained. At pH 3 and 5, the turbidity and UV absorbance were increased, which was possibly due to the inability of aluminium ions to form aluminium hydroxide flocs which could not settle and float.

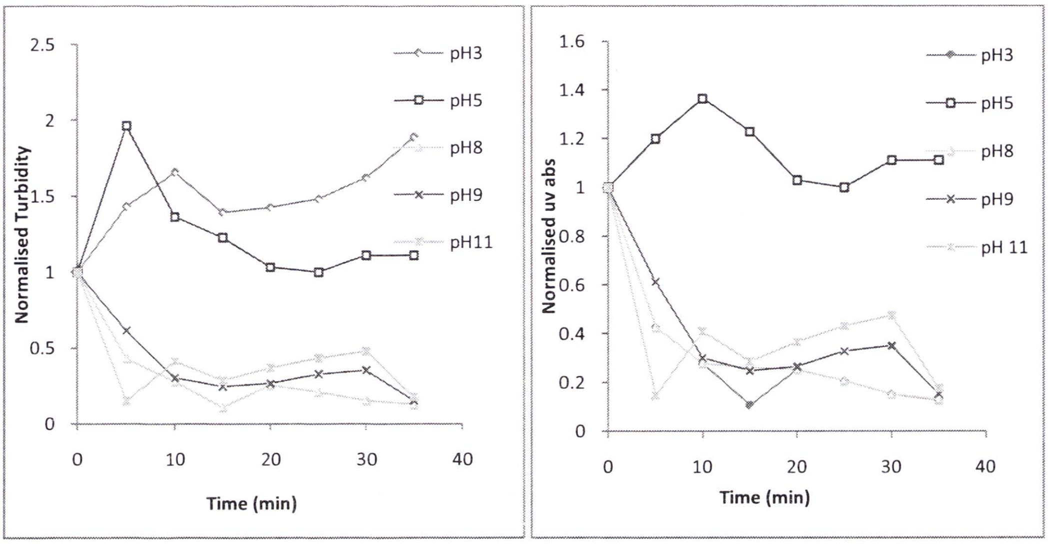

Figure 4.17 Variation of turbidity (left) and UV removal (right) at different pH (Current density= 11.5 mA cm^{-2}, initial turbidity=80 NTU, initial UV= 0.150 cm^{-1} and electrodes gap = 2 cm).

4.4.1.3 Effect of electrodes gap

The variation of turbidity and UV at different gaps between the two aluminium electrodes was investigated (Figure 4.18). The experiments were performed separately by varying the gap or distance between the two electrodes between 0.5 cm and 2.5 cm. The results showed that, the electrode gap did not influence on the performance of EC. Initially, between 0 to 10 min of EC operation, turbidity and organic removal efficiency was higher with smaller gap of electrodes as the current density increased. However, after 35 min of EC, the removal efficiency remained constant.

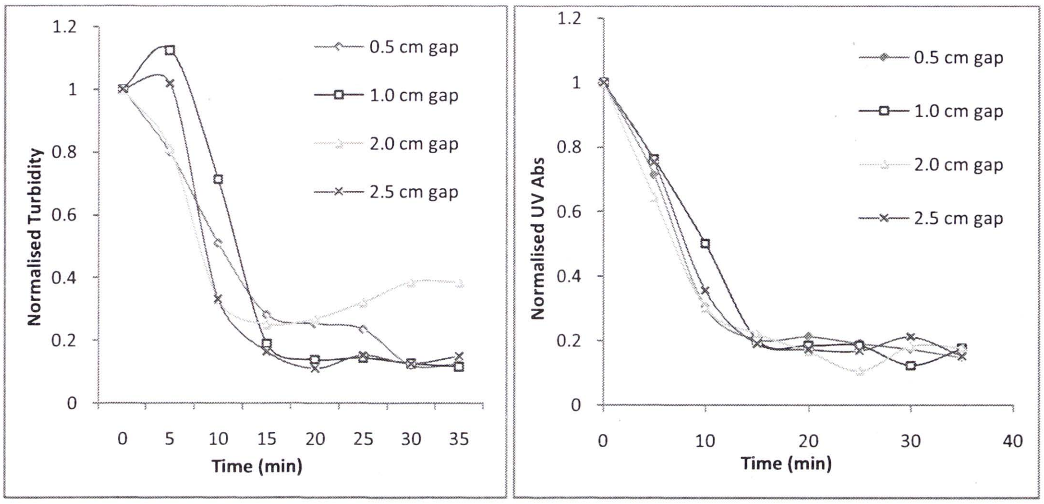

Figure 4.18 Variation of turbidity (left) and UV removal (right) at different gaps of electrodes (Current density = 11.5 mA cm^{-2}, initial turbidity = 80 NTU, initial UV = 0.150 $cm^{-1}$and pH = 8.0).

4.4.1.4 Effect of initial organic loading

The variation of turbidity and UV absorbance at different concentrations of HA is presented in Figure 4.19. There is no significant difference in removal of turbidity due to change of the initial HA concentration except for the fact that the initial removal efficiency (0-10 min) of HA was slightly higher at higher initial HA concentration. This may be due to the generation of aluminium ions for 35 min which was sufficient to coagulate HA easily at this Al release rate. This indicates that EC is suitable for water treatment of high organic concentration.

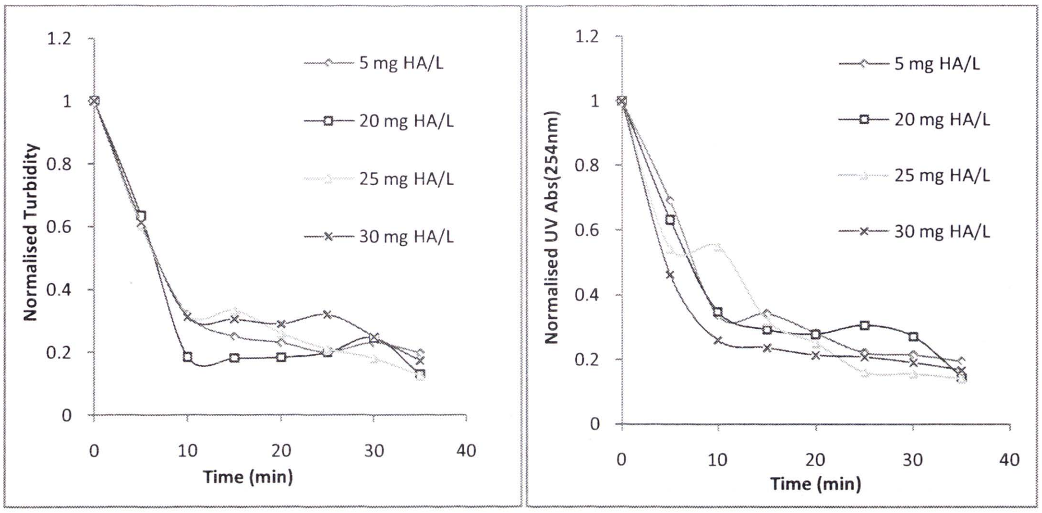

Figure 4.19 Variation of turbidity (left) and UV removal (right) at different concentration of humic acid (Current density = 11.5 mA cm^{-2}, initial turbidity = 80 NTU, initial UV = 0.150 cm^{-1}, electrodes gap = 2 cm and pH = 8.0).

4.4.2 Electrocoagulation with power directly from photovoltaic panel without charge controller

EC was carried out with a PV cell without any charge controller. Due to the fact that the EC is directly connected to the PV panels, the EC process system was found sensitive to variations on solar irradiation. The current intensity that the electrodes provide depends on the solar irradiation and the temperature of the PV module which in turn is affected depending on the weather conditions. The variation of turbidity and UV absorbance for EC conducted at five different times on 4 April 2010 starting from 10:15 AM in the morning to 19:00 PM in the evening is shown in Figures 4.20 and 4.21. The weather was fine on the day of the experiment. The temperature was between 25-30°C and relative humidity between 60-80%. The results show the variation in turbidity and organic removal dependent on solar irradiation. The maximum turbidity removal (87%) and HA removal (85%) were obtained at midday (10:00 AM-2:00 PM) when the sunlight intensity was maximum.

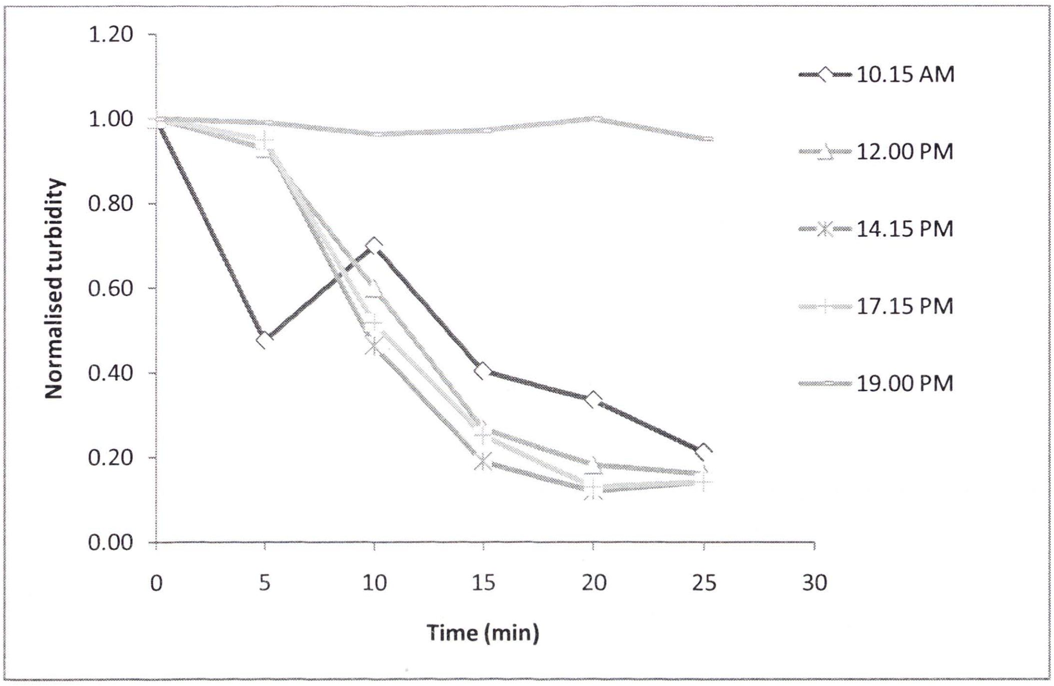

Figure 4.20 Variation of turbidity at five different times in a day (Initial turbidity = 80 NTU, initial UV= 0.150 cm^{-1}, electrodes gap= 2 cm and pH= 8.0. Experiment conducted = 4th April 2010. Weather condition = fine).

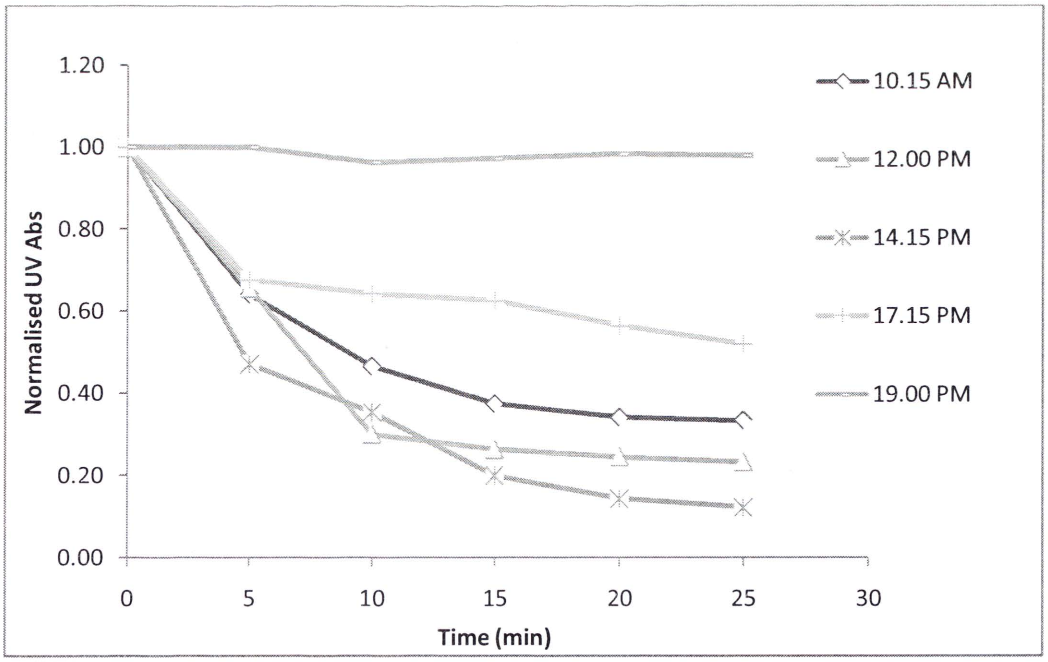

Figure 4.21 Variation of UV absorbance (254 nm) at five different times in a day (Initial turbidity = 80 NTU, initial UV = 0.150 cm^{-1}, electrodes gap = 2 cm, pH = 8.0, Experiment conducted = 4th April 2010, Weather condition = fine).

4.4.3 Electrocoagulation with power from PV panel using battery and charge controller

In this study, power supply of the EC was controlled by connecting PV panel to a series of batteries connected to a charge controller before supplying to the electrodes. By this configuration, the current through the solar panel did not depend on weather conditions or solar irradiation which eliminated the change in the removal of pollutants in the solution. The power was stored in a battery and utilised by the electrodes through the solar panel when the condition of solar radiation fluctuated during the course of the day. This happened since the charge controller supplied a constant voltage of 12 V throughout the experiment irrespective of weather conditions or the times of the day.

The variation of turbidity and UV at different times of the day (9 April 2010) using a charge controller is presented in Figures 4.22 and 4.23 respectively. This resulted in improved and consistent performance of EC. The current intensity didn't fluctuate during the experiments as the power was taken from the battery during times of fluctuating intensities. The result showed maximum turbidity removal of 90% at 10:30 A.M in the morning and maximum UV removal of 95% at 12:30 PM on the same date.

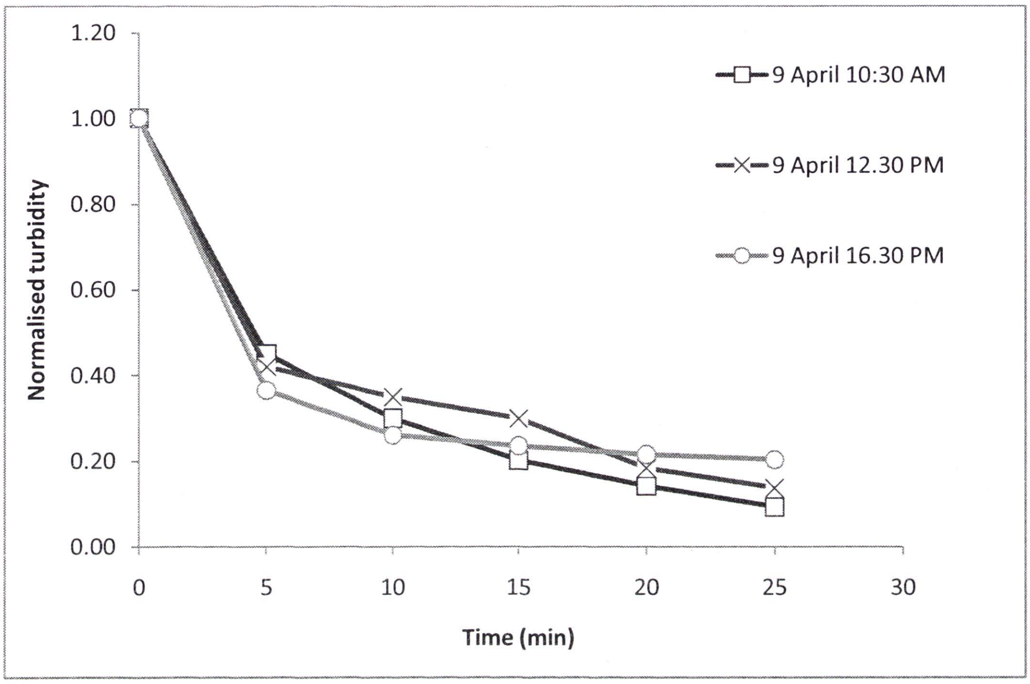

Figure 4.22 Variation of turbidity at three different times in a day (Initial turbidity = 80 NTU, initial UV = 0.150 cm^{-1}, electrodes gap = 2 cm and pH = 8.0, current density = 2.11 mA/cm^{-2}).

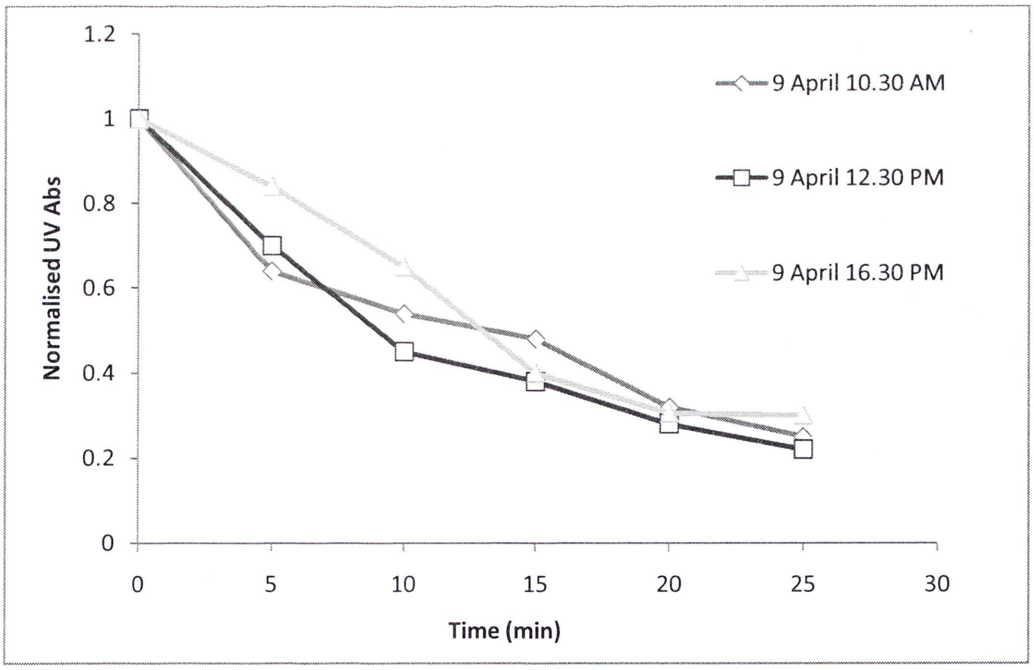

Figure 4.23 Variation of UV at three different times in a day (Initial turbidity = 80 NTU, initial UV = 0.150 cm^{-1}, electrodes gap = 2 cm, pH = 8.0, current density = 2.11 mA cm^{-2}).

4.5 Solar powered electrocoagulation and microfiltration hybrid system as a sustainable pretreatment option

Water availability and quality are a major problem in many Australian remote locations (Schafer and Richards, 2005). In some areas high levels of treatment are required either due to contamination of waters or due to high salinity. In remote communities the operation of such facilities may be limited by the availability of electricity. Solar or PV energy is the ideal source of energy in Australia to overcome this problem. There has been several renewable solar energy-powered desalination systems designed to produce 100–3000 L of clean drinking water per day using RO membranes (Matthew et al., 2000; Keefer, Hembree and Schrack, 1985). Study was done for system design and performance testing of a standalone hybrid membrane-photovoltaic desalination system (Masson and Schafer 2005) where several parameters such as feed water salt concentration, operating pressure, system recovery, specific energy consumption were examined in order to optimise the system performance. With specific energy consumption varying from 2.2 to 7.7 $kWh.m^{-3}$, the installation designed for remote villages is able to produce up to 1.2 $m^3.d^{-1}$. Also a study had been done for the feasibility of EC photovoltaic energy (David et al., 2008). But no study has been done yet for SPEC as a pretreatment for membrane filtration. The objective of this study is to demonstrate the feasibility of SPEC system powered by PV panel as a sustainable pretreatment for MF.

4.5.1 Optimisation of electrocoagulation process

The effects of specific process variables, such as initial pH, mixing, current, initial organic loading, and electrodes gap were first studied using direct current as a source of power. The optimum values for each variable were determined based on the highest removal of HA (DOC, UV254 absorbance) and turbidity. The optimum values for the process variables are shown in Table 4.1.

Table 4.1 Optimum parameters of EC operation in terms of removal of HA and turbidity:

Parameters	Tested range	Optimum condition
Current density ($mA\ cm^{-2}$)	0.5-14.5	14.5
Initial pH	3-11	8
Stirring speed (rpm)	50-1000	500
Electrodes gap (cm)	0.5-2.5	no effect
Initial HA loading ($mg\ l^{-1}$)	5-30	no effect

Within 10 min of EC, turbidity and organic removal were seen to depend on the current density, with higher current achieving higher removal efficiency but after 35 min of EC, the removal efficiency remained at almost the same level. The effect of initial pH was significant. At lower pH (3-5), the removal efficiencies were very low. This may be due to the solubility of Al ions at low pH preventing the formation of Al flocs. As the pH approached the neutral region (pH 7), Al starts to form a stable hydroxide ($Al(OH)_3$) that starts to precipitate.

With the initial HA organic loading, the initial removal efficiency (0-10 min) of HA and turbidity was slightly higher at higher initial HA concentration and there was no significant difference in the removal efficiencies due to change of the initial HA concentration. This might be due to the generation of aluminium ions for 35 min which was sufficient to coagulate HA easily at this Al release rate. The result indicates that EC with aluminium electrodes is suitable for wastewater of any organic concentration. The turbidity removal by EC under optimum conditions was between 85% and 90%. The organic matter removal efficiency in terms of DOC under optimum conditions was in the range of 65% and 75%.

4.5.2 Electrocoagulation with direct current from a PV panel without charge controller

EC was carried out with power supply coming directly from the PV cells without any charge controlling system. The current intensity that the panels provided depended on the solar irradiation and the temperature of the PV module. Figure 4.24 shows the variation of normalised DOC for the EC conducted at five different times on 4 April 2010 starting from 10:15 AM in the morning to 19:00 PM in the evening. Normalisation for turbidity and DOC was done by dividing the obtained value after EC pretreatment with value without pretreatment. The results show the variation in turbidity and organic removal depended on solar irradiation. The maximum DOC removal (75%) was observed at midday (10:00 AM-2:00 PM) when the sunlight intensity was maximum. At 19:00 PM the removal was almost zero due to the absence of sunlight.

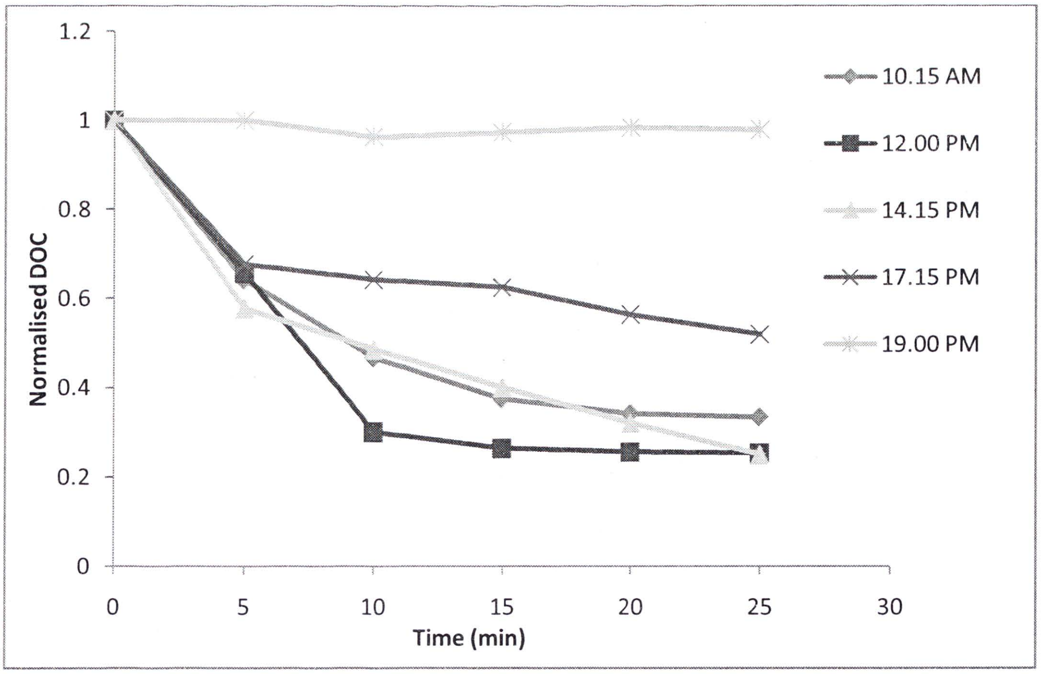

Figure 4.24 Variation of DOC at five different times in a day (Initial turbidity = 80 NTU, initial DOC = 5.5 mg l^{-1}, initial UV= 0.150 cm^{-1}, electrodes gap= 2 cm and pH= 8.0. Experiment conducted = 4th April 2010, weather condition = fine).

4.5.3 Electrocoagulation with direct current from PV panel using battery and charge controller

Power supply for the EC was controlled by connecting a PV panel to a series of batteries connected to a charge controller before supplying to the electrodes. By this configuration, the current through the panel became independent of weather conditions or solar irradiation which helped to stabilise the fluctuation in the removal of pollutants. The power was stored in a battery and utilised by the panel when the condition of solar radiation fluctuated during the course of the day. This happened since the charge controller supplied a constant voltage of 12 V throughout the experiment irrespective of weather conditions or the different times of the day.

Figure 4.25 shows the variation of turbidity and DOC with experiments conducted at different times on 9 April 2010 using battery and charge controller. This resulted in improved and consistent performance of the EC. The current intensity didn't fluctuate during the experiments as the power was taken from the battery during times of fluctuating intensities. The result showed maximum DOC removal of 90% at 12:30 P.M (9 April 2010).

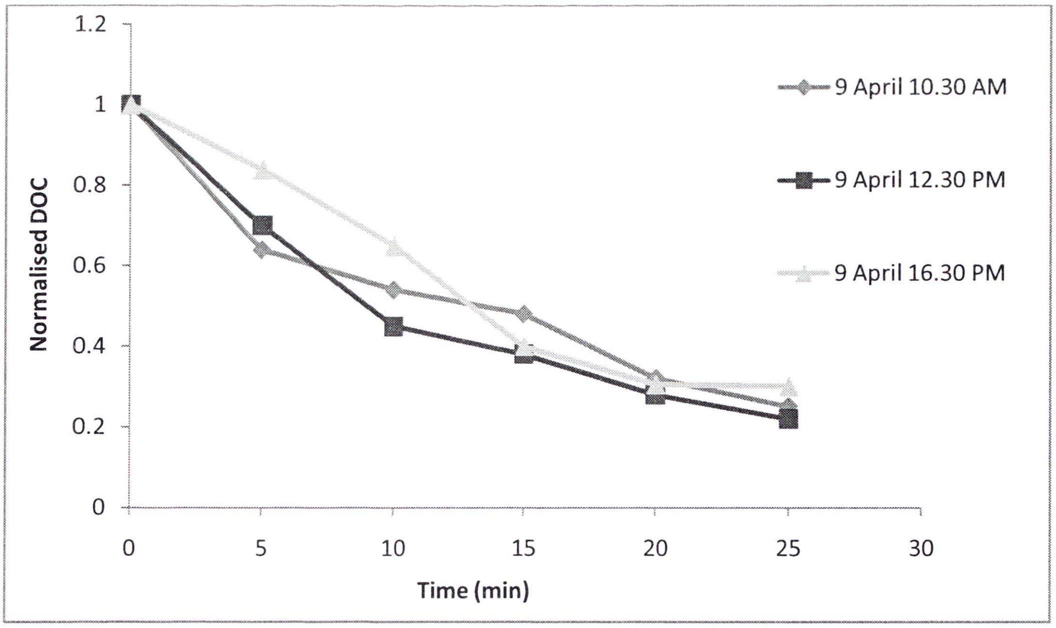

Figure 4.25 Variation of DOC at three different times in a day. (Initial turbidity = 80 NTU, initial UV= 0.150 cm^{-1}, electrodes gap= 2 cm, pH= 8.0 and current density= 2.11 mA cm^{-2}).

4.5.4 Performance of microfiltration with solar powered electrocoagulation pretreatment from photovoltaic panel without charge controller

Figure 4.26 shows the normalised permeate flux profile for 60 min of operation for SPEC at different times of the same day (4 April 2010) at pH 8.0. The current density was kept constant at 14.5 mA cm^{-2} for all the experiments.

Without pretreatment the flux decline was 90%. It can be seen that with SPEC pretreatment, the flux decline fluctuated with the variation of solar intensity. In all cases, the flux decline was observed with time. The decline was rapid at an initial stage (0-20 min) followed by more gradual decline. The significant flux decline occurred towards the evening after 4 PM where 37% flux decline was observed. The decline was minimum at 12:00 to 2 PM where only around 10% flux decline was observed. At this point we also observed highest turbidity and organic removal (DOC and UV abs). Increase of solar irradiation increases the aluminium ion released to the system. As the experiment was conducted under optimum conditions determined previously by optimisation by DC power supply, it was believed that the released ion converted to $Al(OH)_3$ floc quickly.

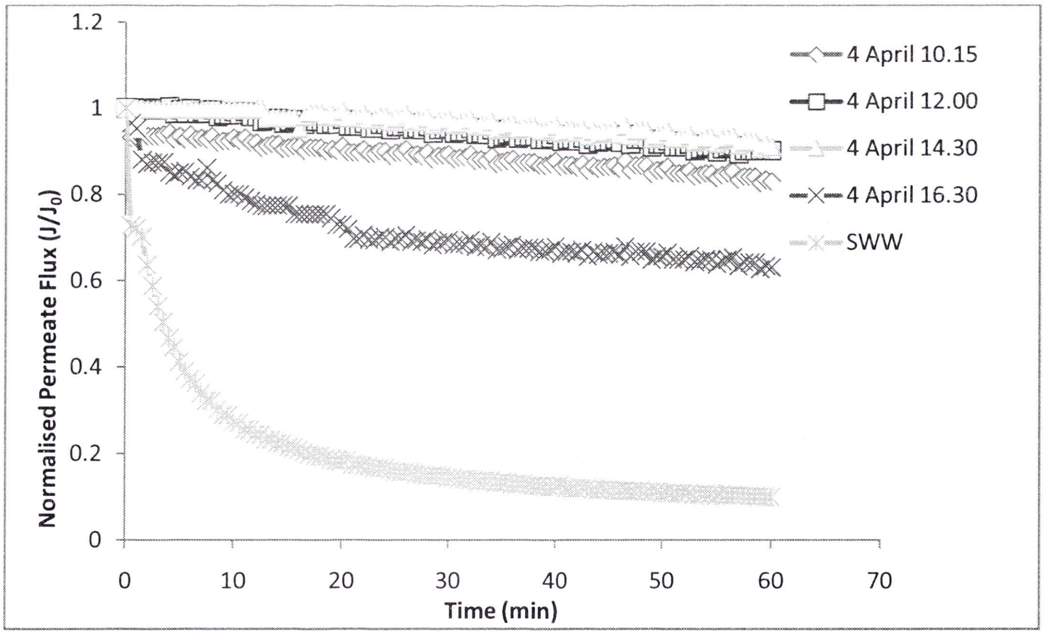

Figure 4.26 Normalised permeate flux after SPEC pretreatment at five different times in a day (SPEC operation: 35 min, transmembrane pressure: 10 kPa, cross flow velocity: 0.5 l min^{-1}, pH 8).

4.5.5 Performance of microfiltration with solar powered electrocoagulation pretreatment using battery and charge controller

Crossflow MF was carried out after pretreatment by SPEC using battery and charge controller. The power supply for the SPEC was controlled by connecting PV panel to a series of batteries connected to a charge controller before supplying to the electrodes. Through this configuration, the flux through the MF did not rely on the weather conditions and solar radiation. Thus the flux through MF was stable even for different times in a day. The power was stored in a battery and utilised by the electrodes when the condition of solar radiation fluctuated during the course of the day. This happened since the charge controller supplied a constant voltage of 12 V throughout the experiment irrespective of weather conditions or the times of the day.

The normalised permeate flux for 60 min of operation for crossflow MF after pretreatment with SPEC at different times for a day (9 April 2010) is presented in Figure 4.27. The current density was kept constant at 14.5 mA cm^{-2}. 90% of flux decline took place without pretreatment. As batteries were used in conjunction with the charge controller for SPEC pretreatment, fluctuation in flux decline was not observed with the variation of solar intensity during different times of the day. Flux decline remained in the range of 10-14%, which was increased by more than 80% compared to no pretreatment. Thus improved performance of MF was observed by this configuration. As the current through the electrodes was controlled, the release of aluminium ions was also controlled. Under optimum conditions, all parameters were favourable for the pollutants to be removed by settling, adsorption and floatation resulting in improved performance.

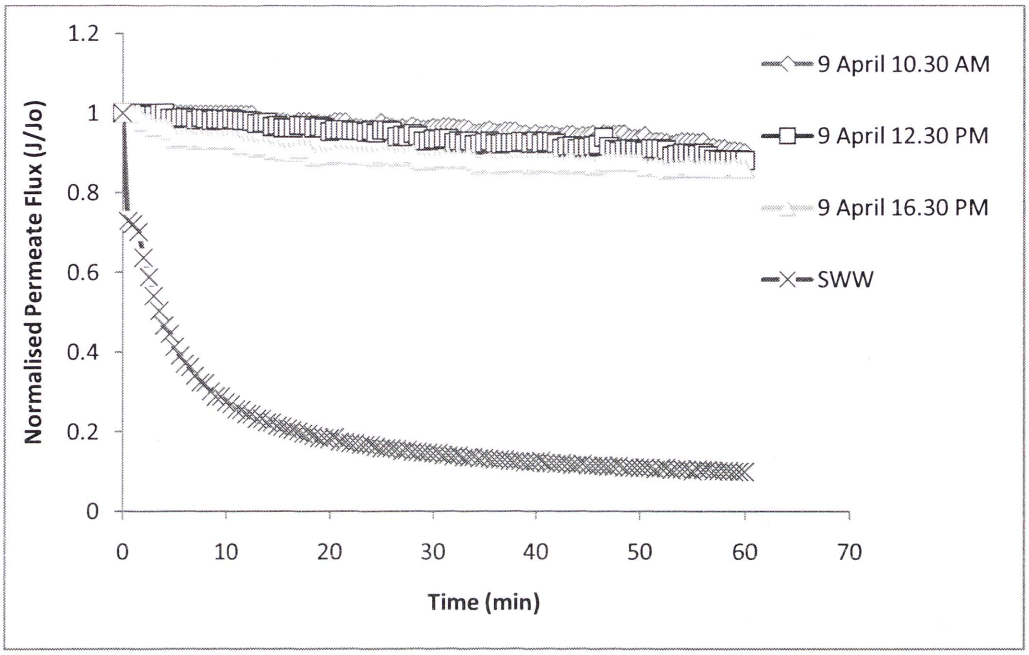

Figure 4.27 Normalised permeate flux after SPEC pretreatment at three different times in a day (SPEC operation: 35 min, transmembrane pressure: 10 kPa, cross flow velocity: 0.5 l min^{-1}, pH 8)

4.6 Study of fouling mechanism in electrocoagulation-crossflow microfiltration system

Crossflow or tangential flow is a process in which the formation of a filter cake is limited or suppressed by a flow of the suspension parallel to the filtration surface. Since this system is pressurised, water is forced through the filter. Particles deposited on the filter medium are swept away by the cross-flow velocity action, which produces shear and lift forces on the particles as they become attached to the filter medium. Generally in most practical applications of crossflow MF, a wide range of colloids and particles exist in the solution to be treated. The flux decline is believed to be a major hindrance to the wide implementation of crossflow MF for water and wastewater treatment. In crossflow MF process, there occurs a formation of a secondary or dynamic membrane on top of the primary membrane. Kaolin, lime and diatomaceous earth were used as dynamic membranes in crossflow MF of activated sludge (Elkebir, 1991). Holdich and Boston (1990) investigated the application of dynamically formed membrane in the MF of tap water using mineral species. The mineral species included fluorspar, diatomite, kaolin, silicate flakes and limestone. The formation of dynamic membrane was divided into three categories (Tanny, 1978).

Class 1 dynamic membranes are formed when the particle have a particle size greater than the pore size of the membrane. This phenomenon is widely known as concentration polarisation.

Class 2 dynamic membranes are created when filtering dilute suspensions of colloidal particles much smaller than the pore size of the membrane. In this case, the flux decline mechanism was found to behave according to an internal pore clogging phenomenon rather than cake build-up on the membrane surface.Visvanathan and Ben Aim (1989), Tanny et al. (1979) and Hermia (1982) reported similar results. All of the above investigators reported the following model:

$$t/V = 1/ Q_0 + k_1 t/2 \qquad \text{(Eq. 4.1)}$$

Where V is the permeate volume (ml), t is the filtration time (min), Q_0 (ml min^{-1}) is the initial flux rate and k_1 is the filtration constant. The development of this model equation is based on the assumption that the pore volume decreases proportionately to the filtrate volume.

After some time, the colloidal particles will be brought-up to the membrane surface, and the flux behaviour will proceed in accordance with the following classical cake filtration model (Murkes and Carlsson, 1988):

$$t/V = 1/K_1 (V - 2V_f) \qquad \text{(Eq. 4.2)}$$

Where V_f(l) is the volume of permeate which produces a hydraulic resistance equal to that of the membrane, and K_1 ($l^2 \text{min}^{-1}$) is the cake filtration constant.

The formation of dynamic membranes was investigated by Al-Malack and Anderson (1996) with crossflow MF. They found that dynamic membrane formation obeys the standard law of filtration in the first few min of membrane formation (15 min). As time passes, the dynamic membrane formation was found to proceed according to the classical cake filtration model. In another study, the removal of phosphate from water by red mud using crossflow MF was investigated (Akay et al., 1998). This study evaluated specific cake resistance in crossflow MF as a function of phosphate concentration by using cake filtration model.

Class 3 dynamic membranes are formed when filtering polymers or polyelectrolyte molecules of equal size to the membrane size.

The objective of this study is to investigate the fouling mechanism of crossflow MF after pretreatment of water containing kaolin suspension with EC using aluminium EC. The study will be useful for developing fouling control mechanisms if fouling mechanism can be properly understood. The findings that the fouling proceeds according to standard law of filtration and classical cake filtration model could prove that fouling of primary membrane is mainly caused by colloids, which precipitate within the pores of the membrane rather than the deposition of particles on the membrane surface.

4.6.1 Fouling Mechanisms

Both the standard law of filtration and classical cake filtration model were used for carrying out the evaluation of fouling mechanism for the crossflow MF. Figures 4.28, 4.29 and 4.30 show the relationship between t/V and t for a kaolin concentration of 100 mg l^{-1}, 400 mg l^{-1} and 800 mg l^{-1} respectively at different CFV. For all the cases (Figures 4.28-4.30), it shows that the fouling mechanism of the primary membrane was proceeding according to the standard law of filtration which is due to the permeation of kaolin colloidal particles into the pores of the primary membrane. The standard law of filtration states that when filtering a suspension where the size of particles is less than that of the membrane pores, then the particles pass through the pores where it is assumed that the volume of the pores decreases in proportion to the volume filtered (Vishvanathan and Ben, 1989). However, fractions of the particles are deposited on the internal pore surface, which results in clogging of the pores.

The summary of the fouling investigation is presented in Table 4.2. From the table; it was observed that the filtration constant k_1 decreased with increase in CFV and increase of kaolin concentration. It is explained by the fact that increase of CFV decreased the hydraulic resistance of the membrane due to the shear effect of the

CFV on particles. Also increasing the kaolin concentration resulted in increasing the hydraulic resistance of the membrane due to the building up of particles inside the pores and on the membrane surface. It was also observed that the initial flux Q_0 was found to increase with increasing CFV.

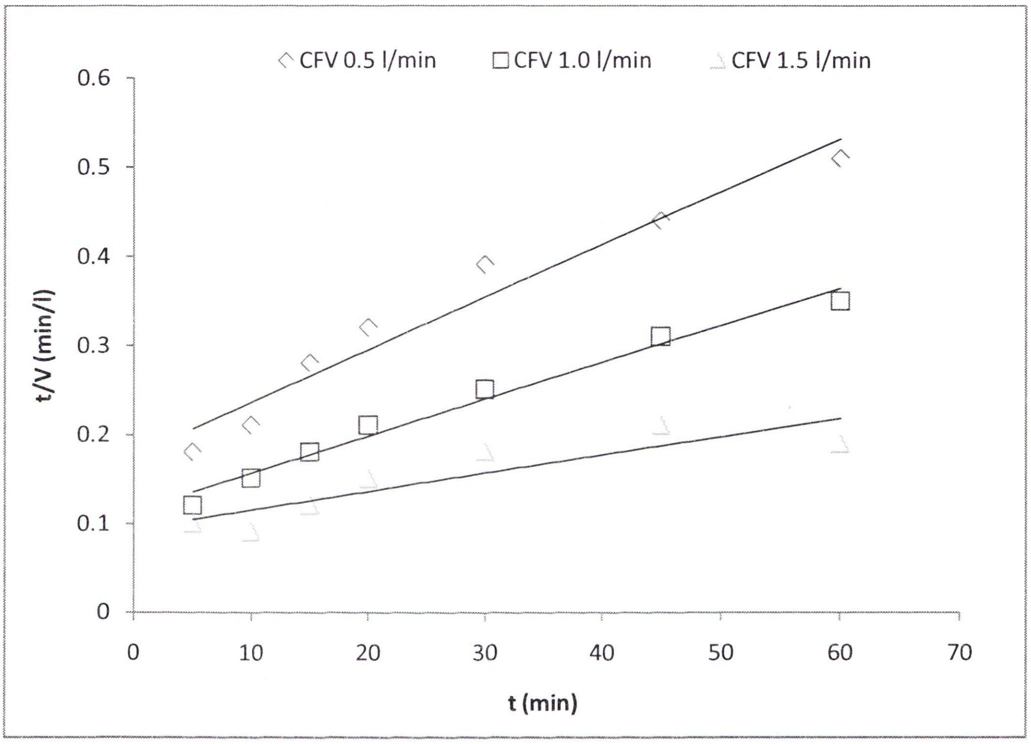

Figure 4.28 Relationship between t/V and t for kaolin concentration of 100 mg l^{-1} at three different CFV.

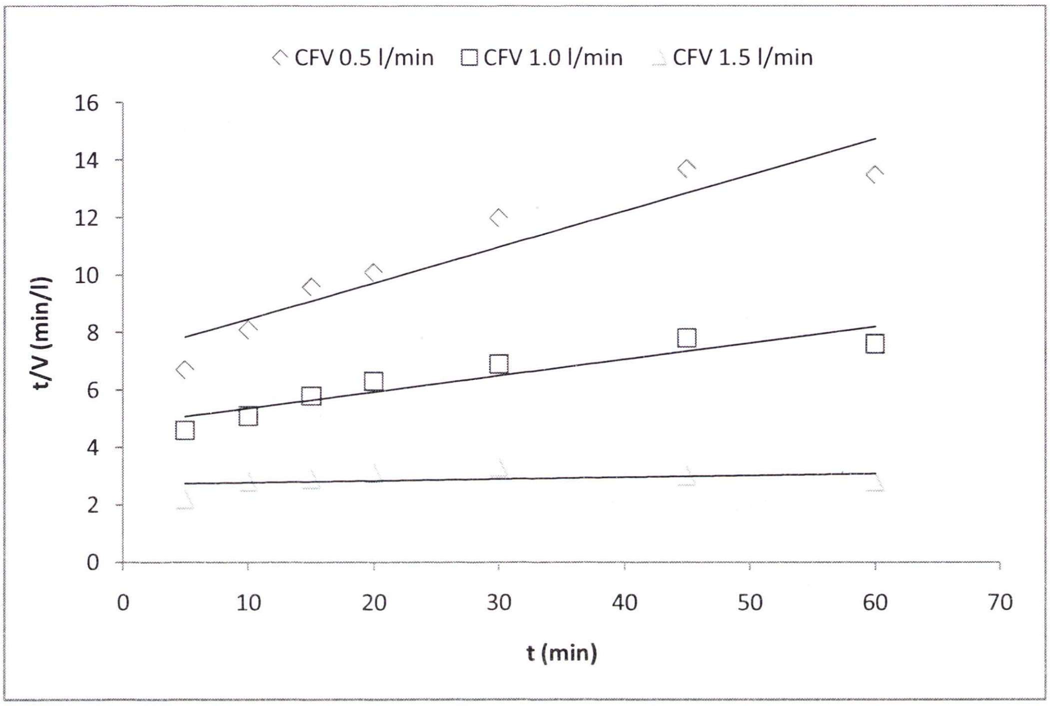

Figure 4.29 Relationship between t/V and t for kaolin concentration of 400 mg l^{-1} at three different CFV.

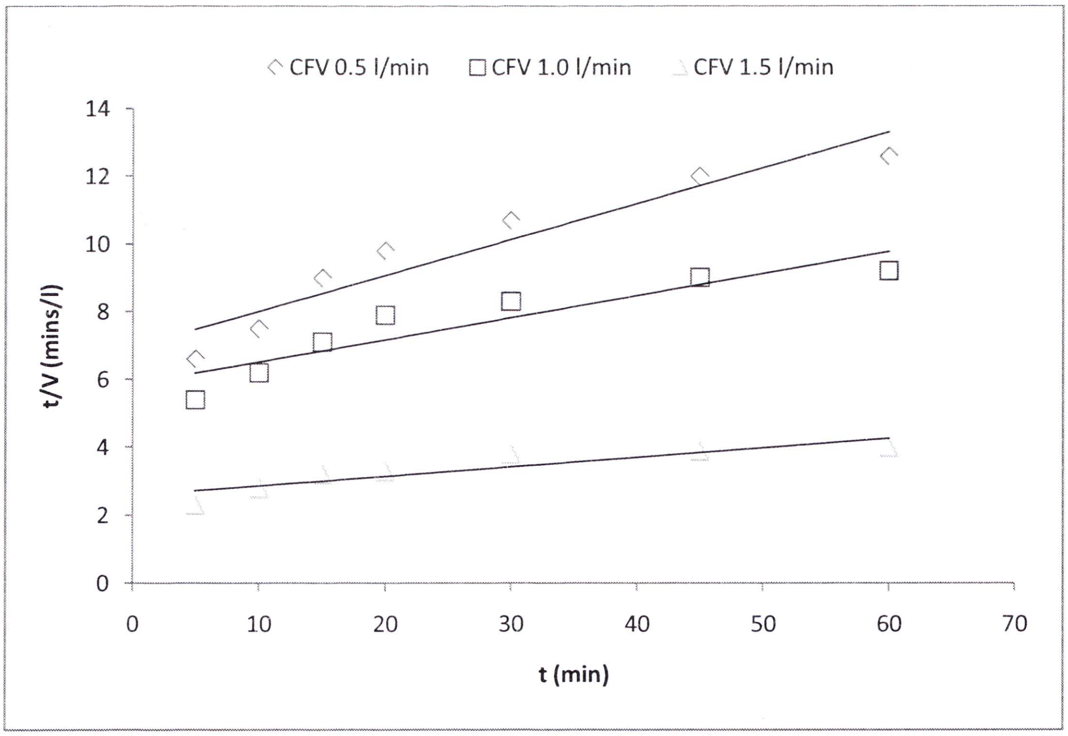

Figure 4.30 Relationship between t/V and t for kaolin concentration of 800 mg l^{-1} at three different CFV.

Table 4.2 Results for the fouling mechanisms

Kaolin concentration (mg l^{-1})	Crossflow velocity (l min^{-1})	Equation	R^2	Q_o (ml min^{-1})	k_l (l/l)
100	0.5	(t/V) = 0.129 x t + 2.26	0.95	442	0.259
100	1	(t/V) = 0.080 x t + 1.78	0.98	561	0.161
100	1.5	(t/V) = 0.015 x t + 1.60	0.85	622	0.030
400	0.5	(t/V) = 0.184 x t + 2.32	0.91	431	0.369
400	1	(t/V) = 0.075 x t + 2.05	0.88	487	0.150
400	1.5	(t/V) = 0.020 x t + 1.91	0.87	521	0.040
800	0.5	(t/V) = 0.079 x t + 4.44	0.91	225	0.159
800	1	(t/V) = 0.074 x t + 2.92	0.86	342	0.148
800	1.5	(t/V) = 0.018 x t + 2.57	0.88	388	0.036

4.6.2 Fouling Mechanisms with electrocoagulation

The crossflow MF process was investigated for the effect of EC at kaolin concentration of 400 mg l^{-1} and at CFV velocity of 1.0 l min^{-1}. The EC time was varied in the range between 0 min to 30 min. Figure 4.31 shows the results of the MF permeate flux under different EC time. When EC as a pretreatment was not used, the initial flux was 198 l/m^2 h and decreased to 70 l/m^2 h after 60 min of operation. However, the flux improved significantly when the feed water was pretreated by EC. When pretreated by EC for 10 min, the initial flux increased to 305 l/m^2 h, which is about 77% increase from the untreated feed. The optimum EC time was found to be about 30 min and the corresponding MF flux reached 855 l/m^2 h, which represents more than 300 percent increase from the untreated feed. The flux did not change significantly when the EC time was increased beyond 30 min which may be due to the reversing the destabilisation of the colloidal particles. As the experiment was done at pH 8, it is believed that the ions released are converted to $Al(OH)_3$ floc quickly causing the particles and organics to agglomerate, float, settle which can then be easily removed from the synthetic water. Tables 4.3 and 4.4 present the summary of results for the crossflow MF.

It was observed from the Table 4.3 that the fouling mechanism for all feed water conditions followed the standard filtration law which is possibly due to the permeation of colloidal particles into the primary membrane. As the MF has an enormous internal surface area of pores, at the initial stages of the operation the colloids with size range much smaller than that of the pores will pass through the pores. Once within the pores of the membrane, these colloids become deposited or adsorbed due to various forces such as the electrical double layer effect and hydrodynamic attraction forces, and form a film of colloids on the internal pore surface (Visvanathan and Ben, 1989).

Table 4.4 indicates that besides the standard filtration law the fouling mechanism also followed the classical filtration model which indicates that besides the infiltration of colloidal particles, a dynamic membrane was formed on top of the primary membrane due to the agglomerated solids. The values for Q_0 and V_f shows the effect of coagulation on membrane performance. The increase in coagulant dose increased the initial flux value (Q_0) and the volume of permeate which produces a hydraulic resistance (V_f) equal to that of the membrane. Table 4.3 also shows that the k_l value was found to decrease with increase in EC time until it reached the lowest value at optimum condition. The results is in agreement with the investigation performed by Grace (1956) who concluded that in general all microporous filter media exhibit an initial period of filtration in which fine particles appear in the filtrate. After this initial period, the number of particles in the filtrate decreases rapidly, and the flux decay follows the standard law of filtration, which is then followed by a prolonged period conforming to the cake filtration model.

When the internal surface of the pores becomes saturated with fine colloids, the colloids accumulate on the membrane surface, leading to the formation of a colloidal film on the external membrane surface. At the early stages of filtration, the colloids can be deposited on the membrane surface between the pores, and thus accumulate. Later, these aggregates of colloids can form bridges over the pore openings, resulting in the partial blocking of the pores, a smaller pore structure available to subsequent colloids and particle retention. This bridging of aggregated colloids leads to the eventual formation of a film on the membrane surface (Visvanathan and Ben, 1989).

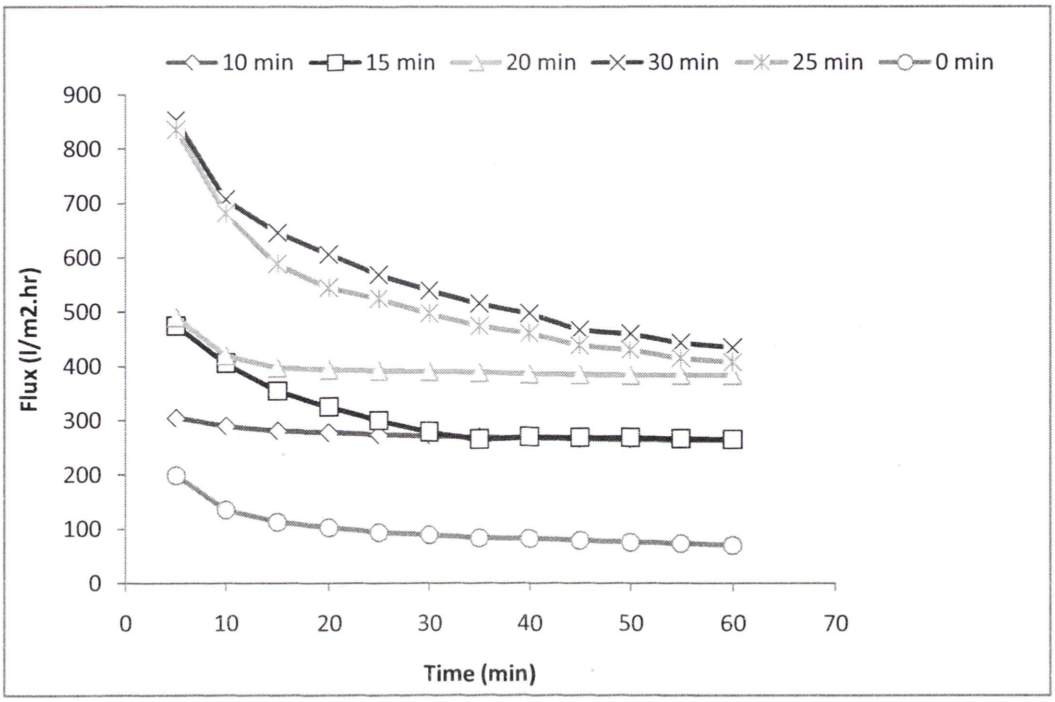

Figure 4.31 Permeate flux with respect to time at various EC time.

Table 4.3 Results of the fouling mechanism for EC-MF according to standard law of filtration

EC Time (min)	Equation	R^2	Q_o (ml min^{-1})	k_I (l/l)
0	(t/V) = 0.051 x t + 0.56	0.91	1780	0.102
10	(t/V) = 0.047 x t + 0.49	0.92	2030	0.094
15	(t/V) = 0.041 x t + 0.21	0.96	4804	0.083
20	(t/V) = 0.022 x t + 0.16	0.92	6010	0.044
25	(t/V) = 0.014 x t + 0.124	0.99	8050	0.028
30	(t/V) = 0.013 x t + 0.119	0.96	8360	0.026

Table 4.4 Results of the fouling mechanism for EC-MF according to classical cake filtration model

EC Time (min)	Equation	R^2	V_f (l)	K_1 (l^2 min^{-1})
0	(t/V) = 0.015 x t + 1.60	0.96	0.20	52
10	(t/V) = 0.184 x t + 2.32	0.88	0.42	153
15	(t/V) = 0.075 x t + 2.05	0.91	2.10	456
20	(t/V) = 0.020 x t + 1.91	0.95	4.24	642
25	(t/V) = 0.079 x t + 4.44	0.98	6.85	718
30	(t/V) = 0.074 x t + 2.92	0.97	7.20	805

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CHAPTER 5

CONCLUSIONS

Membrane filtration has become an indispensible technology for water treatment and wastewater reuse. However, membrane fouling has remained one of the most serious challenges. Pretreatment of feed water is considered one of the most effective means to reduce membrane fouling. In this study, electrocoagulation (EC) using iron and aluminium electrodes has been studied as an attractive pretreatment method for membrane filtration. The potential for using EC with renewable energy such a solar power has been demonstrated which has given rise to this new solar powered EC (SPEC) for applications in remote communities. The possibility for using SPEC as pretreatment for membrane filtration has also been demonstrated. As colloidal fouling is one of the major hurdles for the successful applications of membrane technology, an investigation into the fouling mechanism for crossflow was performed comparatively with feed water containing kaolin suspension with and without EC pretreatment which could be useful for developing fouling control mechanisms if fouling mechanism can be properly understood.

5.1 Electrocoagulation with iron electrodes as pretreatment to microfiltration

The feasibility of electrocoagulation (EC) for water treatment with iron electrodes was evaluated. Performance of EC as pretreatment for microfiltration (MF) was investigated in terms of organic and turbidity removal and membrane flux.

- EC with iron electrodes generated soluble ferrous ions (Fe^{2+}) that introduced a green colour into the treated synthetic water and which then turned yellow and turbid. The Fe^{2+} ions oxidises to Fe^{3+} in acidic or neutral conditions. The formation of $Fe(OH)_3$ as a result of the reaction of Fe^{3+} with OH^- ions gave yellow colour to the water and increased turbidity. Also the presence of organic matter in synthetic water was highly detrimental to iron EC as Fe^{2+}-organic matter complexation prevented $Fe(OH)_3$ precipitation and floc formation. Therefore iron EC was not recommended for treating synthetic water under similar conditions of investigation.
- Pretreatment of feed water by EC with iron electrode did not improve the performance of MF for the entire range of experimental conditions investigated. However, when EC with iron electrodes was followed by fast

mixing, slow mixing and sedimentation using flocculator, significant improvement in the performance of MF was observed (turbidity removal of 93%, DOC removal of 78% and UV (254 nm) absorbance removal of 95% at optimum duration of 20 min). Since EC with iron electrodes simply could not improve the performance of MF without slow mixing, fast mixing and sedimentation using flocculator. Therefore, iron electrodes were not used for further study.

5.2 Electrocoagulation with aluminium electrodes as pretreatment to microfiltration

The effectiveness of EC as pretreatment with aluminium electrodes for MF was studied in terms of permeate flux and organic and turbidity removal and the performance was compared with the conventional chemical coagulation using aluminium sulphate as pretreatment for MF. It is believed that, employing aluminium electrodes will generate Al^{3+} ions during EC producing $Al(OH)_3$ precipitates which is capable of destabilising colloids and organics in the process improving the membrane performance when used as a pretreatment process for MF.

- Without pretreatment, MF experienced a significant flux decline, 94% within 160 min of operation. However, after EC pretreatment at optimum conditions, the MF flux improved by 55%. With chemical coagulation under optimum conditions as pretreatment, MF did not experience any flux decline.
- MF flux was found to be sensitive to pH of the feed solution. MF flux was highest at isoelectric point (pH 8) for both EC and chemical coagulation. Organic and turbidity removal were also maximum at isoelectric points.
- Pretreatment by EC was found to enhance the organic and turbidity removal of the feed solution. At optimum conditions (30 min EC time and pH 8), the DOC and UV abs removal were 78% and 85% respectively.

5.3 Solar powered electrocoagulation

The feasibility of solar powered electrocoagulation (SPEC) for water treatment was investigated using aluminium electrodes. The process parameters of the EC system were first optimised using direct electrical current. SPEC was performed with photovoltaic panel (PV) connected to aluminium electrodes either directly or through a set of batteries and charge control system.

- When EC reactor was directly connected to the PV panels without charge control system, EC process system was found sensitive to variation on solar irradiation. The SPEC performance varied depending on the solar intensity of the day and the highest removal efficiency was observed at around midday (10:00 AM-2:00 PM) under optimum operating conditions (DOC removal of 75%, UV abs 85% and turbidity 87%).
- The use of batteries and charge control system with the EC reactor resulted in more efficient and consistent performance of EC. The variation in organic and turbidity removal was found within the range of only 10% for experiments conducted on three different times in a day. At optimum conditions, the maximum organic removal (78% DOC and 95% UV abs) and turbidity removal (90%) yielded at 10:30 AM in the morning.
- SPEC was assessed to demonstrate the feasibility for its application as a sustainable pretreatment option for MF. Without pretreatment, the MF flux decline was severe, about 90% within 60 min of operation. The SPEC system tested with power supplied directly from PV panel (without charge control system) improved MF permeate flux however; fluctuation in the performance of MF was observed due to variation of solar intensity. A significant flux decline (by up to 37%) occurred towards the evening after 4 PM (4 April 2010) when the solar intensity was at its lowest. The flux decline was minimum (about 10% only) between 12:00 and 2 PM. The connection of batteries and charge control system to the SPEC improved the performance of MF and the performance became more stable. Flux decline remained almost stable within 12% (78% flux increase compared to without

pretreatment) for three different times in a day (9 April 2010, 10:30 AM to 16:30 PM).

- The study demonstrated that SPEC is feasible for small scale decentralised water treatment system which has potential for application in remote Australian communities where renewable energy such as solar power is abundant. The potential for using SPEC as a sustainable pretreatment option for membrane filtration process is also demonstrated.

5.4 Fouling mechanism in electrocoagulation-crossflow microfiltration system

The fouling mechanism of crossflow MF after EC pretreatment for water containing kaolin suspension was investigated. Both the standard law of filtration and classical cake filtration model were used for carrying out the evaluation of fouling mechanism for the crossflow MF. The study will be useful in developing fouling control mechanisms if fouling mechanism can be properly understood.

- After EC pre-treatment, the fouling mechanism for MF was observed to follow the standard law of filtration which is possibly due to the permeation of colloidal particles into the primary membrane. Besides the standard filtration law, the fouling mechanism also followed the classical cake filtration model which indicates that besides the infiltration of colloidal particles, a dynamic membrane was formed on top of the primary membrane probably due to the formation of a colloidal film on the membrane surface.

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APPENDIX

List of publications based on this research

Peer Reviewed Journal Articles

1. **G. Sharma**, H.K. Shon, R. Aryal, S. Phuntsho, "Performance evaluation of microfiltration with electrocoagulation and chemical coagulation pretreatment". Desalination and Water Treatment. In press (doi: 10/5004/dwt.2011.2882).
2. Do Hee Kim, H.K. Shon, **G. Sharma**, J. Cho, "Charge effect of natural organic matter for ultrafiltration and nanofiltration membranes". Journal of Industrial and Engineering Chemistry 17 (2011) 109-113.
3. **G. Sharma**, J. Choi, H.K. Shon, S. Phuntsho, "Solar-powered electrocoagulation system for water and wastewater treatment". Desalination and Water Treatment (accepted February 2011).
4. **G. Sharma**, H.K. Shon, "Solar-powered electrocoagulation and microfiltration hybrid system as a sustainable pretreatment option". Submitted for publication in Desalination and Water Treatment in 2011.

Referred Conference Papers

1. **G. Sharma**, J. Choi, H.K. Shon, S. Phuntsho, "Solar-powered electrocoagulation system for water and wastewater treatment". Conference on Challenges in Environmental Science and Engineering (CESE 2010), Cairns, Australia, September 26-October 1.

2. **G. Sharma**, H.K. Shon, R. Aryal, S. Phuntsho, "Performance evaluation of microfiltration with electrocoagulation and chemical coagulation pretreatment". The 7th International Membrane Science and Technology Conference (IMSTEC 2010), Sydney, Australia, November 22-26 2010.

3. **G. Sharma**, H.K. Shon, S. Phuntsho, "Electrocoagulation-Microfiltration Hybrid System for Water Treatment". The 6th IWA Specialist Conference on Membrane Technology for Water and Wastewater Treatment, Aachen, Germany 4-7 October 2011. Submitted for attendance.