TREATMENT OF INDUSTRIAL DETERGENT WASTEWATER VIA MEMBRANE SEPARATION

BAHRUN BIN MOHD SHAKIR

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Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang

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ABSTRACT

This thesis presents the experimental study of the potential of Nanofiltration membrane in treating industrial detergent wastewater that contains high Linear Alkylbenzene Sulfonate (LAS). LAS is the most common synthetic anionic surfactant used in domestic and industrial detergents and can cause significant environmental problems. This study was focused on treated wastewater sample from FPG Oleochemical Sdb Bhd based on decreasing the parameters so it can comply with the regulation of Environment Quality Act (EQA), 1974 before it can release to discharge. LAS, Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), Total Suspended Solid (TSS) and Turbidity were used as a parameters used in this study. The Polyamide Nanofiltration membrane performance was characterized by varying the Trans Membrane Pressure (TMP) 3, 4, 5 and 6 bars. The results showed that the optimum operating condition of the Nanofiltration membrane was achieved at TMP 6 bar. The removal percentage of the parameters is high which is more than 88%. However, only the Turbidity and TSS has achieved the EQA regulation. It is concluded that the wastewater from the production of Dynamo in FPG Oleochemical Sdn Bhd can be fully treated by using Nanofiltration membrane in addition some pre treatment or further treatment.

ABSTRAK

Tesis ini menyajikan kajian eksperimental potensi Nanofiltrasi membran dalam mengolah sisa cair industri yang mengandungi detergen Linear Alkylbenzene Sulfonate (LAS). LAS adalah surfaktan anionik sintetik yang paling biasa digunakan dalam industri detergen dan domestik dan ia boleh menyebabkan masalah persekitaran yang signifikan. Penelitian ini difokuskan pada perawatan sampel air sisa dari FPG Oleochemical SDB Bhd berdasarkan penurunan parameter sehingga dapat memenuhi syarat-syarat Environmental Quality Act (EQA), 1974 sebelum dilepaskan. LAS, Chemical Oksigen Demand (COD), Total Organic Carbon (TOC), Total Suspended Solid (TSS) dan Turbidity dijadikan sebagai parameter yang digunakan dalam kajian ini. Prestasi Polyamide Nanofiltrasi membran diuji dengan memvariasikan Trans Membran Pressure (TMP) 3, 4, 5 dan 6 Bar. Keputusan kajian menunjukkan bahawa keadaan operasi optimum membran Nanofiltrasi ialah pada TMP 6 Bar. Peratusan penghapusan parameter adalah tinggi iaitu melebihi 88%. Namun, hanya Turbidity dan TSS mencapai kehendak peraturan EQA. Dapat disimpulkan bahawa air sisa hasil daripada pengeluaran Dynamo di FPG Oleochemical Sdn Bhd boleh sepenuhnya dirawat dengan menggunakan membran Nanofiltrasi denagan kombinasi beberapa rawatan pra atau rawatan tambahan.

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CHAPTER 1

INTRODUCTION

1.1 Background

Increased water consumption for both industrial and domestic purposes has led to a shortage of good quality surface and groundwater resources and to an increase in the costs of water and wastewater treatment. As a consequence of this shortage it would be prudent for any rational water management authority to secure the purest water sources for direct human consumption and to encourage the reuse of processed water for industrial applications (Rozi *et al*., 1999). Environmental risks associated with detergent manufacture, its use and disposal are of great concern due to the relative toxicity of detergent products and its core ingredients (surfactants) on aquatic life (Lin *et al*., 1999). Surfactants have also been widely used in textile, fiber, food, paints, polymers, plant protection, cosmetics, pharmaceuticals as well as mining, pulp and paper industries (Lin *et al*., 1999). Among wide range of surfactant types, linear alkylbenzene sulfonate (LAS) is the most common synthetic anionic surfactant used in domestic and industrial detergents. The majority of detergent products reach the environment with domestic and industrial wastewater. The high and varied pollution loads of these effluents are mainly due to the residual products in the reactor, which have to be washed away in order to use the same facility for the manufacture of other products. Detergent solution can cause significant environmental problems because detergent product and its ingredients can be relatively toxic to aquatic life. That’s why the detergent solution needs to be treated before release to discharge.

In this study, the wastewater sample is the excess solution from the batch process on production of liquid detergent Dynamo. Basically, this detergent solution contains very high LAS. This study was focused on treated this wastewater sample based on decreasing the parameters so it can comply with the regulation of environment quality act, 1974 before it can release to discharge. This wastewater sample is treated using membrane separation process. The membrane use is Turbular Nanofiltration membrane. This method will reduce the anionic surfactant and also the Chemical Oxygen Demand (COD) in the detergent solution. The LAS is the main parameter in this study. Besides the LAS and COD, the Nanofiltration membrane also can remove the viruses, bacteria and the suspended solid.

The type of Turbular Nanofiltration used in this study is Polyamide membrane with dimension 4 inch D x 4ft L. This process will reduce the COD contain in the solution and also can remove the heavy metal and solid that a common use in wastewater treatment. Table 1.1 below shows the detail characteristics of Nanofiltration membrane use.

Table 1.1: Characteristics of Nanofiltration membrane used

Make	PCI – Memtech (UK)
Type	AFC 40 Membrane
Material	Polyamide
Housing	SS 316
Max pH range	1.5 – 9.5
Max Pressure	60 bar
Retention character	60% $CaCl_2$
Dimension	4” D x 4ft L

1.2 Problem Statement

The wastes that have been produced need to be treated before discharge to prevent our environmental from pollution. Untreated waste may damage our environment and also present serious hazard to human and other living thing. The wastewater in this study is the linear alkylbenzene sulfonate (LAS), commonly used in the formulation of detergents and present in industrial wastewaters. The detergent solutions that contain high LAS are harmful to environment if they are not fully treated before discharge. To solve this problem, the wastewater needs to be treated before it is allowed for release to the drainage system. This work aim to evaluate the performance of Nanofiltration membrane for treating LAS contaminated wastewater from FPG Oleochmical Sdn Bhd.

1.3 Objective

The objective of this project is to evaluate the effectiveness of Nanofiltration membrane in treating the LAS contaminated wastewater from FPG Oleochemical Sdn Bhd.

1.4 Scope of Study

To achieve the objective of this project, the treated and untreated wastewater needs to be characterized. Besides that, the membrane performance is also studied by analyzing it surfactant retention and the permeate flux. The factor that affects the surfactant retention and permeates flux is the Trans membrane pressure (TMP), the crossfow velocity and the surfactant concentration. Therefore, optimum operating condition of the membrane may be obtained by varying the TMP.

1.5 Outline of This Thesis

The main part of this thesis is the experimental studies of Nanofiltration membrane treatment. The experimental part is explained in chapters 3 and 4. A schematic of the thesis outline is presented in Figure 1.1

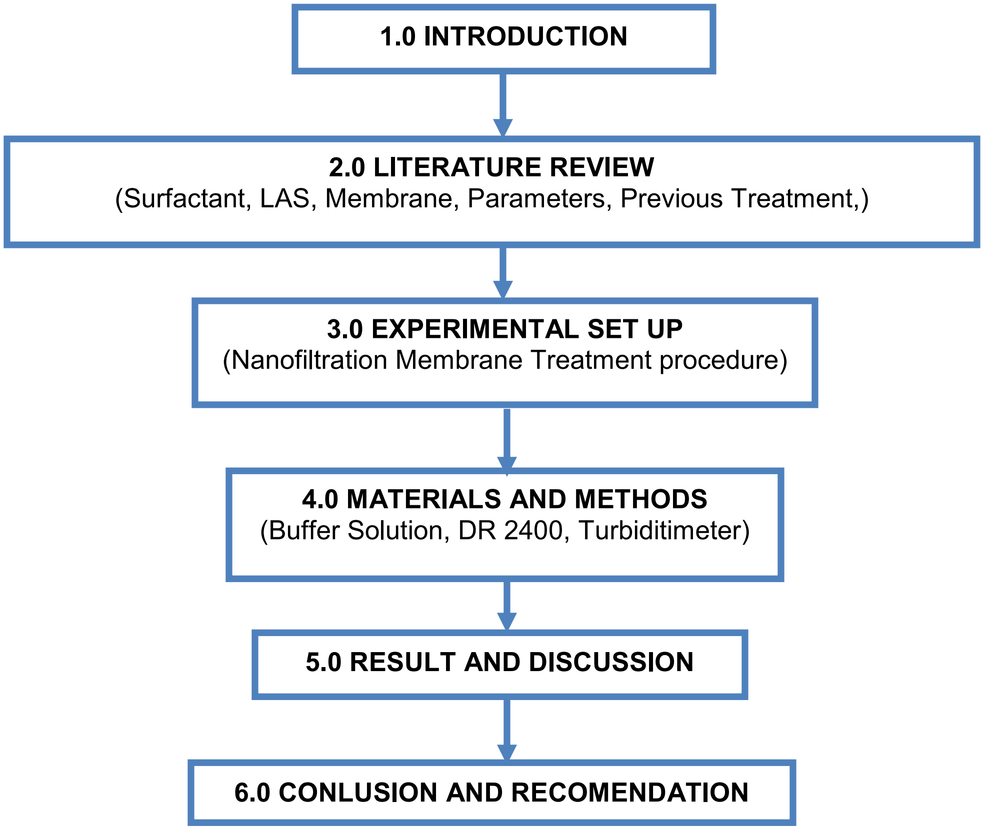


Figure1.1: Road Map for the Thesis

CHAPTER 2

LITERATURE REVIEW

2.1 What is surfactant?

Surfactant is an abbreviation for surface active agent, which literally means active at a surface (Porter, 1994). Surface active agents are compounds having a hydrophobic and a hydrophilic group (Falbe, 1987) and, hence, they show a tendency to adsorb at liquid/solid, liquid/liquid and air/liquid interfaces. They are mainly used in aqueous solutions and are classified according its hydrophilic group in anionic, cationic, nonionic, and amphoteric surfactants. Due to their chemical structure, surfactants are strongly adsorbed at an interface or they form colloid aggregates in solution at very low concentrations, lowering the interfacial tension. Surfactants have found many industrial applications, such as detergency, wetting, cleaning, emulsification, foam control and lubricity in industrial systems (Chen *et al*., 1992). Some novel separation techniques using biodegradable surfactants (such as colloid-enhanced ultrafiltration, admicellar chromatography and surfactant-enhanced carbon regeneration) are also used in wastewater cleanup and groundwater remediation (Canselier *et al.,* 1995). The worldwide surfactant consumption was of the order of 10.4M tons in year 2000 (Crabb *et al* 1999) and consequently large amounts are discharged into the environment. Therefore, the treatment of effluent streams containing surfactants is an important issue, either for environmental or economic reasons.

2.2 Linear alkylbenzene sulfonate

LAS are produced by sulfonation of linear alkylbenzene with sulfur trioxide. LAS is a mixture of closely related isomers and homologues, each containing an aromatic ring sulfonated at the *para* position and attached to a linear alkyl chain with the length which varies between C_{10} and C_{14} (Dealmedia *et al.*, 1994). Detergents usually contain 5 - 25 % of LAS. From the environmental point of view, it is the major anthropogenic source of organic compounds in primary sludge of the municipal wastewater treatment plants. It can be adsorbed onto suspended solids ranging from 30 to 70 % and, hence, escaping aerobic treatment (www.heraproject.com). It has also been identified in surface water supplies in the concentrations lower than 1 µg dm^{-3} (Berna *et al.*, 1989), and in the drinking water with the concentrations of 0.001 - 0.008 mg dm^{-3} (Delmedia *et al.*, 1994). It has been reported that LAS at higher concentrations, between 20 and 50 mg dm^{-3}, such as in detergent manufacturing wastewaters, is not biodegradable (Tabrizi *et al.*, 2006). It is implied that some of chemical processes need to be used to degrade aqueous LAS.

2.3 Membrane

Membrane systems have been used in specialized 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. The demand for membranes in the water and wastewater industry is projected to increase at a 9% annual rate and reach $540 million by year 2000. About two-thirds of the market will be for water, and one-third for wastewater. Membrane technologies are receiving special recognition as alternatives to conventional water treatment and as a means of polishing treated wastewater effluent for reuse applications. Membrane technologies are energy intensive.

New membrane technologies feature the use of low pressure systems that significantly reduce energy use and operation and maintenance costs. Membranes are commonly used for the removal of dissolved solids, color, and hardness in drinking water.

2.3.1 Membrane Separation

Membrane technology utilizes a semi permeable membrane for the separation of suspended and dissolved solids from water. There are two basic types of membrane separation processes; pressure-driven and electrically-driven. A comparison of their features is given in Table 2.1. Pressure-driven processes use hydraulic pressure to force water molecules through the membranes. Impurities are retained and concentrate in the feed water, which becomes the reject water or concentrate stream. The permeate, the water that passes through the membrane, is recovered as product or pure water. In the electrically-driven membrane process, electric current is used to move ions across the membrane, leaving purified water behind. In this process, the ions are collected in the concentrate stream for disposal. The product water is the purified feed water.

Table 2.1: Comparison of Membrane Features

	Pressure-driven membrane	**Electrically-driven membrane**
Matter crossing membrane	water	Ion
Matter removed from water	Inorganic, most organics, silica, suspended solids, and microorganisms	Ion only
Matter not removed	Gases	Gases, silica, organics. and suspended solids

2.3.2 Pressure Driven Membrane

Membranes are made of several materials in several configurations and they can be thought as a kind of filter under certain pressure. The most important duty of a membrane is to act as a selective barrier (Cheryan. 1998). Membrane filters are usually used to separate the compounds of dimensions smaller than 10 micrometer from the liquor. The flow on the membrane surface is in two directions; parallel to the membrane axis and in a radial direction (cross-flow). Particles having greater dimensions than the membrane pores are held-back on the surface of the membrane and carried out by the parallel flow and collected as concentrate. Particles having smaller molecular sizes than the membrane pores pass through the membrane with the cross-flow and collected as permeate. Consequently, the molecules in the liquor are separated physically according to their molecular dimensions (Dickenson, 1997). The most popular membrane processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) which separates the compounds in the liquor according to molecular dimensions under hydrostatic pressure. Figure 2.1 illustrates the separating action according to the pore size.

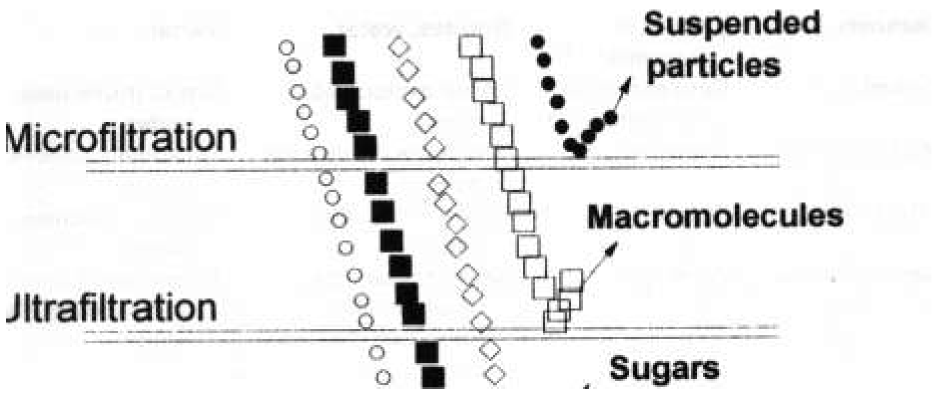
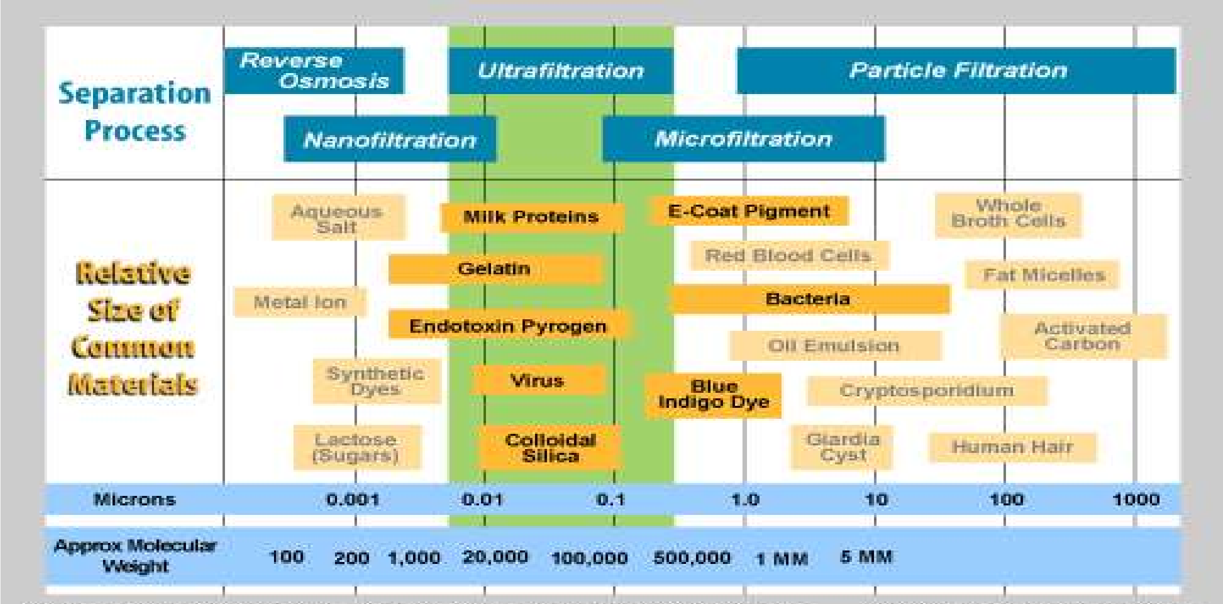


Figure 2.1: The separation of the membranes according to their pore dimensions (Cheryan, 1998)

The range of sizes of selected constituents in water and wastewater and the performance capabilities of the different membranes are illustrated in Figure 2.2. MF and UF often serve to remove large organic molecules, large colloidal particles, and many microorganisms (see Table 2.2). MF performs as a porous barrier to reduce turbidity and some types of colloidal suspensions. UF offers higher removals than MF, but operates at higher pressures. In wastewater reclamation, MF UF might provide a suitable level of treatment. In drinking-water treatment, MF or UF might be used in tandem with NF or RO to remove coarser material so that fouling of the less permeable membranes is minimized.



Note: 1 micron (micrometer) = 4 x 10-5 inches = 1 x 104 Angstrom units

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Figure 2.2: Filtration spectrum

a. Microfiltration Membrane

Microfiltration membranes remove all bacteria. Only part of the viral contamination is caught up in the process, even though viruses are smaller than the pores of a micro filtration membrane. This is because viruses can attach themselves to bacterial biofilm. Micro filtration can be implemented in many different water treatment processes when particles with a diameter greater than 0.1 mm need to be removed from a liquid. Membranes with a pore size of 0.1 – 10 µm perform micro filtration. (www.lenntech.com)

b. Ultrafiltration Membrane

Ultrafiltration or UF is a pressure driven membrane separation process that separates particulate matter from soluble components in the carrier fluid (such as water). UF membranes typically have a high removal capability for bacteria and most viruses, colloids and silt (SDI). The smaller the nominal pore size, the higher the removal capability. Most materials that are used in UF are polymeric and are naturally hydrophobic. Common polymeric materials used in UF include: Polysulfone (PS), Polyethersulfone (PES), Polypropylene (PP), or Polyvinylidenefluoride (PVDF). Although these materials can be blended with hydrophilic agents, they can reduce the membranes ability to be cleaned with high strength disinfectants such as hypochlorite that impacts removal of bacterial growth.

c. Nanofiltration Membrane

Nanofiltration is a liquid separation membrane technology positioned between reverse osmosis (RO) and ultrafiltration. While RO can remove the smallest of solute molecules, in the range of 0.0001 micron in diameter and smaller, nanofiltration (NF) removes molecules in the 0.001 micron range. NF refers to a membrane process that rejects solutes approximately 1 nanometer (10 angstroms) in size with molecular weights above 200. Because they feature pore sizes larger than RO membranes, NF membranes remove organic compounds and selected salts at lower pressures than RO systems. NF essentially is a lower-pressure version of RO where the purity of product water is not as critical as with pharmaceutical grade water, or the level of dissolved solids to be removed is less than what typically is encountered in brackish water or seawater. (www.wwdmag.com)

d. Reverse Osmosis Membrane

Reverse osmosis is a filtration process that is often used for water. It works by using pressure to force a solution through a membrane, retaining the solute on one side and allowing the pure solvent to pass to the other side. Liquid phase pressure-driven separation process in which applied transmembrane pressure causes selective movement of solvent against its osmotic pressure difference (Koros et al., 1996). This is the reverse of the normal osmosis process, which is the natural movement of solvent from an area of low solute concentration, through a membrane, to an area of high solute concentration when no external pressure is applied.

Table 2.2: Comparison of Pressure driven Membrane Systems

PARAMETERS	Membrane System			
	MF	UF	NF	RO
Product particle size, pm	0.008 to 2.0	0.005 to 0.2	0.001 to 0.01	0.0001to 0.001
Retained compounds Operating	Very small suspended particles, some colloids, most bacteria	Organics >l000 MW, pyrogens, viruses, bacteria, colloids	Organics > 300 MW, THM Precursors, some dissolved solid, divalent > monovalent	Ion, Organic > 100 MW

Pressure, psi	1 to 15	10 to 100	80 to 125	125 to 1000
Maximum temperature, "F ("C)	80 (27)	80 (27)	80 (27)	100 (38)
Recovery rate, %	100	75	85	50-85

2.3.3 Electrically Driven Membrane

Electro dialysis reversal (EDR) is an improvement over the original electro dialysis process. In EDR, the direct-current driving force is periodically reversed to prevent scaling and fouling of the membrane surface. This innovation improves both the efficiency and the operating life of membranes. Ion exchange membranes are the heart of the process. Cation-selective and anion-selective membranes are alternately placed in a membrane “stack”. Water flows between the membranes, and when direct current is applied across the stack, positive Ions move toward the cathode and negative ions move toward the anode. Due to the alternating membranes, salt is removed from every other compartment and collected in intervening compartments. The salt-laden water is then discharged as a brine concentrate; desalted water is discharged to the purified-water collection system.

2.4 Cross Flow System

Crossflow filtration also known as tangential flow filtration (Millipore Technical Library) is a type of filtration. Crossflow filtration is different from dead-end filtration in which the feed is passed through a membrane or bed, the solids being trapped in the filter and the filtrate being released at the other end. Cross-flow filtration gets its name because the majority of the feed flow travels tangentially *across* the surface of the filter, rather than into the filter (Koros et al., 1996). The principle advantage of this is that the filter cake (which can blind the filter) is substantially washed away during the filtration process, increasing the length of time that a filter unit can be operational. It can be a continuous process, unlike batch-wise dead-end filtration. This type of filtration is typically selected for feeds containing a high proportion of small particle size solids (where permeate is of most value) because solid material can quickly block (blind) the filter surface with dead-end filtration. Industrial examples of this include the extraction of soluble antibiotics from fermentation liquors.

In crossflow filtration, the feed is passed across the filter membrane (tangentially) at positive pressure relative to the permeate side. A proportion of the material which is smaller than the membrane pore size passes through the membrane as permeate or filtrate; everything else is retained on the feed side of the membrane as retentate. With crossflow filtration the tangential motion of the bulk of the fluid across the membrane causes trapped particles on the filter surface to be rubbed off. This means that a crossflow filter can operate continuously at relatively high solids loads without blinding. Figure 2.3 show the flow of Crossflow and conventional Filtration.

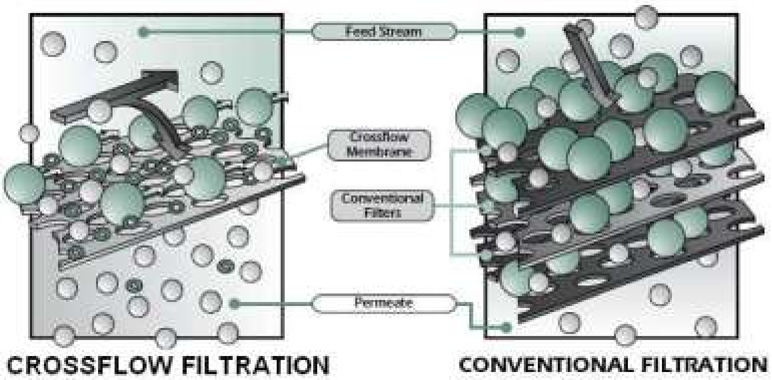

Figure 2.3: Crossflow and Conventional Filtration

2.5 Advantages and disadvantages of membrane

Advantages:

1. Membrane separation consistently separates a wide variety of emulsion, surfactant, and chelating chemistries and various mixtures.
2. It requires no specific chemical knowledge.
3. Complex instrumentation is not required.
4. The method does not require constant attention.
5. The basic concept is simple to understand.

Disadvantages:

1. Membranes are expensive.
2. Certain solvents can quickly and permanently destroy the membrane.
3. Certain colloidal solids, especially graphite and residues from vibratory deburring operations, can permanently foul the membrane surface.
4. The energy cost is higher than chemical treatment, although less than evaporation.
5. Oil emulsions are not "chemically separated," so secondary oil recovery can be difficult.
6. Synthetics are not effectively treated by this method.

2.6 Parameters

2.6.1 Anionic Surfactant (Linear alkyl benzene sulfonate)

The LAS is the most widely used type of surfactant for laundering, dishwashing liquids and shampoos because of its excellent cleaning properties and high sudsing potential. The surfactant is particularly good at keeping the dirt away from fabrics, and removing residues of fabric softener from fabrics. Anionic surfactants are particularly effective at oily soil cleaning and oil/clay soil suspension. Still, they can react in the wash water with the positively charged water hardness ions (calcium and magnesium), which can lead to partial deactivation. The more calcium and magnesium molecules in the water, the more the anionic surfactant system suffers from deactivation. To prevent this, the anionic surfactants need help from other ingredients such as builders (Ca/Mg sequestrants) and more detergent should be dosed in hard water. The most commonly used anionic surfactants are alkyl sulphates, alkyl ethoxylate sulphates and soaps.

2.6.2 Chemical Oxygen Demand (COD)

The chemical oxygen demand is a measure of the oxidizability of a substance, expressed as the equivalent amount in oxygen of an oxidizing reagent consumed by the substance under fixed laboratory conditions. COD measurements are commonly made on samples of waste waters or of natural waters contaminated by domestic or industrial wastes. Chemical oxygen demand is measured as a standardized laboratory assay in which a closed water sample is incubated with a strong chemical oxidant under specific conditions of temperature and for a particular period of time.

A commonly used oxidant in COD assays is potassium dichromate ($K_2Cr_2O_7$) which is used in combination with boiling sulfuric acid (H_2SO_4). Because this chemical oxidant is not specific to oxygen-consuming chemicals that are organic or inorganic,