ULTRASONICALLY AIDED CROSS-FLOW MEMBRANE FILTRATION SYSTEM FOR LATEX WASTEWATER

by

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		Unit
a	value of J_P / J_{P0} at the beginning of one cycle	
k	coefficient value	
K	fouling coefficient	
J	flux	l/m^2.sec
J_0	initial flux	l/m^2.sec
J_p	Permeate flux	l/m^2.sec
J_W	Water permeate flux	l/m^2.sec
μ	Viscosity	cP
ρ	Density	kg/m^3
A_m	Effective membrane surface area	m^2
T	Temperature	˚C
T_c	length of one cycle	min
t	time	sec
F	Frequency	kHz

LIST OF ABBREVIATION

ABS	Acrylbitrile Butadiene Styrene
AFM	Atomic Force Microcopy
ANOVA	Analysis of Variance
ATR	Attenuated Total Reflectance
AS	Activeted Sludge
BOD_5	Biological Oxygen Demand
CAS	Conventional Activated Sludge
CCD	Central Composite Design
COD	Chemical Oxygen Demand
DO	Dissolve Oxygen
DR	Decay ratio
SBR	Styrene Butadiene Rubber
NBR	Nitrile Butadiene Rubber
PVC	Polyvinyl Chloride
MF	Microfiltration
RO	Reverse Osmosis
UF	Ultrafiltration
F/M	Food per Microorganism
HRT	Hydraulic Retention Time
TOC	Total Organic Compound
RSM	Response Surface Methodology
3D	Three Dimensional

TSS	Total Suspended Solid
TS	Total Solid
TEM	Transmission Electron Microscopy
FTIR	Fourier Transform Infra Red Spectroscopy
SEM	Scanning Electron Microscopy
PG	Pressure Gauge

ALIRAN SILANG PENAPISAN MEMBRAN DENGAN BANTUAN ULTRASONIK BAGI SISA BUANGAN LATEKS

ABSTRAK

Dalam kajian semasa, satu sistem membran penapisan dengan bantuan ultrasonik dibangunkan bagi menawarkan membran yang bersih selepas melalui penapisan oleh air sisa lateks. Pencirian air sisa lateks telah disiasat untuk memutuskan membran terbaik dan sesuai bagi digunakan dalam sistem penapisan ini di bawah keadaan optimum. Beberapa langkah pencirian telah dilakukan seperti analisis saiz zarah, dengan menggunakan Mikroskop Transmisi Elektron (TEM) dan Mikroskop Pasukan Atom (AFM), pH, jumlah pepejal (TS), pepejal terampai (TSS), Keperluan Oksigen Biologi (BOD5) , Permintaan Oksigen Kimia (COD) dan kelikatan. Untuk mendapatkan kebolehtelapan tinggi membran, selulosa asetat membran telah digunakan sebagai penapis selepas pencirian sisa lateks dijalankan. Berdasarkan literatur, sistem penapisan membran ultrasonik bantuan telah disediakan. Hasil daripada analisis sudut sentuh permukaan membuktikan bahawa membran adalah membran hidrofilik yang baik. Ini merupakan salah satu ciri penting membran yang digunakan dalam kajian ini. Analisis Fourier Transform Infra Red (FTIR) telah dilakukan untuk menyiasat keberkesanan pembersihan gelombang ultrabunyi ke permukaan membran yang telah ditutupi oleh zarah air sisa. Model proses pengotoran ditentukan dari trend fluks meresap. Kesan beberapa parameter penting untuk mendapatkan keadaan optimum untuk proses pembersihan telah dikaji dengan teliti. Kesan frekuensi gelombang ultrasonik, suhu air mandi dan masa untuk ultrasonik disiasat. Semua parameter dibandingkan berdasarkan pengiraan nilai pekali *k* dan DR%. Frekuensi rendah (35 kHz) memberikan kecekapan pembersihan yang lebih baik daripada frekuensi yang tinggi (130 kHz) dengan perbezaan nilai DR% sebanyak 12.2%. Frekuensi berbeza memberikan bentuk kesan yang berbeza bagi setiap masa untuk sonikasi. Pada frekuensi tinggi, lebih lama masa untuk sonikasi akan mengurangkan keberkesanan pembersihan. Pada frekuensi rendah, 5 minit masa untuk sonikasi memberi kesan terbaik untuk membersihkan membran dengan nilai DR% adalah 64.68%. Semakin meningkat suhu air mandi, semakin meningkat suhu cecair masukan. Oleh itu, ia mengurangkan kelikatan cecair masukan. Semakin kelikatan menurun, semakin meningkat fluks. Kualiti air hasil penapisan diukur oleh kekeruhan air tertapis tersebut. Walaupun kualiti air penapisan selepas penapisan oleh membran yang dibersihkan oleh ultrasonik adalah sedikit lebih rendah daripada penapisan oleh membran yang tidak dibersihkan, perbezaan oleh kedua-dua ini masih boleh diterima dengan 1% perbezaan kadar penolakan. Dari Mengimbas imej mikrofotokopi Elektron (SEM), permukaan membran menunjukkan tiada kerosakan diperhatikan selepas membran dibersihkan. Satu analisis interaksi antara cecair masukan dan permukaan membran telah dijalankan dengan menggunakan analisis potensi zeta. Ia menunjukkan bahawa koloid dan permukaan membran mempunyai kestabilan sederhana dengan bacaan -37.64 mV. Satu analisis pengoptimuman telah dijalankan dengan menggunakan perisian Design Expert dan Kaedah Permukaan Respon (RSM) telah digunakan sebagai satu kaedah untuk mendapatkan keadaan optimum sistem untuk beroperasi pada keberkesanan yang paling tinggi. Selepas interaksi ketiga-tiga faktor telah dipertimbangkan dalam analisis ini, model yang signifikan menunjukkan bahawa proses pembersihan adalah pada keadaan yang optimum apabila beroperasi pada 130 kHz, 10 minit masa untuk sonikasi dan 40 ˚ C suhu mandi air dengan kebaikan sebanyak

0.986. Dapatan adalah berbeza antara analisis RSM dan hasil eksperimen kerana interaksi antara semua parameter yang telah diperhatikan oleh RSM analisis kajian lanjut mengenai interaksi tersebut perlu dijalankan pada masa akan datang. Sebagai kesimpulan, kebolehtelapan membran telah meningkat dengan sistem penapisan membran bantuan ultrasonik.

ULTRASONICALLY AIDED CROSS-FLOW MEMBRANE FILTRATION SYSTEM FOR LATEX WASTEWATER

ABSTRACT

In this current study, an ultrasonically-aided membrane filtration system that offers cleaned membrane after being fouled by latex wastewater was developed. Characterizations of latex wastewater were investigated to decide the best and suitable membrane used for this filtration system under optimum condition. Some characterization steps were done such as the latex particle size analysis, by using Transmission Electron Microscopy (TEM) and Atomic Force Microscope (AFM), pH, total solid (TS), total suspended solid (TSS), Biological Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD) and viscosity. In order to obtain high permeability of the membrane, cellulose acetate membrane was used as the filter after characterized the latex wastewater based on the hydrophilicity of the membrane. Based on the literature, an ultrasonic-aided membrane filtration system was set up. The result from surface contact angle analysis proves that the membrane was a good hydrophilic membrane which is one of the crucial characteristic of a membrane used in this study. Fourier Transform Infra Red (FTIR) analysis was done to investigate the cleaning effectiveness of ultrasound waves to the fouled-membrane surface. The model of the fouling process was determined from the permeate flux trends. The effects of several important parameters to obtain an optimum condition for the cleaning process were thoroughly investigated. The effect of frequency of the ultrasound waves, water bath temperature and the sonication time were investigated. All the parameters were compared based on the calculation of coefficient k value and the DR%. In overall, low frequency (35 kHz) gives better cleaning efficiency than high frequency (130 kHz) with DR% differences value of 12.2%. Different frequency gives different trends of effect for each sonication time. At high frequency, longer of sonication time reduce the cleaning effectiveness. At low frequency, 5 minutes of sonication time gives the best effect to clean the membrane with DR% of 64.68%. Roughly, as the water bath temperature increase, the feed solution temperature was increased. Thus, reduce the viscosity of the feed solution. As the viscosity decreased, the permeate flux increase. The permeate water quality was measured by the permeate turbidity. Even though, the quality of permeate flux after the filtration by cleaned-membrane was lower than the filtration by uncleaned-membrane, the differences of these two were acceptable with 1% differences of rejection rate. From Scanning Electron Microcopy (SEM) images, the membrane surface shows no damaged was observed after sonication. An interaction analysis between feed solution and the membrane surface was conducted by using zeta potential analysis. It shows that the colloid and the membrane surface have moderate stability with -37.64 mV. An optimization analysis was carried out by using Design Expert software and Response Surface Methodology (RSM) was used as a method to get the optimum condition of the system to operate at highest effectiveness. After the interactions of all three factors were considered in this analysis, the significant model shows that the process of the cleaning procedure was at optimum condition when were operated at 130 kHz, 10 minutes of sonication time and 40˚C of water bath temperature with desirability of 0.986. The finding was different between RSM analysis and experimental result because of the interaction between all the parameters was observed by RSM analysis which further study on these interactions should be conducted in future. As a conclusion, the membrane permeability was increased with ultrasonic-aided membrane filtration system.

CHAPTER ONE

INTRODUCTION

1.0 Latex wastewater treatment

Latex can be found in nature as milky sap of plants that coagulates when exposed to air. Alternatively, it can be produced synthetically by polymerizing a monomer that has been emulsified with surfactants. The annual production of synthetic latexes/rubbers is close to 12 million tons. Styrene Butadiene Rubber (SBR) is the most common synthetic latex with a global annual consumption of around 2.4 million tons. Common applications for latex are adhesives, paints and sealing.

Nitrile Butadiene Rubber (NBR) is actually a complex family of unsaturated copolymers of acrylonitrile and butadiene. By selecting an elastomer with the appropriate acrylonitrile content in balance with other properties, the rubber compounder can use NBR in a wide variety of application areas requiring oil, fuel, and chemical resistance. On the industrial side NBR finds uses in roll covers, hydraulic hoses, conveyor belting, graphic arts, oil field packers, and seals for all kinds of plumbing and appliance applications. Worldwide consumption of NBR is 368,000 metric tons annually in the year 2005 and the number is expected to grow.

One of the key problems in the latex production is the latex wastewaters form stable emulsions, which are not easily biodegradable and have colouring effects even at low concentrations. An example of conventional method used to treat these streams is coagulation with aluminium sulphate followed by settling, filtration and biological treatment of the waste streams. Usually it is comprises a series of big anaerobic ponds followed by oxidation ponds which requires large area. The Biological Oxygen Demand (BOD_5) of the treated wastewater was much more greater than 20mg/L (the regulation limit is not greater than 20mg/L). This would pollute the public rivers when accidentally or intentionally discharged and the rotten-egg odor of hydrogen sulfide and the mercaptans characteristic from anaerobic ponds annoyed the inhabitants who live close to the factory or may be kilometers away from the factory if were in the wind direction. By changing the anaerobic ponds to aeration ponds, only the bad odor problems was solved but not the BOD_5 of the treated wastewater and the treatment still required large area.

Alternatively, ultrafiltration can be applied to concentrate latex to over 20 wt% and solids. The concentrated latex wastewater can be use as the raw material for latex products. The latex concentration in the permeate can be maintained below 50 ppm which can be recycled as rinse water. Ultrafiltration has been found suitable for concentration of diluted artificial latexes such as polyvinyl chloride (PVC) latex, styrene butadiene rubber (SBR) or acrylnitrile butadiene styrene (ABS).

1.1 Membrane technology

Membrane are commonly refers to a thin, film-like structure that separates two fluids and acts as a selective barrier, allowing some particles or chemicals to pass through, but not others. These can be described by Figure 1.1. Membrane separation technology is used to separate, purify, or enrich some kinds of multicomponent gases or liquids with selective permeability. It is a current "proven technology" within a few main areas, i.e., food and dairy industry, water purification and treatment of liquid fluent streams, and it is presently being introduced into a wide variety of other applications (Maskooki et al., 2010).

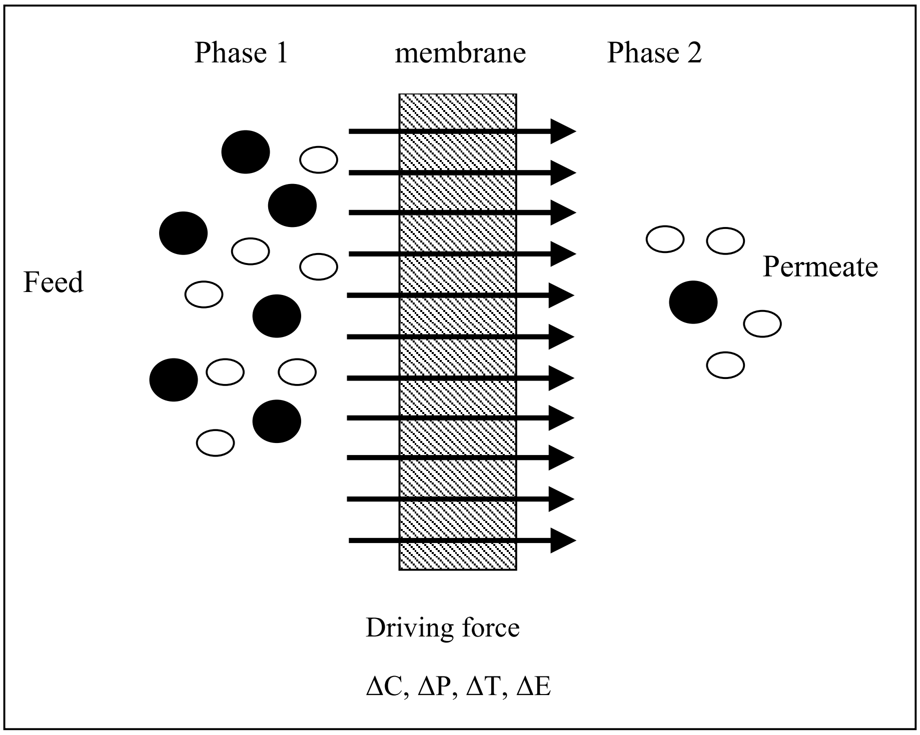

Figure 1.1: Membrane filtration schematic diagram

Membranes are widely used as a flexible, clean and valuable separation processes. Different types of membranes are utilised for the removal of suspended particles and microorganisms in different applications ranging from microfiltration (MF) to reverse osmosis (RO). Each type of membrane is distinguished by its pore size.

Most membrane processes are characterised by two key process parameters, namely, flux and selectivity. Selectivity is controlled by the intrinsic nature of the membrane material and depends on the manufacturing technique. It is calculated using the permeability of the membrane to the species at issue. The flux of a membrane rises with the operating area of the membrane and with the pressure applied. It can be determined using the specific resistance of the membrane material under a given differential pressure across the membrane.

1.2 Problem statement

In practice, there are a number of operational problems that affect the performance of a membrane. These problems involve the resistance to corrosion, membrane mechanical strength, resistance to temperature, feed quality, solid handlings, permeate treatments and energy consumption. The major drawback in membrane processes is flux decline, which results from fouling. Fouling is caused by the deposition of slimy solids, which are present in the feed, on the upstream membrane surface that eventually leads to blocking of the surface. This phenomenon increases operating costs because higher pressures are needed to maintain the permeate flux, time and materials are needed for cleaning of the membrane (Espinasse et al., 2002) and the membrane needs to be replaced (Chen et al., 2006). The drop in flux is normally connected to two phenomena, namely, concentration polarisation and fouling (Kyllönen et al., 2005)

Membrane fouling is due to plugging and adsorption of rejected macromolecules or other substance solutes in porous membranes (Kobayashi et al., 2003). There are several factors that contribute to membrane fouling. Membrane fouling is dependent on the feed suspension properties (e.g. particle size, particle concentration, pH and ionic strength), membrane properties (hydrophobicity, charge and pore size) and hydrodynamics (cross-flow velocity, transmembrane pressure) (Kyllönen et al., 2005). Fouling will results in a continuous drop in the membrane permeation rate, an increased elimination of low molecular weight solutes and the blocking of flow channels. For an ultrafiltration (UF) process, reduction of the membrane permeation rate to 10-30 % that of pure water is common after a few minutes of operation. It is often followed by a more steady decrease. Fouling is partly due to the blocking of the membrane surface or a reduction in the effective diameter of the membrane pores; it is also due to the development of a slowly thickening layer on the membrane surface (J. M. Coulson, 2002).

The problems associated with fouling are commonly reduce by the following main membrane fouling strategies: (1) modification of the membrane material, (2) changing of the hydrodynamic conditions in the flow channel, and (3) application of an external force, e.g. electrical field. (Handbook of Membrane Separations, 2009)

An application of external force by ultrasonic-assisted membrane filtration process has been developed recently. This technology has been extensively used as a method of cleaning materials because of the cavitation phenomenon. It was reported that the permeability enhancement resulted from the acoustic pressure, agitation and micro-current of feed fluid by ultrasound irradiation. Chai et al. found that the increase in permeate flux could be ascribed to the increase in bulk mass transfer in the concentration polarisation layer near the membrane (Chai et al., 1998).

Ultrasound irradiation does not influence the intrinsic permeability of membranes. It increases the flux by breaking the concentration polarisation and cake layer at the membrane surface.

In general, power ultrasound is characterised by an ability to transmit substantial amounts of mechanical power through small mechanical movements. Power ultrasound is a section of sound spectrum from 20 kHz through to around 1 MHz. The passing of ultrasonic waves of a suitably high intensity through liquid and gaseous media is accomplished by primary phenomena such as cavitation, radiation pressure, acoustic streaming; and secondary phenomena of a physicochemical nature such as dispersion, coagulation, and change in liquid properties. In many cases the effect of ultrasound is due to a combination of many effects acting synergistically.

Therefore, membrane fouling problems can be solved by introducing the ultrasound transducer in the membrane separating system . An optimal condition of the filtration process can reduce operating and maintenance cost. Thus, the technique and operation condition are crucial to be studied and identified. The focus of this study is the effect of ultrasonic frequency, ultrasound irradation time, and water bath temperature towards the permeate flux.

1.3 Objectives of research

The objectives of this study are stated as following:

1) To investigate the membrane permeability towards latex wastewater at different ultrasonic frequency, sonication time, and water bath temperature.
2) To characterize the membrane using SEM in order to get the surface characteristic after each sonication procedure.
3) To optimize the ultrasonic-aided cross flow membrane filtration for latex wastewater by using statistical method.

1.4 Organization of the thesis

The thesis comprises of five chapters providing all the details and findings of the research. Chapter one briefly introduces the latex wastewater treatment, membrane technology, problem statement, research objectives and thesis organization.

Chapter two reviews all necessary literatures where it is divided into four sub-chapters. The first sub-chapter contains information on latex wastewater treatment that have been studied or used in the industry. The second sub-chapter focused on membrane separation technique. Third sub-chapter goes for the membrane fouling mechanism and controlled technique. The fourth sub-chapter goes to introduction to ultrasonic cleaning, the mechanism and the factors influence the process. Final sub-chapter for this chapter is focusing on optimization process by using statistical method.

Chapter three is about the methodology applied to run the experiment. All details about the amount and concentration of the chemicals, experimental procedures, analysis, characterization techniques, and equipments used towards the object of study are described.

Chapter four presents the experimental results and discussion. The chapter is basically divided into four sub-chapters. The results and discussion covers the characterization of latex wastewater, membrane selection, and their performance evaluation. Several parameters and their influences on the membrane permeate flux has been investigated. Certain parameter has been studied using cellulose acetate membrane as the subject which is water bath temperature, frequency and sonication time. The optimum conditions are carried forward for the performance evaluation by using the data obtained from the RSM analysis.

The last chapter concludes the findings in the current work with several recommendations for improvement for future work.

CHAPTER TWO

LITERATURE REVIEW

2.0 Latex wastewater treatment

The wastewater from concentrated latex skim crepe industry contains sulfate which comes from sulfuric acid in the skimming process with its concentration ranges between 644 and 1688 mg/l and has the pollutants expressed in term of Biological Oxygen Demand (BOD_5) at the value of about 7000 – 15000 mg/l. The conventional treatment plant of this industry usually comprises the series of big anaerobic ponds followed by oxidation ponds. Instead of the anaerobic ponds, the aeration ponds were used to solve the bad odor problems but this method cannot overcome the BOD_5 of the treated wastewater and large area problems. (V. Thonglimp 2005).

Another example of latex wastewater treatment is by using the activated sludge (AS) system that is one of the biological wastewater treatment process which the organic substances in the wastewater are digested by the aerotrope microorganism suspended in the aeration pond which was aerated by mechanical aerators or air diffuser. The well treated wastewater from aeration pond flow to the sedimentation tank, clear water was overflow at the upper part of the tank and the concentrated microorganism at the bottom, called sludge, is return to the aeration pond in order to control the microorganism concentration in this pond at the design value. The excess sludge was dried in the sand drying bed or further digested in a sludge digester (V. Thonglimp 2005). The schematic diagram of the conventional activated sludge system (CAS) is shown below.

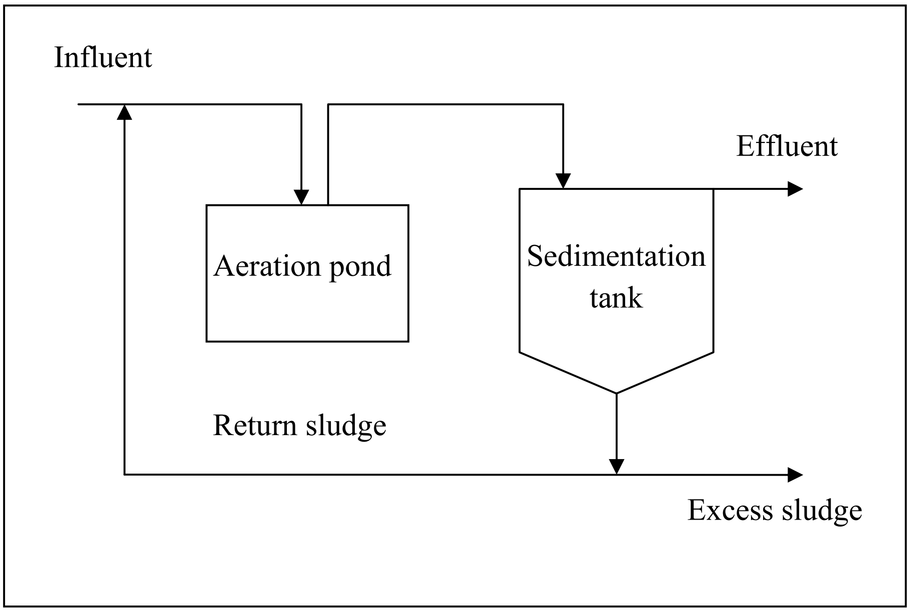

Figure 2.1: The schematic diagram of a CAS

V. Thonglimp et. al. (2005) carried out batch aeration at various food over microorganism (F/M) ratios, hydraulic retention time (HRT), and concentrations of sulfate and calcium. The results showed that the highest BOD_5 and Chemical Oxygen Demand (COD) removal efficiencies were at the $0.4 day^{-1}$ of F/M ratio and longer HRT led to the improvement of the removal efficiencies. The optimum HRT for batch aeration at F/M of $0.4 day^{-1}$ was 12 hours. The BOD_5 and COD removal efficiencies were 98.6 and 89.3 % respectively. The optimum condition in the batch aeration was used in the continuous activated sludge reactor and was run at steady state for two month with the optimum HRT of 2 days. It was found that the average BOD_5 and COD removal efficiencies were 93.24 and 92.37 % respectively (V. Thonglimp 2005).

There are many improvement have been made by researchers for this treatment method in order to increase its efficiency. Jin Anotai et al. (2007) used a series of chemical and biological processes without any addition of acid or base for pH adjustment. The study was conducted to investigate an integrated scheme for rubber thread wastewater using sulfide precipitation followed by anaerobic and aerobic processes. This study shows that the integrated treatment strategy has proven to be an effective treatment for highly polluted and toxic rubber thread wastewater with reduction of BOD value of 99.4%.

Vijayaraghavan et al. (2008) found that the operating optimum conditions were found to be at initial pH 4.5, sodium chlodride content 3% and current density 74.5 mA/cm^2 of latex wastewater. At the end of 90 min electrolysis period for the above operating condition, the treated wastewater had the following characteristic; pH 7.3, COD 78 mg/L, BOD$_5$ 55 mg/L, TOC 45 mg/L, residual total chlorine 136 mg/L, turbidity 17 NTU and temperature 54˚C. During the electrochemical oxidation process, the latex wastewater undergoes in-situ disinfection due to the generated hypochlorous acid, where it was generated using a graphite rod as the anod and stainless sheet as the cathode in an undivided electrolytic reactor. Furthermore, the excess chlorine concentration can be reduced either by storing the treated wastewater in a holding tank or by the addition of bisulfate.

For treatment of skim serum effluent from natural rubber latex centrifuging units, biochemical analysis revealed that electrolysis in the present of Fenton's reagent is effective in removing soluble protein, phenols and sugars especially from anaerobically treated effluent (Abraham et al., 2009). In this study, the result of microbiology analysis showed the complete removal of total bacteria by 20 min electrolysis in the present of Fenton's reagent. It is also proven that the electrochemical treatment is a simple method and at the same time ensures rapid processing since it takes only 30 to 45 min for treatment compared to conventional biological treatment like activated sludge (AS) process and other aerobic oxidation method. It removes very fine colloidal particles through coagulation and the quantity of the sludge generated and water bound to the sludge is less and therefore easy for dewatering. The use of solar energy for electrolysis with the help of photovoltaic cells is one of the advantages for this method as it can be applied in rural areas too. It will reduce the running cost of the treatment process instead using electricity as the main supply power.

Alternatively, membrane filtration could become a method for isolating value added product from latex wastewater and discharging minimal amount of effluent, thus making latex processing an environmental friendly process. This process could achieve 'zero discharge' as all the products from the concentration process have commercial value (Veerasamy et al., 2009). The retentate can be used as part of latex product's raw material while the permeate water can be used as rinse proposes.

2.1 Membrane separation

There are several types of membrane processes that can be considered in separation processes which are reverse osmosis, nanofiltration, ultrafiltration and microfiltration. The summary of these four processes can be described from Table 2.1. There are two different modes of operation in membrane filtration methods which are cross flow and dead end filtration. Both of these modes differ from each other at the point of the direction of feed water flow, in relation to the membrane surface (Michael Pilutti, 2003). In a dead end filtration system, the feed water effectively contacts the membrane surface at a perpendicular angle. On the other hand, feed water in a cross flow system flows parallel to the membrane surface. These two modes may experience differences in fouling rate, flux and recovery, and finished water quality.

Table 2.1: Summary of membrane filtration methods (Wagner, 2001)

	Reverse osmosis	**Nanofiltration**	**Ultrafiltration**	**Microfiltration**
Membrane	Asymmetrical	Asymmetrical	Asymmetrical	Symmetrical Asymmetrical
Thickness	150 µm	150 µm	150 250 µm	10 – 150 µm
Thin film	1 µm	1 µm	1 µm	
Pore size	0.0001 – 0.001 µm	0.001-0.01 µm	0.1 – 0.005 µm	0.1 – 10 µm
Rejection particles	HMWC, LMWC, sodium chloride, glucose, amino acids	HMWC, mono-, di, and oligosaccharides, polyvalent neg. ions	Macromolecules, proteins, polysaccharides, viral	Particles, clay, bacteria
Membrane material(s)	Cellulose Acetate (CA), Thin film	CA, Thin film	Ceramic, Polysulfone (PSO), Polyvinylidene fluoride (PVDF), CA, Thin film	Ceramic, Polypropelene (PP), PSO, PVDF
Membrane module	Tubular, spiral wound, plate-and-frame	Tubular, spiral wound, plate-and-frame	Tubular, hollow fiber, spiral wound, plate-and-frame	Tubular, hollow fiber
Operating pressure	15-150 bar	5-35 bar	1-10 bar	<2 bar

In order to get the optimal separation to occur, the correct process has to be selected. All the criteria in Table 2.1 are crucial and need to be considered before the separation process are chosen. There are other factors that contributed to the optimization of the separation process such as the feed quality, membrane properties and fouling control system. Membrane fouling is the most crucial problem. It has to be put into a full attention as it cost lots of money and energy in order to overcome this problem.

2.1.1 Membrane characteristic

Membranes can be manufactures in a wide variety of materials. These materials differ in their performance characteristics including mechanical strength, fouling resistance, hydrophobicity, hydrophilicity, and chemical tolerance. For the perspective of hydrophobicity and hydrophilicity of the membrane, hydrophilic membranes tends to exhibit greater fouling resistance than hydrophobic membranes. Hydrophobic particles such as latex particles tend to cluster or group together to form colloidal particles because this lowers the interfacial free energy due to surface area exposure. To prevent fouling, a membrane requires a surface chemistry which prefers binding to water over other materials. This implies that the material must be very hydrophilic. From the Table 2.2 below, the calculated of some polymeric materials are shown. Higher surface tension of a material presents higher hydrophilicity.

Table 2.2: Calculated surface tension of some polymeric materials (Michael Pilutti, 2003)

Chemical name	Surface tension (dynes/cm)
Polytetrafluoroethelyne (Teflon)	18
Polyvinylidene Fluoride	25
Polypropylene	29
Poly Vinyl Chloride	39
Polysulfone	41
Polycarbonate	42
Polyacrylonitrile	44
Cellulose	44

Despite the pore size and membrane morphology, the degree of hydrophilicity or hydrophobicity influences the wettability and applied pressure requirements for water flow through the membrane. There is wide variety of materials that available in the markets that vary chemical and mechanical properties including mechanical strength, burst pressure, oxidant tolerance, VOC tolerance, pH operating range, and so forth (Michael Pilutti, 2003). The membrane selection is crucial. Thus, compatible material with raw water quality, pretreatment requirements, and other operating conditions is important. There are several example of the material construction for membrane such as polypropylene, polyethersulfone, polysulfone, cellulose derivative and many others.

2.2 Membrane fouling

Membrane fouling is due to plugging and adsorption of rejected macromolecules or other solutes substance in porous membranes (Kobayashi et al., 2003). There are several factors that contribute to membrane fouling. Membrane fouling is affected by the factor of the feed suspension properties (e.g. particle size, particle concentration, pH and ionic strength), membrane properties (hydrophobicity, charge and pore size) and hydrodynamics (cross-flow velocity, transmembrane pressure) (Kyllönen et al., 2005). Fouling will cause a continuous drop in the membrane permeation rate, an increased elimination of low molecular weight solutes and the blocking of flow channels. For an ultrafiltration (UF) process, reduction of the membrane permeation rate to 10-30 % that of pure water is common after a few minutes of operation. It is often followed by a more steady decrease. Fouling is partly due to the blocking of the membrane surface or a reduction in the effective diameter of the membrane pores; it is also due to the development of a slowly thickening layer on the membrane surface (J. M. Coulson, 2002).

In MF/UF fouling mainly occurs on porous membranes that are implicitly susceptible to fouling are used. On the other hand, with dense membrane used in pervaporation and gas separation, fouling is practically absent. Therefore, pressure driven processes will be emphasised. In such processes, the nature of the separation problem and the type of membrane used also determine the extent of fouling. Roughly, three types of foulant can be distinguished:

- Organic precipitates (e.g., macromolecules and biological substances)
- Inorganic precipitates (e.g., metal hydroxides and calcium salts)
- Particulates

The occurrence of fouling is very difficult and complicated to describe theoretically. Even for a given solution, fouling will depend on physical and chemical parameters such as concentration, temperature, pH, ionic strength and specific interactions (hydrogen bonding, dipole-dipole interaction). However, reliable values of flux decline are necessary for process design. Flux may also be described by a resistances-in-series model, in which a resistance of a cake layer is in series with the membrane resistance (Mulder, 1997).

To minimise the fouling problem that occurs in the membrane filtration system, several techniques can be applied. These techniques can be divided into two sections: controlling methods and cleaning methods. In controlling method, there are several techniques that have been used by researchers such as feed pretreatment (Williams and Wakeman, 2000), membrane material selection (Goosen et al., 2004) and membrane surface modification(Flemming and Schaule, 1988; Jenkins and Tanner, 1998). For cleaning methods, it includes chemical (Lim and Bai, 2003), mechanical and hydrodynamic (turbulent promoters (Xu et al., 2003; Auddy et al., 2004), backfulshing, plushing, shocking (Sondhi et al., 2000), pulsatile flow (Gupta et al., 1993; Howell et al., 1993), gas sparging (Youravong et al.), electrical (Ahmad and Ibrahim, 2002; Handbook of Membrane Separations, 2009) and ultrasonic cleaning (Chai et al., 1998)) cleaning.

2.2.1 Mechanism of membrane fouling

Understanding the membrane fouling mechanism is important for the development of new approaches that counter or minimise it and maintain high system performance (Handbook of Environmental Engineering, 2007). A flux decline in membrane filtration results from the increase of the membrane resistance and the development of another resistance layer, which are related to pore blockage and cake formation, respectively (Song, 1998). The permeate flux decreases with time as retained particles build up on and within the membrane. Accumulation of discarded particles on the top surface of the membrane occurs and leads to external fouling or cake formation. This accumulation is usually reversible. On the other hand, deposition and adsorption of small particles within the internal pore structure of the membrane (internal fouling) is often irreversible. These additional resistances lead to a flux decline in membrane filtration (Song, 1998; Williams and Wakeman, 2000). Colloidal fouling is caused by accumulation of particles and macromolecules on, in and near the membrane. Materials accumulated on the membrane surface create an additional layer of resistance to permeation. Larger particles tend to be swept away in bulk flow rather than deposit on the membrane surface. In addition to surface deposition, some particles may be small enough to penetrate and remain within the pores of the membrane. Figure 2.2 explained the concentration polarisation phenomenon.

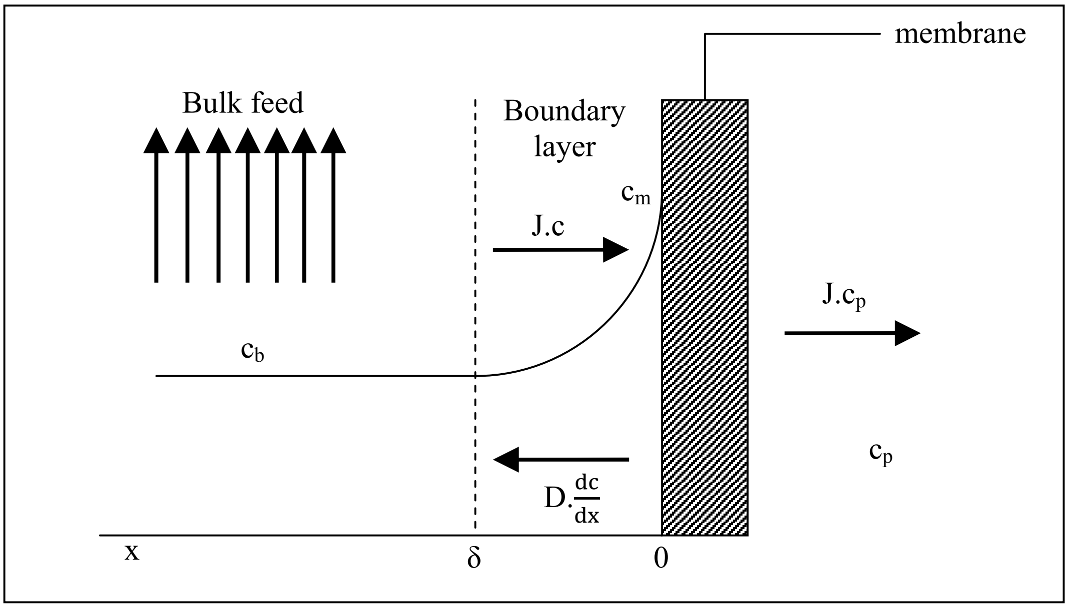

Figure 2.2: concentration polarisation; concentration profile under steady-state conditions (Mulder, 1996)

Other factors, such as solute adsorption, particle deposition within the membrane pores and characteristic changes of the cake layer, can affect membrane fouling by enhancing or modifying cake formation and pore blockage. Among various types of membrane foulants, inorganic colloidal particles are one of the particular interest (Zhu and Elimelech, 1997) because they are small enough to pass through most pretreatment systems and can thus block membrane pores or form a compact cake layer on the membrane surface (Chen et al., 2006).

As shown in Figure 2.3, a typical flux-time curve of UF and MF starts with a rapid initial slump (I) from the flux of pure water filtration. It is followed by a long steady flux decrease (II) and ends with a steady-state flux (III). Stage II occurs in all membrane fouling processes regardless of the operating conditions. Stages I and III may not be observed in some experiments. For instance, a steady-state flux can only be attained after a long operation time if the pressure is sufficiently high and the feed concentration is sufficiently low. It will not be observed if the experiment is stopped before the steady state is reached (Song, 1998). There are several techniques that can be performed in order to control the membrane fouling phenomena. These methods can usually reduce the fouling from the perspective of the chances of the membrane to foul.

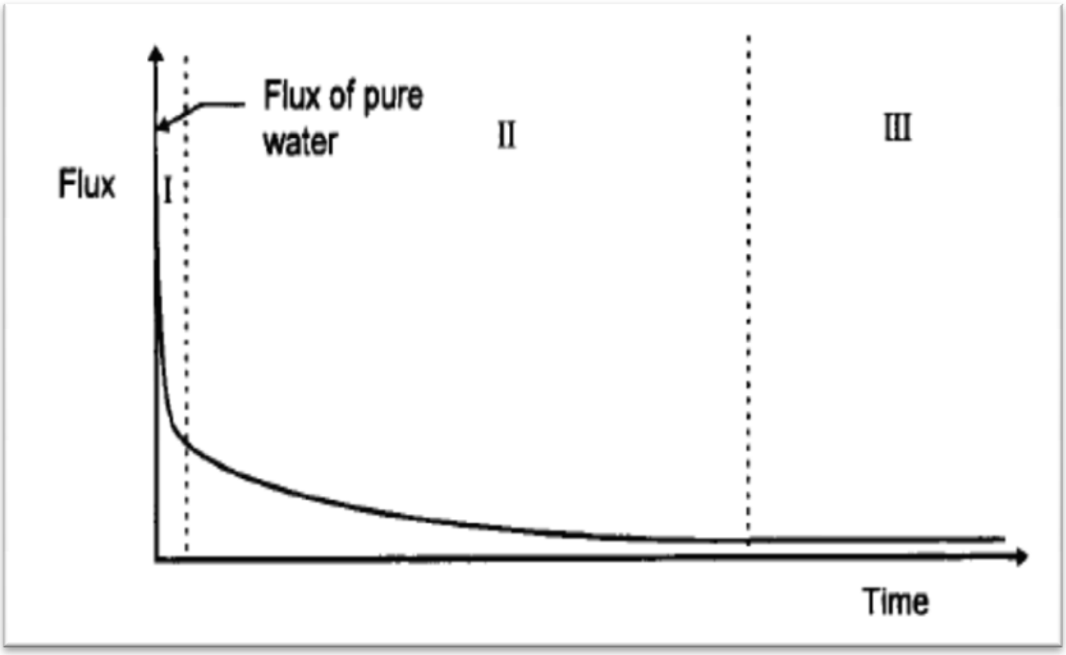

Figure 2.3: A schematic presentation of three stages in flux decline. (I) initial quick drop from the flux of pure water filtration; (II) long term steady flux decline; and (III) time dependent steady state flux (Song, 1998)

2.3 Ultrasonic cleaning

An ultrasonic-assisted membrane filtration process has been developed recently (Cai et al., 2010; Popovic et al., 2010; Ahmad et al., 2012; Mirzaie and Mohammadi, 2012). This technology has been extensively used as a method of cleaning materials because of the cavitation phenomenon (Masselin et al., 2001). It was reported that the permeability enhancement resulted from the acoustic pressure, agitation and micro-current of feed fluid by ultrasound irradiation. Chai et al. (1998) found that the increase in permeate flux could be ascribed to the increase in bulk mass transfer in the concentration polarisation layer near the membrane. This cleaning procedure will be further discussed in the next section.

2.3.1 Mechanism of ultrasonic waves

Similarly to sound waves, ultrasounds are spread by a series of compression and rarefaction (decompression) waves stimulated in the molecules of the medium through which it passes (Ahmad et al., 2012). The rarefaction cycle may exceed the repulsive forces of the liquid molecules, and cavitation bubbles (empty, gas and/ or vapour-filled bubbles) will form with an adequately high power (Kyllönen et al., 2005). Cavitation bubbles are formed when the pressure amplitude exceeds the tensile strength of liquid during the rarefaction of sound waves (Chen et al., 2006). This cavity may dissipate back into the liquid, grow to a resonant size and fluctuate about this size or grow to a size at which the surface tension forces of the liquid cause it to collapse on itself (Lamminen et al., 2004). Bubble dissolution is important because a bubble must be present in the system for the cavitation to occur. If dissolution occurs, bioeffects caused by cavitation will not be a concern.

In aqueous systems, the collapse of the cavitation bubble has important mechanical and chemical effects. Each cavitation bubble acts as a contained "hot spot" that engendered temperatures of about 4000-6000 K and pressures of 100-200 MPa at the bubble core (Yasui et al., 2002; Ashokkumar and Grieser, 2005). These high temperatures and pressures dissociates water into hydrogen atoms ($H^{\bullet}$) and hydroxyl radicals ($OH^{\bullet}$). The implosions occur with lifetimes of < 10 μs (Lickiss, 1994). The most effective bubble collapse arises at a bubble size of several micrometers. The cavitation threshold is the level of energy that is necessary to reach cavitation. These processes result in fluid movement and may be able to remove parts of the foulant layer from the membrane surface and/or avoid the deposition of particles that lead to membrane fouling.

Cavitational collapse also produces a number of phenomena that result in high velocity fluid movement. Proposed mechanisms for particle removal and detachment observed with ultrasonic cleaning are illustrated in Figure 2.4.

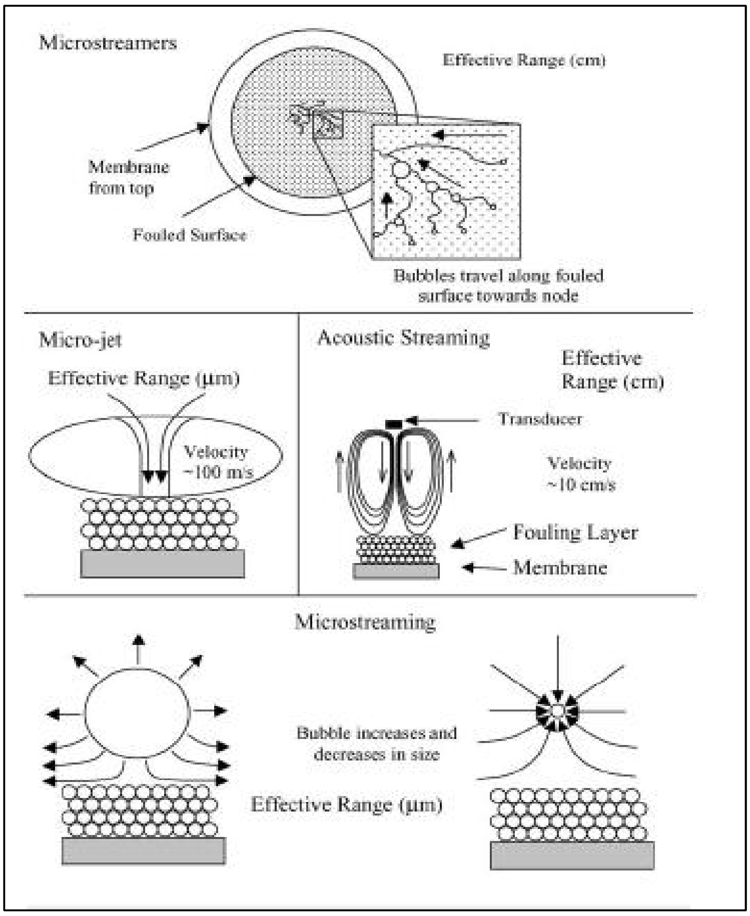

Figure 2.4: Possible mechanism for particle removal/detachment observed with ultrasonic cleaning (Lamminen et al., 2004).

Acoustic streaming is part of the detachment process. It is defined as the adsorption of acoustic energy resulting in fluid flow and does not require the collapse bubbles. Higher frequency ultrasound tends to have higher energy absorption and thus greater acoustic streaming flowrates than lower frequencies for the same power intensities. Furthermore, higher power intensities lead to greater acoustic streaming flowrates due to higher energy gradients in solution between acoustically and non-acoustically stimulated areas. These may scour the particles from the membrane surface.

Microstreaming is a time dependent circulation of fluid occurring in the vicinity of bubbles set into motion by oscillating sound pressure. It is occur when a microbubble, surrounded by a liquid media, undergoes direct oscillatory action when exposed to ultrasound. Oscillatory action causes rapid, toroidal eddy currents to form as a result of the displacement of liquid around the bubble. These eddying currents decrease in size as the ultrasonic frequency is increased; that is, less microstreaming occurs at higher frequencies. Therefore, it is consequence of low-frequency, low-pressure response to oscillations of microbubbles.

Microstreamers is the action of the cavitation bubbles that form at the nucleation sites within the liquid and are subsequently translated to a mutual location (antinodes)(Lamminen et al., 2004). The bubbles travel in ribbon like structures along tortuous paths at velocities approximately an order of magnitude faster than average velocity of the fluid (Luther et al., 2001), coalescing as they collide with other bubbles. The migration of the bubbles is caused by the Bjerkness force existing between pulsating bubbles in a pressure field (Laborde et al., 1998). Thus, these may result in bubbles scouring away the particles while translating to these antinodes. These streamers have an effective range on the order of millimetres (Luther et al., 2001).

A liquid jet is created and targeted at the surface, i.e., a membrane surface, when a collapse near it produces a nonsymmetrical inrush of fluid to fill the void. In addition to these phenomena, there are other mechanisms that may lead to particle release from a fouled surface as a result of ultrasound irradiation.

Lamminen et al. studied the cleaning of fouled ceramic membranes in a dead-end filtration cell (Lamminen et al., 2004). According to them, the cavitational mechanisms, i.e. microstreaming, and microparticles played a significant role in detaching particles from the membrane surface, while turbulence linked with ultrasound, i.e., acoustic streaming, was important for the transport of particles away from the surface after detachment, especially in dead-end filtration. In addition, there is a divergence in the literature regarding the integrity of membranes following exposure to ultrasound. Masselin et al. observed damage to polyethersulfone membranes by ultrasound (2001), while other researchers (Chai et al., 1998; Li et al., 2002; Muthukumaran et al., 2004; Muthukumaran et al., 2005; Chen et al., 2006; Chen et al., 2006) showed that the integrity of membranes was maintained during sonication. The integrity of membranes during sonication is of critical importance for the practical application of this technology to membrane fouling control.