Removal of Cr (VI) and Cr (III) From Water by Reduction and Micellar Enhanced Ultrafiltration Techniques

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Abstract

Removal of Cr (VI) and Cr (III) from water by reduction and micellar enhanced ultrafiltration

Elham Abbasi- Garravand

Nowadays, hexavalent and trivalent chromium are two forms of heavy metals that have raised a serious concern due to their high toxicity, low biodegradability and carcinogenesis and their ability to pollute groundwater and soil. In this research, reduction and micellar enhanced ultrafiltration (MEUF) methods were used for removing hexavalent and trivalent chromium from water respectively. Rhamnolipid (JBR 425) was also applied as a reducing agent in reduction and a biosurfactant in MEUF techniques because of its low toxicity and biodegradability in the environment.

In this study, batch experiments were done in two parts (reduction and MEUF) to investigate the efficiency of rhamnolipid (JBR 425) for removing Cr (VI) and Cr (III). In the first part of the experiments, initial concentration of hexavalent chromium, pH, and rhamnolipid concentration were examined to observe the effect of these parameters on the reduction of Cr (VI). The maximum reduction of hexavalent chromium was 98.3 % at a 10 mg/L Cr (VI) initial concentration of 10 mg/L, pH 6, and a rhamnolipid concentration of 2 %. In the second part of the trials, the operating factors such as temperature, transmembrane pressure (TMP), fouling, and rhamnolipid concentration in removing trivalent chromium and also the behavior of rhamnolipid in the presence of Cr (III) were studied. TMP and temperature had a positive effect on the performance of MEUF system. In all experiments for both parts, it has been illustrated that rhamnolipid (JBR 425) had an extremely good efficiency for removing hexavalent and trivalent chromium from waters which was the main purpose of this research.

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List of Abbreviations

C_f	Feed Concentration
C_p	Permeate Concentration
CMC	Critical Micelle Concentration
Cr	Chromium
Cr (III)	Trivalent Chromium
Cr (VI)	Hexavalent Chromium
EPA	Environmental Protection Agency (U.S)
IUPAC	International Union of Pure and Applied Chemistry
MWCO	Molecular Weight Cut Off
MEUF	Micellar Enhanced Ultrafiltration
R	Rejection Ratio
R^2	Square Linear Regression
RO	Reverse Osmosis

T	Temperature
TMP	Transmembrane Pressure
WHO	World Health Organisation

Introduction

1.1 General Remarks

Wide introduction of industries into areas and improper disposal are two important factors which play a significant role in releasing the heavy metals into the ecological system. Bioaccumulation of released heavy metals affects the food chain in higher trophic levels. Heavy metals cause acute and chronic problems for living creatures, when they exist greater than the normal levels in the environment. Heavy metals are not degradable and are persistent and their natural mineralization happens slowly. Industries such as metal coating, smelting and refining of non-ferrous metals, paint, ink and associated products, petroleum refining, iron and steel manufacturing, photographic production and developing, leather tanning, wood pre-serving, and battery manufacturing discharge the main amount of heavy metals such as aluminum, arsenic, cadmium, chromium, copper, lead, nickel, silver, mercury and zinc to the ecosystem (Chaychian *et al.*, 1998).

One of these heavy metals is chromium which has considerable effects on the environment. The two major oxidation states of chromium that exist in the environment are hexavalent chromium and trivalent chromium. Cr (VI) is more toxic than Cr (III). Although Cr (III) in high amounts is toxic, it is a useful and essential element for humans as well (Sahmoune *et al.*, 2011). Chromium is found more in industries like electroplating, leather tanning, metal finishing, nuclear power plant, textile and chromate preparation manufacturers. Chromium is considerably carcinogenic and causes problems such as chromosomic abnormality, and bioaccumulation into flora and fauna(Rengaraj *et al.*, 2001). Chromium existence in natural ground water has been observed in many countries all around the world. Among the US states, California, Washington, Indiana, South Carolina, North Carolina and New Jersey were those that have been reported to have Cr (VI) ground-water pollution. As well, water sources in some other cities around the world such as Leon in Mexico, Kanpur and Lucknow in India, Wuhan City in China, Glasgow in Scotland, La Spezia in Italy and the province of Ontario in Canada, were found to be contaminated by hexavalent chromium. As chromium is a very toxic compound, guideline values have been set for Cr (VI) concentration in the water. World Health Organization (WHO) has determined a temporary guideline concentration of 50 μg/L for total chromium. The US Environmental Protection Agency (USEPA) which has categorized the chromium in the group A of contaminant compounds, has recommended a Maximum Contaminant Level (Chaychian *et al.*) of 100 μg/L for total chromium and Canadian drinking water quality guidelines has determined the value of 50 μg/L for total chromium as a maximum permitted level (Sharma *et al.*, 2008).

There are a large number of conventional technologies for removing chromium from water and wastewaters. The membrane separation process is an interesting and appropriate technology for removing heavy metals like chromium. This technique is being used regularly because it is relatively very easy to include it as a part of the whole process. Reverse osmosis (RO) or nanofiltration can be utilized for separation of ions because of the ion size in aqueous phase, but they are not economic processes. In RO membranes for having a regular permeate flux; a high transmembrane pressure is required and this makes the process very costly (Baek *et al.*, 2003). Micellar enhanced ultrafiltration technology (MEUF) which is a surfactant-based process, has been evaluated for separation of multivalent metal ions (Samper *et al.*, 2010). In this method, a surfactant is added to the polluted aqueous solution (Chaudhari and Marathe, 2010). The structure of a surfactant is the composition of a hydrophilic head and a hydrophobic tail. When the concentration of the surfactant is more than the critical micelle concentration (CMC), a micelle which is a formation of a spherical or cylindrical group of monomers is created. Based on the electrostatic forces, heavy metal ions bind to the surface of opposite charged micelles (Rahmanian *et al.*, 2010).

Synthetic and biologically produced are two different types of surfactants. Synthetic surfactants are the result of chemical synthesis and are originated from petrochemicals and biosurfactants are biogenic surfactants that are microbially produced by bacteria, yeast and fungi (Edwards *et al.*, 2003). Biosurfactants in comparison with synthetic surfactants have some benefits such as low toxicity, high biodegradability, low irritancy, and compatibility with human skin. The characteristics of biosurfactants do not change under excessive conditions of pH, temperature, and salinity (Pornsunthorntawee *et al.*, 2008). Leakage into the permeate during filtration is a potential problem of using synthetic surfactants which in the long term has the risk of secondary pollution. Biosurfactants are potential substitutions for synthetic surfactants in micellar enhanced ultrafiltration technique. As biosurfactants are environmentally compatible and nontoxic compounds, the leakage does not make another sort of contamination. The other advantage of using biosurfactant enhanced ultrafiltration membrane processes is its application in a large range of pH, pressure, and temperatures (El Zeftawy and Mulligan, 2011).

1.2 Objectives

The main goal of this study is to develop a method for the removal of hexavalent chromium and trivalent chromium from contaminated water. For achieving this purpose, Cr (VI) was reduced to Cr (III) and then Cr (III) was removed by using the biosurfactant enhanced ultrafiltration membrane process technique. The biosurfactant that was used in this research was rhamnolipid (JBR 425) for both reduction and micellar enhanced ultrafiltration (MEUF) experiments.

The objectives of this study are classified as follows:

- To evaluate the feasibility of applying rhamnolipid JBR 425 for the reduction and removal of hexavalent chromium in water.
- To evaluate the factors affecting the reduction productivities
- To investigate the operating conditions influencing the permeate flux and removal efficiency.
- To determine the effect of rhamnolipid on rejection of Cr (III).

1.3 Organization of the Research Study

There are five chapters in this thesis. In chapter one, the introduction and purposes of the research are presented. Chapter two describes the literature review on chromium, membrane technology, surfactants and biosurfactants, and micellar enhanced ultrafiltration. Chapter three includes materials, instruments, and methods which were used in the experiments. In chapter four, the results of different experiments are demonstrated and discussed. Chapter five summarizes the conclusions of this study and introduces the recommendations for future work. This thesis is completed by the list of references.

2 Literature Review

2.1 Heavy Metals

When an element has four characteristics such as electrical conductivity, high thermal conductivity, high density, malleability and ductility then it is known as a metal (Watts, 1998). Heavy metals are elements with atomic numbers greater than iron and metals with densities greater than 5.0 $^{g}/_{cm^3}$ (Watts, 1998). Heavy metals include a large range of elements that pose an important threat on the environment. Production of heavy metals and developing industries has grown in parallel. Some of heavy metals are useful for microorganisms, plants, and animals such as Mn, Cu, Zn, Cr, Mo and Ni, but in low amounts because high concentrations of these metals contaminate the environment. Contamination by heavy metals causes an undesirable change in the physical, chemical or biological characteristics of water, soil and air and these changes, pose risk to humans, animals and plants (Tahar and Keltoum, 2011).

Contamination of the aquatic ecosystem by heavy metals damages living organisms' lives and the environment. Toxic heavy metals such as Cr, Cd, Hg, Ni, Pb and Zn as inorganic effluents pollute wastewater. High toxicity, non-biodegradability, accumulation in the food chain and carcinogenic are some of the negative effects of heavy metals (Albadarin *et al.*, 2011).

Therefore, treating and removing the heavy metals is very important and it has received attention by many researchers all over the world (Pagana *et al.*, 2011).

Effluents of industries and domestic wastes include large amounts of heavy metals or nutrient substances that enter the land ecological system and natural aquatic environment (Xu *et al.*, 2011).

In North America, pollution of some sites by metal ions continues and occurs more for those areas which are close to mining facilities and industrial waste discharge points. In most of the contaminated sites in U.S., heavy metals play an important role. Based on the U.S. Environmental Protection Agency Superfund, heavy metals have polluted around 65% of soil and ground water contaminated sites (El Zeftawy and Mulligan, 2011).

2.1.1 Chromium

The French chemist Louis Vauquelin discovered chromium in 1797. As the chromium compounds exist in many different colors, it was called chromium (in Greek, Chroma means color) (Mohan and Charles, 2006). Chromium is known as one of the elements that exist in the periodic table in group 6. Its symbol is Cr and its atomic number is 24. Chromium is a hard shiny steely-gray metal and is highly polished. Chromium ranks 21st among the most abundant elements on earth and also between the most abundant transition metals it is sixth. Some physical properties of chromium are mentioned in Table 2-1.

Table 2-1: Chromium physical properties (Papp and Lipin, 2010)

Property	**Value**
Atomic weight ($^{g}/_{mol}$)	51.996
Vapor pressure at 1610 ℃ (Pa)	130
Specific gravity at 20 ℃ ($^{g}/_{cm^3}$)	7.18- 7.20
Oxidation states	6, 5, 4, 3, 2, 1, -1, -2
Density at 20 ℃ ($^{g}/_{ml}$)	7.19
Thermal conductivity at 20 ℃ ($^{W}/_{m.K}$)	91
Electrical resistivity at 20 ℃ ($\mu \cap . m$)	0.129
Melting point (℃)	1907
Heat of fusion ($^{kJ}/_{kg}$)	14.6
Boiling point (℃)	2671
Electron affinity of Cr-Cr bond (ev)	0.666

Mining chromite ($FeO\ .Cr_2O_3$) is the main source of chromium and also crocoite, $PbCrO_4$, and chrome ochre, Cr_2O_3, are the other sources of chromium (Mohan *et al.*, 2011). Chromium oxidation states change from 2- to 6+. Less important states of chromium are the 1- and 2- and the most common ones are the 2+, 3+ and the 6+. Between these three states, the 6+ state is commercially more important because it has high oxidation potential. Cr (VI) is often present as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) in aqueous solutions and this state of chromium is thermodynamically stable. However, the 3+ state is stable and insoluble in water (Watts, 1998).

Cr (III) and Cr (VI) have different toxic effects. Cr (III) is an essential trace element for animals and humans, but large concentrations of trivalent chromium are toxic (Qin *et al.*, 2005).Cr (VI) is harmful and carcinogenic for humans. Cr (III) often converts to Cr (VI) in wastewater treatment processes and this shows the importance of removing both Cr (III) and Cr (VI) to protect the environment and human health (Konczyk *et al.*, 2010). Chromium is used in many industries such as the preservation of wood, textile dyeing, leather tanning, electroplating and metal finishing and thus contaminates the surface and ground waters (Anbia and Mohammadi, 2011). These industries release a large amount of Cr in wastewaters in the range of 0.5 to 270,000$\frac{mg}{L}$. Cr (VI) is 500-1000 times more toxic than Cr (III) and based on this difference, the US Environmental Protection Agency (USEPA) determined the allowable amount of dischargeable Cr (VI) to surface water to below 0.05 $\frac{mg}{L}$, but the regulated concentration of total Cr (Cr(VI), Cr(III) and other forms) is 2 $\frac{mg}{L}$ (Malaviya and Singh, 2011). Also, the recommended concentration of total chromium in drinking water by the EPA is 100 $\frac{\mu g}{L}$ (Mohan *et al.*, 2011). Nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhage, and respiratory problems are some damage that happens for people who are exposed to Cr (VI). Also, irritation and ulceration of the nasal septum and respiratory sensitization may happen because of inhalation of Cr (VI). Ingestion causes kidney and liver problems. The healing of cuts or scrapes is inhibited by touching Cr (VI) and some problems like systemic poisoning damage or even severe burns occurred by skin contact with Cr (VI) as well. If treatment of these diseases takes a long time, it will seriously cause chronic allergies and ulcerations. Eye contact may result in substantial permanent harm (Mohan and Charles, 2006).

Canada does not currently produce chromium ore, but imports different materials containing chromium (e.g. 76.7 tonnes in 2003 (Papp, 2004)). Chromium is used in many industries in Canada and this causes chromium to enter the aquatic environment. Available data indicated that at least 27 tonnes of chromium went into liquid discharges from Canadian base metal smelters and refineries besides iron and steel plants and metal finishing plants (CEPA, 1994).

The median amount of total chromium in unpolluted surface and marine waters is below 1.0 µg/L, but higher amounts of total chromium in contaminated surface waters have been observed in many parts of Canada. For example, a survey done between 1986 and 1988 showed that the average concentration of total chromium in the tributaries of the St. Lawrence River in the province of Quebec was 7.1 µg/L, with a range of 1.5 to 92 µg/L (CEPA, 1994).

2.2 Treatment Technologies

There are several treatment technologies for removing chromium from water and wastewaters. Some of these technologies are chemical precipitation, ion exchange, flotation, electrocoagulation, solvent extraction, sedimentation, electrokinetic extraction, phytoremediation, reduction, dialysis/electrodialysis, adsorption/filtration, evaporation, cementation, dilution, air stripping, steam stripping, flocculation, chelation, and membrane separation (Mohan and Charles, 2006). Some conventional techniques such as chemical precipitation, ion exchange and electrodialysis have several drawbacks which are high operating costs, incomplete removal, low selectivity, high energy consumption and toxic slurries (Samper *et al.*, 2010).

2.3 Membrane Technology

Membrane technology is used in many separation processes because it has a multidisciplinary nature. It is cost effective and safe separation techniques from an environmental standpoint (Beolchini *et al.*, 2006). Membrane technology like every other treatment method has some advantages and disadvantages. Some of the benefits are: continuous separation, low energy consumption, combination with other membrane separation processes, easy scale-up, variable and adjustable properties, and additives are not required. Also, membrane technology has some drawbacks such as concentration polarization, membrane fouling, low membrane lifetime, and low selectivity (Mulder, 1991).

2.3.1 Membranes and Membrane Separation Processes

Semipermeable membranes work as a barrier between two phases and separate metals by limiting the movement of ions and molecules as illustrated in Figure 2-1. Size exclusion, differences in diffusion coefficients, electrical charge, and solubility are the factors that affect these movements. Driving forces control the membrane separation processes such as micro-, ultra-, and nanofiltration, reverse osmosis (RO) by hydrostatic pressure, dialysis by concentration gradient; and gas permeation by pressure and concentration gradients (Malaviya and Singh, 2011). Each membrane process has an effective separation range which is shown in Figure 2-2.

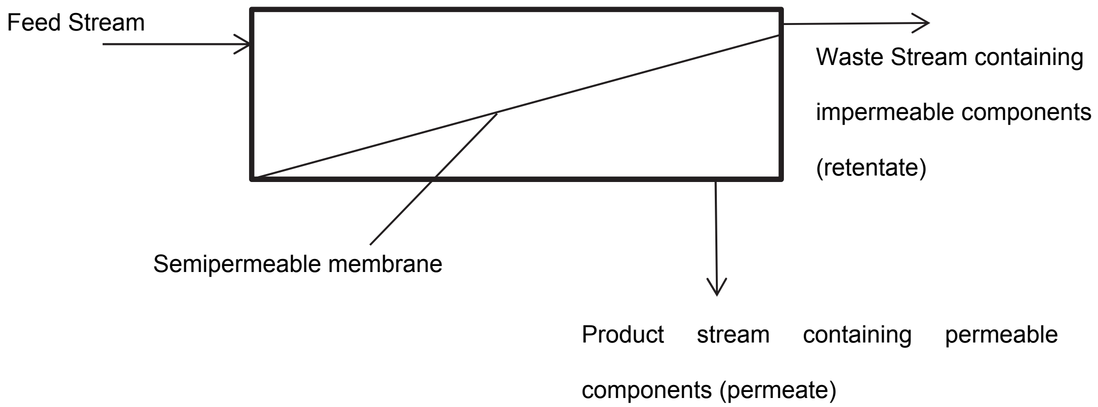


Figure 2-1: Schematic of a Separation Process Through a Semipermeable Membrane (MWH, 2005)

The membrane passes some components into a permeable stream and will retain others in the retentate stream. The structure of membranes is homogeneous or heterogeneous and can have different thicknesses. Classification of membranes can also be done based on the pore diameter. International Union of Pure and Applied Chemistry (IUPAC), has classified three different types of pore diameter size (dp): microporous (dp < 2 nm), mesoporous (2 nm < dp < 50 nm), and macroporous (dp> 50 nm). The status of membranes is either neutral or charged, and that of particle transport is active or passive (Ambashta and Sillanpää, 2012). Membranes have different thicknesses that can be greater than 100 nm and can go up to more than a centimeter. Also, a membrane has an electrical resistance that can start from thousands of megohms and decrease to a fraction of an ohm (Strathmann, 1981). Based on the type of driving forces, the membrane processes are classified and it is shown in Table 2-2.

Table 2-2: Classification of Membrane Processes (Belfort, 1984)

Process	Driving potential	Constituents removed from feedwater	Constituents remaining in the product (other than water)	Possible size ranges of permeable species (kPa)
Hyperfiltration (Reverse osmosis)	Pressure (as high as 3948 kPa)	Water without dissolved and undissolved inorganic and organic constituents	Little salt (owing to membrane leakage BO_3^-, NO_3^-, urea, low MW organics	395 – 29606
Ultrafiltration	Pressure (usually below 987 kPa)	Water without dissolved and undissolved organic constituents	All the salt and low molecular weight organics	1974- 10132500
Electrodialysis	Electrical	Dissolved inorganic ions	Little salt, all the organics (dissolved and undissolved) including viruses, bacteria, etc.	395 – 29606
Transport depletion	Electrical	Dissolved inorganic ions	More than a little salt, all the organics (dissolved and undissolved) including viruses, bacteria, etc.	10 - 1000

Membranes, which are used for separation and concentration of solutes, have some benefits such as ease of operation, reduction in secondary pollution, recovery and reuse of solutes (Malaviya and Singh, 2011).

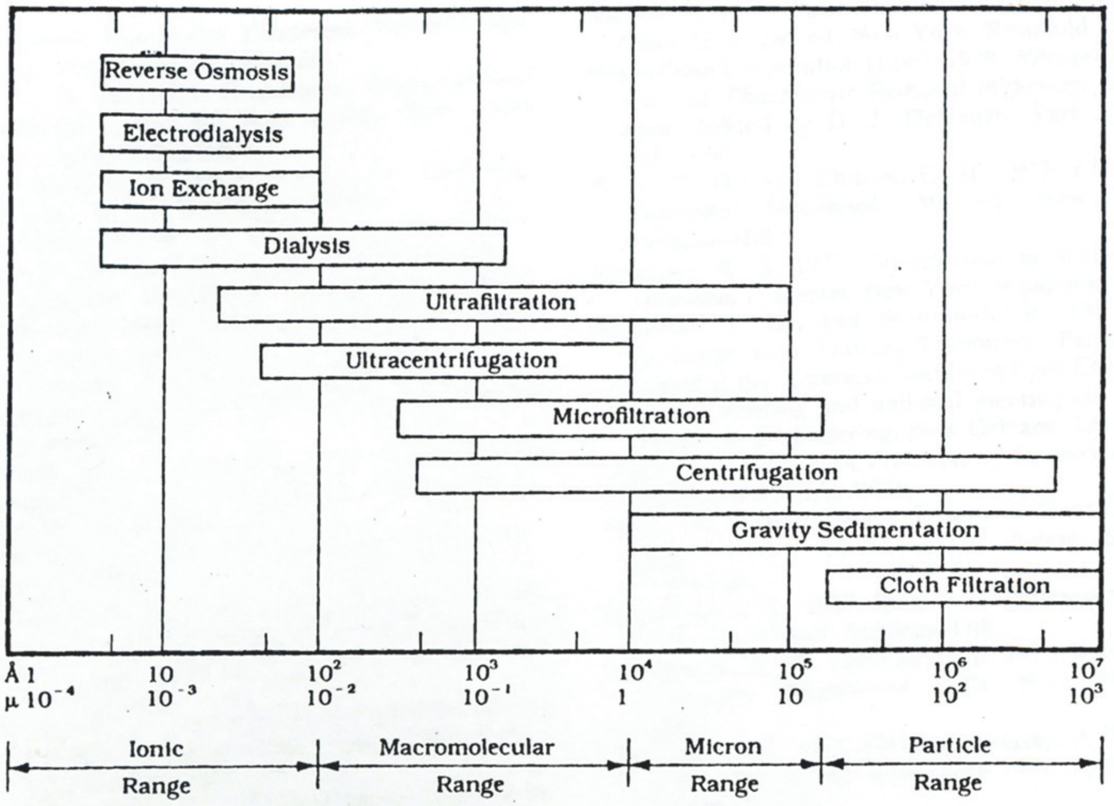


Figure 2-2: Effective Ranges of Some Separation Techniques (Raynolds and Richards, 1995)

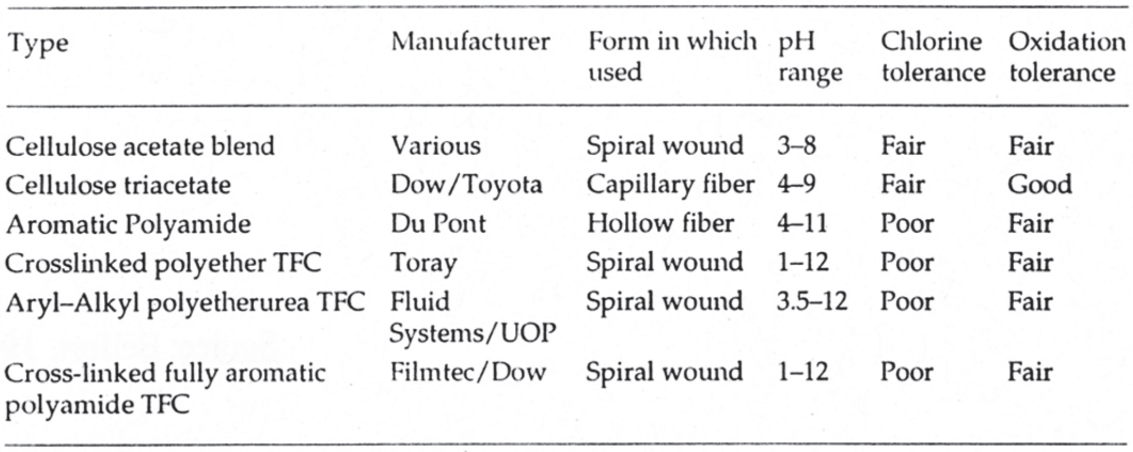
2.3.1.1 Ultrafiltration

Ultrafiltration is defined as a membrane process which is being used for purifying, concentrating and fractioning macromolecules or suspended fine colloidal particles by a pressure driving force at the same time. During this process, the phase does not change (Bhave, 1991). Ultrafiltration membranes are classified based on molecular weight cut-off which is the molecular weight of a dissolved particle when its rejection coefficient is 90% (Mehta and Zydney, 2005). Typically molecular weights range from 1000 to 100000 Da (Malaviya and Singh, 2011). Polymers like cellulose acetate, polysulfone, and polyethersulfone are commonly used to make the asymmetric membranes which are used in ultrafiltration membrane processes (Arthanareeswaran *et al.*, 2007).

2.3.1.2 Reverse Osmosis

Reverse Osmosis (RO) is defined as a membrane permeation process which is applied for separation of the pure solvent from a solution with less purity. In this process the solution is passed over a semipermeable membrane when the pressure is more than osmotic pressure of the feed solution (Lonsdale and Podall, 1972). Particles as small as 10^{-3} to 10^{-4} nm are rejected by RO (Malaviya and Singh, 2011). When water passes through the RO membrane, the heavy metal is retained. RO can be used over a wide range of pH from 3 to 11 and at 450-1500 kPa of pressure and this occurs based on the membrane characteristics such as the porosity, hydrophilicity, thickness, roughness, and charge of membrane (Kurniawan *et al.*, 2006). In Table 2-3 , properties of some RO membranes are shown.

Table 2-3: Properties of Some Commercial Reverse Osmosis Membranes (Fell *et al.*, 1995)

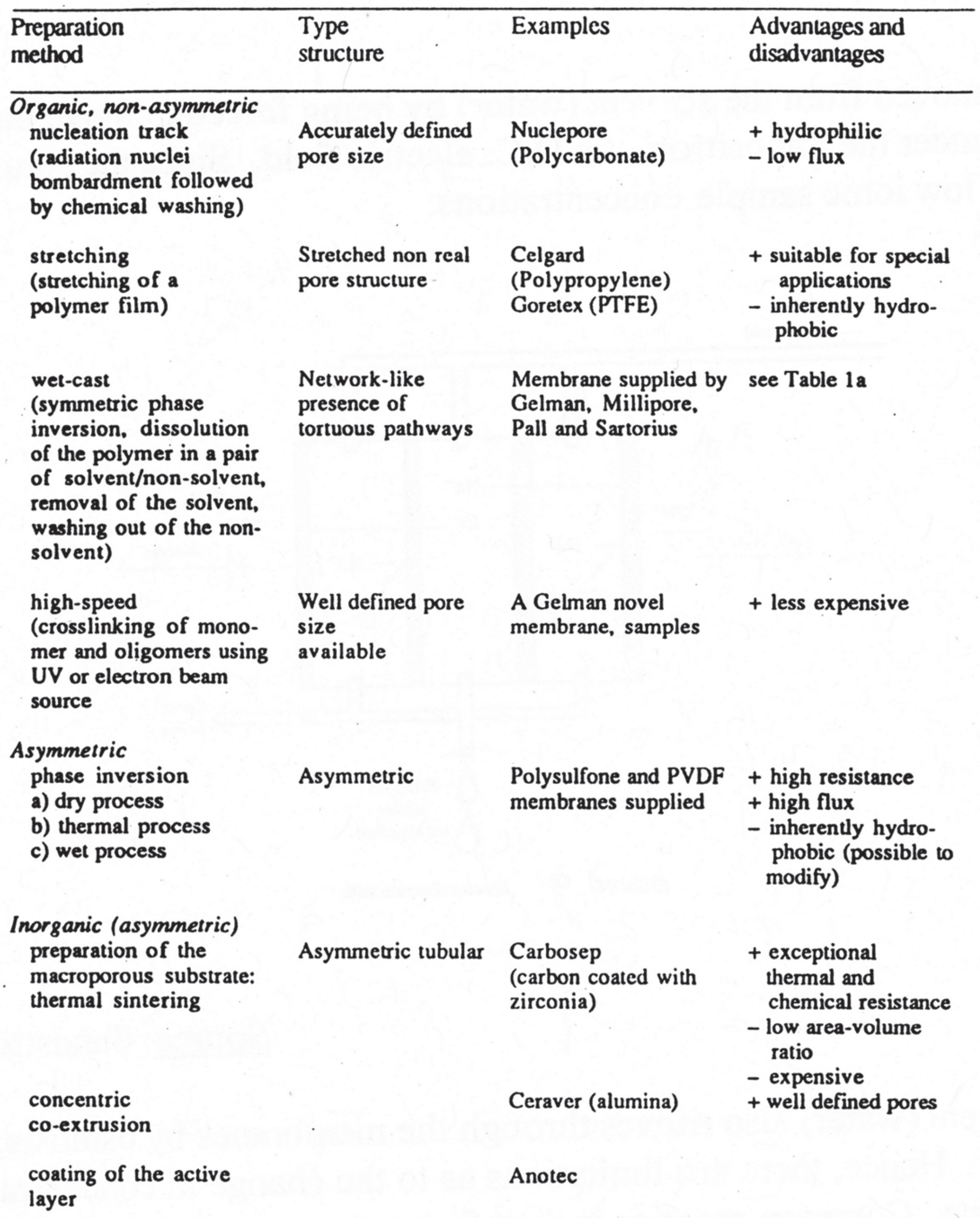


Type	Manufacturer	Form in which used	pH range	Chlorine tolerance	Oxidation tolerance
Cellulose acetate blend	Various	Spiral wound	3–8	Fair	Fair
Cellulose triacetate	Dow/Toyota	Capillary fiber	4–9	Fair	Good
Aromatic Polyamide	Du Pont	Hollow fiber	4–11	Poor	Fair
Crosslinked polyether TFC	Toray	Spiral wound	1–12	Poor	Fair
Aryl–Alkyl polyetherurea TFC	Fluid Systems/UOP	Spiral wound	3.5–12	Poor	Fair
Cross-linked fully aromatic polyamide TFC	Filmtec/Dow	Spiral wound	1–12	Poor	Fair

2.3.1.3 Microfiltration

Microfiltration is defined as a membrane which passes the flow through a micro-porous membrane by using pressure as a driving force for separating and recovering micron or sub-micron-sized particles from fluids (Venkiteshwaran and Belfort, 2010). In microfiltration membrane, pore sizes range from 0.1 to 5 μm and pressures are generally low, 200 – 300 kPa or even under vacuum. Flat microfiltration membranes are applied in many various plants such as waste water treatment, gas separation, and in biotechnology areas. Colloids and particles are also filtered in beverage industries using microfiltration membranes. Some characteristics such as well-defined molecular weight cut off, a high flow rate, and a low fouling tendency are necessary to use microfiltration in applications which have been mentioned above (Reingruber *et al.*, 2011). Some different types of microfiltration membranes are shown in Table 2-4.

Table 2-4: Types of Microfiltration Membranes (Gekas and Hallstrom, 1990)



Preparation method	Type structure	Examples	Advantages and disadvantages
Organic, non-asymmetric			
nucleation track (radiation nuclei bombardment followed by chemical washing)	Accurately defined pore size	Nuclepore (Polycarbonate)	+ hydrophilic – low flux
stretching (stretching of a polymer film)	Stretched non real pore structure	Celgard (Polypropylene) Goretex (PTFE)	+ suitable for special applications – inherently hydrophobic
wet-cast (symmetric phase inversion, dissolution of the polymer in a pair of solvent/non-solvent, removal of the solvent, washing out of the non-solvent)	Network-like presence of tortuous pathways	Membrane supplied by Gelman, Millipore, Pall and Sartorius	see Table 1a
high-speed (crosslinking of monomer and oligomers using UV or electron beam source	Well defined pore size available	A Gelman novel membrane, samples	+ less expensive
Asymmetric			
phase inversion a) dry process b) thermal process c) wet process	Asymmetric	Polysulfone and PVDF membranes supplied	+ high resistance + high flux – inherently hydrophobic (possible to modify)
Inorganic (asymmetric)			
preparation of the macroporous substrate: thermal sintering	Asymmetric tubular	Carbosep (carbon coated with zirconia)	+ exceptional thermal and chemical resistance – low area-volume ratio – expensive
concentric co-extrusion		Ceraver (alumina)	+ well defined pores
coating of the active layer		Anotec	

2.3.1.4 Nanofiltration

Nanofiltration is also known as ultra-low pressure reverse osmosis or membrane softening. The solids, smaller than 400 – 1000 MW, can pass through the NF membranes. The nanofiltration membrane properties change between ultrafiltration and reverse osmosis membrane properties (Hafiane *et al.*, 2000). NF membranes usually have a negative charge and are formed from an ultra-porous support layer coated by a selective layer which has a 1 μm thickness. Diffusion, convection, and donnan potential mechanisms affect all transport properties in the support layer (Muthukrishnan and Guha, 2008). NF membranes are very efficient for removing metals when the pH changes from 3 to 8 and pressure from 300 to 400 kPa based on the membrane characteristics, but UF and RO are used more than NF for the removal of heavy metals (Kurniawan *et al.*, 2006).

2.3.2 Membrane Materials

Many different materials can be used to produce membranes. Membranes are classified into two groups: biological and synthetic membranes. Life on earth is totally dependent on biological membranes as every living cell has a membrane. Synthetic membranes are also divided into two groups: organic (polymeric) and inorganic (Induceramic) membranes which their structure and functionality is totally different from biological membranes (Mulder, 1991). Polymeric and ceramic materials comprise two different types of membrane (Figure 2-3). The membrane materials must be prepared in a way to let water pass through them. A classic membrane has some properties such as anisotropic structure, symmetry just in the flat orthogonal to the membrane surface, high surface porosity, narrow pore size distribution, strong mechanical properties and some resistance to thermal and chemical attack and to fouling. The most common polymers that are used to form membranes include: polyvinylidene difluoride (PVDF), polyethylsulphone (PES), polyethylene (PE), polypropylene (PP) (Judd, 2006).

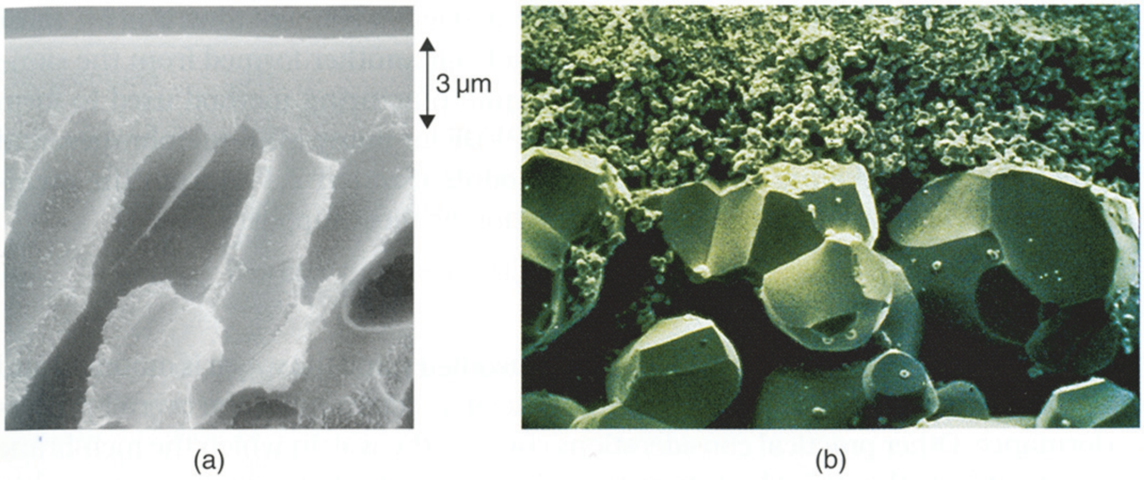


Figure 2-3: Anisotropic UF Membranes: (a) Polymeric and (b) Ceramic (Judd, 2006)

2.3.3 Ultrafiltration Membrane Configurations

The membrane configuration (its geometry and how it's placed in regards to flow of water) is very important to determine the performance of the overall process. The ideal configuration of the membrane is done in a way that it will have: a high membrane area, a high degree of turbulence, low energy expenditure, a low cost per unit membrane area, an easy to clean design, and a modularized design (Judd, 2006). Tubular, hollow fiber, spiral wound, and plate and frame are some common module configurations which are used in cross flow ultrafiltration (Mallevialle *et al.*, 1996). Tubular membrane module has inner channel diameters more than 4 mm. For hollow fibers, inner diameters are between 0.2 mm to 3 mm (Fadhel *et al.*, 2006). Some advantages and disadvantages of these modules are shown in Table 2-5.

2.3.3.1 Tubular Membrane Module

Tubular membranes are very applicable in many different ways when wide flow channels are very important. Three important examples of using tubular membranes in industries are the treatment of oily waste from the metalworking industries, clarifying and concentrating of fruit juices and industrial wastewater treatment. Traditional tubular membranes have been built based on assembling several membrane tubes which are connected in series configuration to create a single long flow channel in a module. Using the parallel configuration is not very common. There are two major reasons for it. First, for achieving a high cross-flow in the many parallel tubes, a large flow is needed and the other reason is related to the large losses of entrance and exit that are occurred in the end caps of the modules (Nordin and Jönsson, 2010). Figure 2-4 exhibits a schematic drawing of a tubular module.

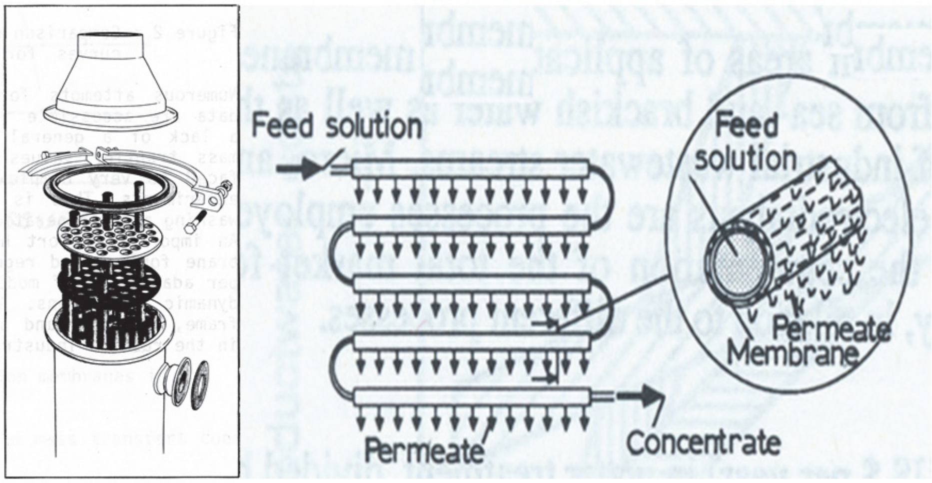


Figure 2-4: Schematic Drawing of a Tubular Module (Cecille and Toussaint, 1989)

2.3.3.2 Hollow Fiber Membrane Module

A bundle of hundreds to thousands of hollow fiber membranes constructs the hollow fiber membrane module (Figure 2-5) (WEF, 2006). Hollow fiber UF membrane filtration process is used in large applications such as industrial processes, groundwater replenishment, and food and beverage processing because it has a large active membrane area per unit volume. Like other technologies, hollow fiber membranes have some disadvantages which include fouling of the membrane. The fouling decreases the performance of the system regarding to permeate flux. By reducing the permeable flux, pressure drop increases and all these happen because of fouling the membrane which affects the membrane filtration efficiency (Li *et al.*, 2011). Hollow fiber membranes have high area packing density and because of this they are one of the most important modules (Fadhel *et al.*, 2006). Additionally, back flushing techniques improve the cleaning of the hollow fibers and aeration reduces particle adhesion and concentration polarization (Mänttäri *et al.*, 2010).

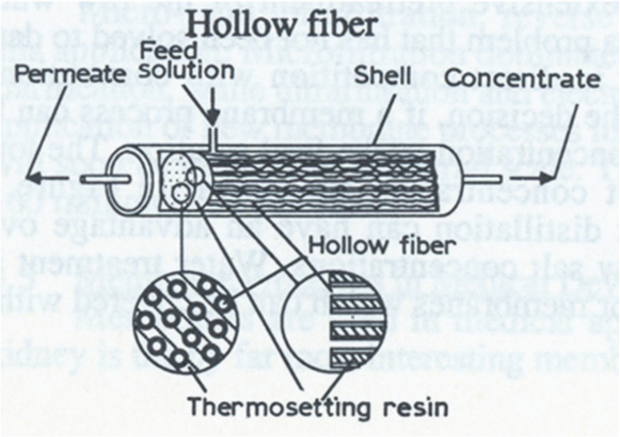
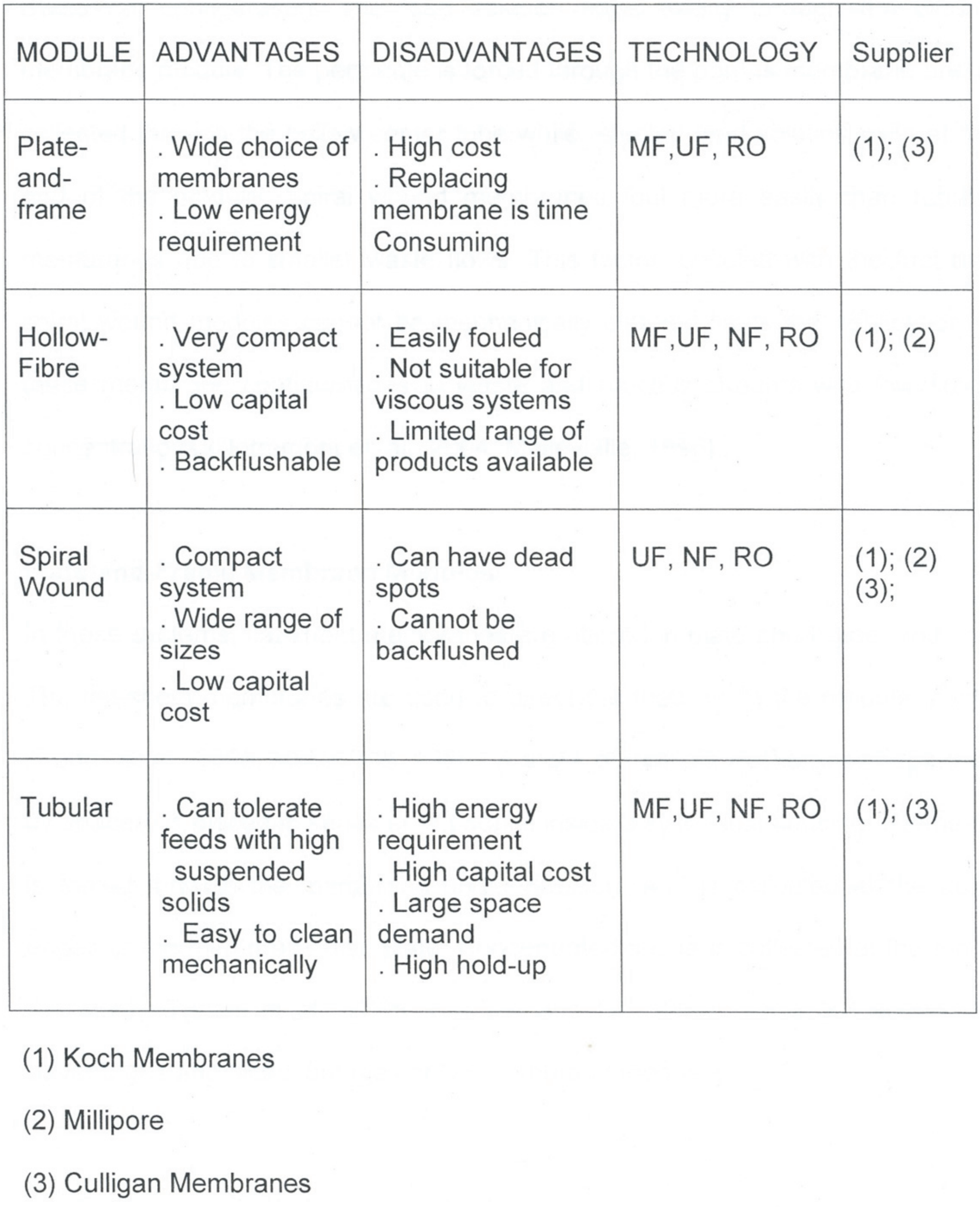


Figure 2-5: Schematic Drawing of a Hollow Fiber Module(Cecille and Toussaint, 1989).

Table 2-5: Advantages and Disadvantages of UF Membrane Modules(El Zeftawy, 2006).



MODULE	ADVANTAGES	DISADVANTAGES	TECHNOLOGY	Supplier
Plate-and-frame	. Wide choice of membranes . Low energy requirement	. High cost . Replacing membrane is time Consuming	MF,UF, RO	(1); (3)
Hollow-Fibre	. Very compact system . Low capital cost . Backflushable	. Easily fouled . Not suitable for viscous systems . Limited range of products available	MF,UF, NF, RO	(1); (2)
Spiral Wound	. Compact system . Wide range of sizes . Low capital cost	. Can have dead spots . Cannot be backflushed	UF, NF, RO	(1); (2) (3);
Tubular	. Can tolerate feeds with high suspended solids . Easy to clean mechanically	. High energy requirement . High capital cost . Large space demand . High hold-up	MF,UF, NF, RO	(1); (3)

(1) Koch Membranes

(2) Millipore

(3) Culligan Membranes

2.3.3.3 Spiral Wound Membrane Module

The structure of spirals consists of plastic bags that contain permeate spacers on the inside, the active membrane surface which is on the outside and a wound round a hollow shaft which are separated from each other by a feed mesh (Cardew and Le, 1998). There are three types of flow paths for a spiral-wound membrane module. The first type is an axial flow which is along the feed spacer-filled channel and the second one is a spiral flow which is parallel to the permeate flow path and the last one is a radial flow which is toward the membranes (Li *et al.*, 2012). The densities of spiral-wound and hollow fiber modules are higher in comparison with tubular modules. Because of their small flow channels, module plugging happens easily and as a result it requires a way to keep the feed streams free from fibers and suspended solids and other particulate contaminants. Plugging of spiral-wound membranes can be decreased by developing open channels and special spacer constructions. Maintaining the high flow rates in the spiral-wound modules is very difficult and it is the other disadvantage of them. The reason refers to the increase of the pressure loss through the module, because of the flow rate, and when the pressure loss exceeds the maximum permissible level, which is typically 0.5 – 1.5 bars, it will destroy the module structure (Mänttäri *et al.*, 2010). A schematic drawing of a spiral-wound module is shown in Figure 2-6.

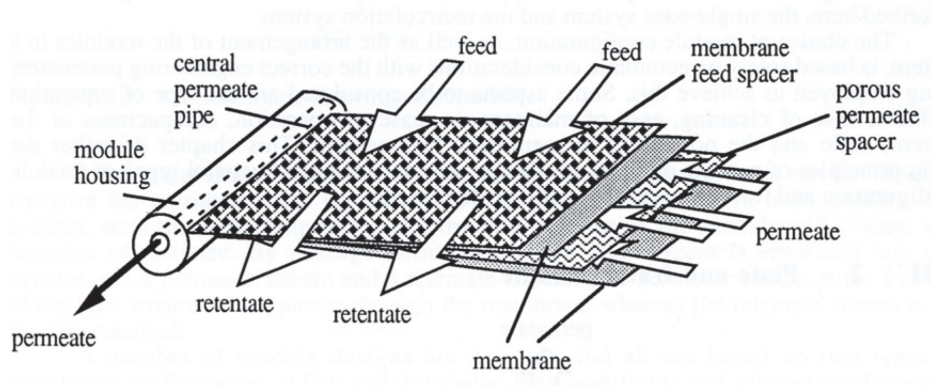


Figure 2-6: Schematic Drawing of a Spiral-Wound Module (Mulder, 1991).

2.3.3.4 Plate and Frame Membrane Module

These modules consist of stacked flat sheet membranes which are supported by plates (Figure 2-7). Circulation of the feed occurs between the membranes of two near plates. The liquid sheet has a thickness that ranges of 0.5 to 3.0 mm (Mallevialle *et al.*, 1996). Plate and frame membrane modules have some benefits such as ease of disassembly, sanitization, and replacement of the membrane sheet. They are widely used in pharmaceutical and food researches (Cardew and Le, 1998). These modules have disadvantages as well such as bulky equipment, discommodious transportation, low loading density, narrow channels and insufficient mass transfer (Zhang *et al.*, 2011).

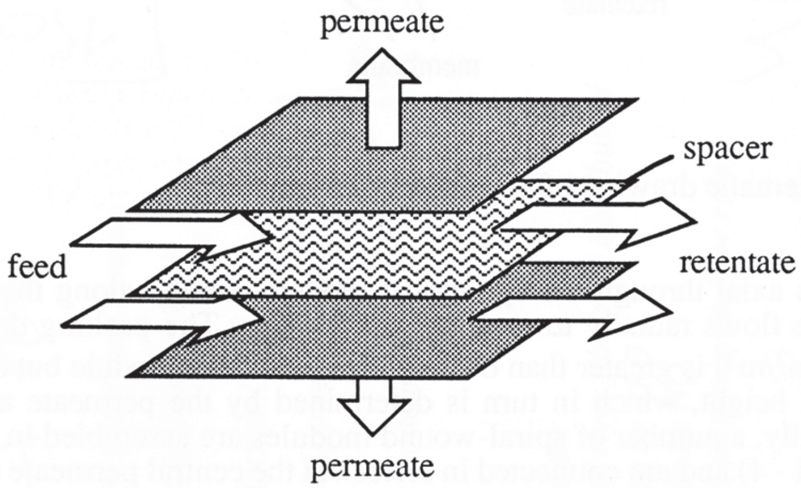
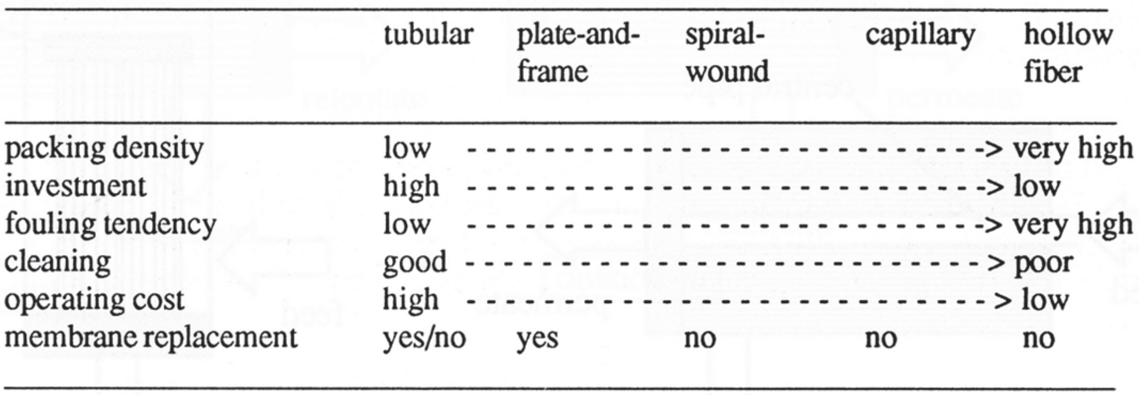


Figure 2-7: Schematic Drawing of a Plate-and-Frame Module (Mulder, 1991).

Table 2-6 shows a qualitative comparison between characteristics of all modules described above.

Table 2-6: Qualitative Comparison of Various Membrane Configurations (Mulder, 1991)



	tubular	plate-and-frame	spiral-wound	capillary	hollow fiber
packing density	low	- - - - - - -	- - - - - - -	- - - - - - ->	very high
investment	high	- - - - - - -	- - - - - - -	- - - - - - ->	low
fouling tendency	low	- - - - - - -	- - - - - - -	- - - - - - ->	very high
cleaning	good	- - - - - - -	- - - - - - -	- - - - - - ->	poor
operating cost	high	- - - - - - -	- - - - - - -	- - - - - - ->	low
membrane replacement	yes/no	yes	no	no	no

2.3.4 Membrane Process Operation

2.3.4.1 Dead-end and Cross Flow Operation

The flow regime of the feed water near the membrane surface is very important because it affects permeate flux and fouling. Cross-flow filtration and dead-end filtration are two filtration strategies which influence the flow regime. In cross flow filtration, the feed water passes tangentially on the membrane surface with high rate. One of the advantages of this mode is operation at higher flux with high turbidity feed water and it has some disadvantages such as clogged lumen, treatment of less water, and high pumping costs. In dead end filtration, all feed water passes through the membrane and solids larger than pore size retain on the membrane surface. It is less expensive in comparison with cross flow mode and clog lumen, and treat less water are some of the drawbacks of this mode (MWH, 2005).

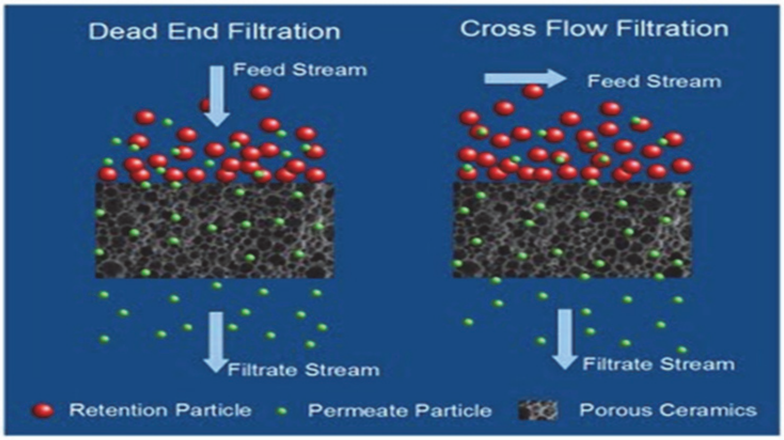


Figure 2-8: Schematic Diagram of Cross Flow Filtration and Dead End Filtration (Induceramic, 2011)

2.3.4.2 Concentration Polarisation

Concentration polarization is defined as the accumulation of solutes nearby boundary layer. Concentration polarization is affected by operating parameters such as velocity, pressure, temperature and feed concentration (Ilias and Govind, 1993).

Formation of concentration polarization boundary layer on the membrane surface affects the driving force efficiency through the membrane. In other words, when the concentration near the membrane surface increases, the driving force decreases (Zhang *et al.*, 2006).

In membranes which work based on pressure as their driving force, the concentration polarization in direction of gel formation usually occurs. These phenomena reduce permeability and transport characteristics. Diffusion layer and laid down gel include various particles which have different diffusivity characteristics. Hydrodynamic and mass transfer properties of membrane process are affected by gel or cake layer which is accumulated on the membrane surface (Agashichev, 2006). Formation of concentration polarization on the membrane surface is shown in Figure 2-9.

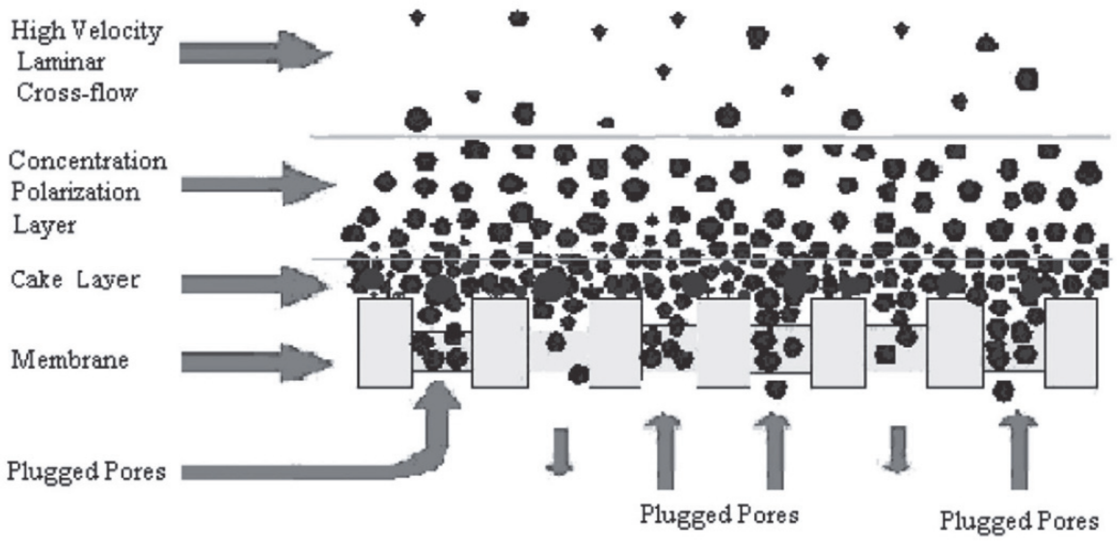


Figure 2-9: Schematic Diagram of Formation of Concentration Polarization on Membrane Surface (Zhan *et al.*, 2004)

2.3.4.3 Membrane Fouling

Membrane fouling is the phenomena in which the ultrafiltration membrane loses its permeability during the filtration and this happens because the impurities such as physic-, chemic-, and bio-substances accumulate on or in the membrane matrices. Foulants play an important role in membrane fouling control, so recognition of them is very significant. Based on the type of foulants, fouling is classified as particle fouling, organic fouling, and bio-fouling. Particle fouling is defined according to two classical plugging laws. Firstly, larger particles which accumulate on the membrane surface and smaller ones go through the membrane pore. Secondly, the cake which is formed by increasing precipitation of particles on the initial layer, causes a high resistance of membrane flux. Organic fouling is created by natural organic matter (NOM) from the source waters, but this type of fouling is not well understood. Bio-fouling comes from organisms which live or grow in water. Algae are a good example of aquatic organisms that create colonies which results in bio-fouling (Gao *et al.*, 2011). Fouling is generally known to be a time-dependent and irreversible phenomenon (Ilias and Govind, 1993). Execution and efficient performance in the production of drinking water are restricted by fouling of the ultrafiltration membrane (Peiris *et al.*, 2010). One of the grave problems of ultrafiltration technology is the membrane fouling which affects the process of commercializing of the membrane processes (Kwona *et al.*, 2008). Changing the operating conditions, chemical additions and pre-treatment are the parameters which can control the membrane fouling (Schafer, 2001).

2.4 Surfactants

A surfactant gets its name from a surface active agent, since the concentration is more in interfacial regions. The structure of surfactants is amphiphilic. An amphiphilic structure consists of hydrophilic and hydrophobic section in molecule. In other words, their structure has two parts, the head or the polar or ionic hydrophilic part and the tail or the nonpolar hydrophobic part. The head can be anionic, cationic, zwitterionic or non-ionic (West and Harwell, 1992). Also, there is another classification of surfactants based on the balance between the different parts of the molecule such as hydrophilic and hydrophobic or lipophilic. A lipophilic substance is defined as a hydrophobic material which has a high affinity to fatty or organic solvents. A high number of hydrophile-lipophile balance (HLB) means the substance is more soluble in water and a low number shows more solubility in an organic solvent (Maturi *et al.*, 2009).

Surfactants based on their environmental chemistry, hydrology, and transport mechanisms are used in subsurface remediation (West and Harwell, 1992). Surfactants decrease the surface and interfacial tension (Figure 2-10). They can ease the transportation of organic contaminants from soils to washing solution. Also surfactants can be used as flocculating, wetting and foaming agents (Mulligan *et al.*, 2001). The molecular weight of surfactants varies from 200 g/mole to 2000 g/mole (Li, 2009).

An efficient surfactant can decrease the interfacial tension of air-water to approximately 30 mN/m (Dahrazma and Mulligan, 2004). Surfactants can be used for increasing the contaminant bioavailability because they are capable of enhancing water solubility and mass transfer (Franzetti *et al.*, 2008).

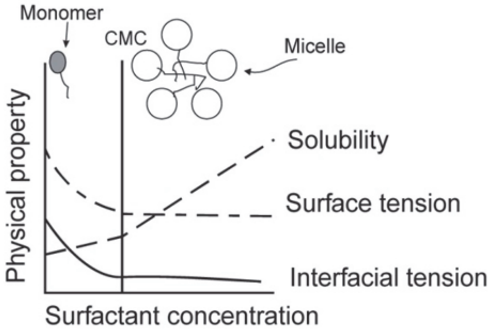


Figure 2-10: Schematic Diagram of the Variation of Surface Tension, Interfacial and Contaminant Solubility with Surfactant Concentration (Mulligan *et al.*, 2001).

2.5 Surfactant Mechanisms

Remediation technologies which are surfactant-based have two mechanisms: micellar solubilization and mobilization (NAPL displacement) (Suchomel *et al.*, 2007).

2.5.1 Micellar Solubilization

A surfactant monomer is a surfactant molecule that exists as a single unit. As the surfactant concentration increases, the concentration of monomers will also increase until it reaches a concentration at which micelles form. The critical concentration of micelle or CMC marks this minimum concentration (Rosen, 1978). Every surfactant has a unique CMC and the typical range of CMC is 0.1 to 10 mM. The number of monomers will remain unchanged at a concentration equal to or above CMC. Thus the extra surfactant molecules aggregate and form micelles. In aqueous conditions, the hydrophobic tail of the micelles will point towards the interior and the hydrophilic head of it will direct towards the aqueous solution (Li, 2009).

Micelles, bilayers and vesicles are supramolecular structures that are formed by amphiphilic molecules, when the concentrations are more than CMC (Lin, 1996).

Formations of micelles, based on properties of the system, are spherical, elongated, cylindrical and rodlike (Nguyen *et al.*, 2008).

2.5.2 Mobilization

One of the features of aqueous surfactant solutions is their ability to remove or mobilize the NAPL residue from porous media. The capillary forces control the NAPL movement in the subsurface (Aman, 2008).

2.6 Biosurfactants

Biosurfactants are used as a new class of commercial surfactants in many industries such as food, household cleaning, cosmetic, microbial enhanced oil recovery, environmental remediation, and agricultural applications (Hung and Shreve, 2001).

Biosurfactants which have different structures are produced by microorganisms (Manickam *et al.*, 2012). Biosurfactants can also be produced by yeast and bacteria which come from different substrates (sugars, oils, alkanes and wastes). The hydrophobic part consists of long-chain fatty acids, hydroxyl fatty acids or α-alkyl-β-hydroxy fatty acids and the hydrophilic head is based on a carbohydrate, amino acid, cycle peptide, phosphate, carboxylic acid or alcohol. The CMCs of biosurfactant typically range from 1 to 200 mg/L and their molecular weights range from 500 to 1500 Da (Mulligan, 2009).

Some advantages of biosurfactants are biodegradability, low toxicity, ecological acceptability, and effectiveness at high temperature and pH (Yin *et al.*, 2009). Also, biosurfactants are very useful for environmental remediation because of some of their abilities in the solubilization, dispersion and desorption of organic and inorganic contaminants from soils and sediments (Wang and Mulligan, 2009). On the other hand, channeling effects, aqueous-phase bypassing, and rate limiting mass transfer are some the known drawbacks of biosurfactants (Wang and Mulligan, 2004).

Similar to synthetic surfactants, biosurfactants decrease the surface and interfacial tensions. Also, they are good for use in detergency, emulsification, foaming, or dispersion (Pinzon and Ju, 2009).

2.6.1 Types of Biosurfactants

Biosurfactants which are produced by microorganisms have many different types such as glycolipids, rhamnolipids, sophorolipids, trehalolipids, phospholipids, lipoproteins and lipopeptides, polymeric biosurfactants, and fatty acids (Rahman and Gakpe, 2008). Some of these biosurfactants and their original microorganisms have been shown in Table 2-7.

Table 2-7: Type and Microbial Origin of Biosurfactants (Mulligan, 2005).

Type of biosurfactant	Microorganism
Trehalose lipids	*Arthrobacter paraffineus*
	Corynebacterium sp.
	Mycobacterium sp.
	Rhodococcus erythropolis, *Norcardia* sp.
Rhamnolipids	*Pseudomonas aeruginosa*
	Pseudomonas sp., *Serratia rubidea*
Sophorolipids	*Candida apicola*, *Candida bombicola*
	Candida lipolytica
	Candida bogoriensis
Glycolipids	*Alcanivorax borkumensis*
	Arthrobacter sp., *Corynebacterium* sp.
	R. erythropolis, *Serratia marcescens*
	Tsukamurella sp.
Cellobiose lipids	*Ustilago maydis*
Polyol lipids	*Rhodotorula glutinus*
	Rhodotorula graminus
Diglycosyl diglycerides	*Lactobacillus fermentii*
Lipopolysaccharides	*Acinetocbacter calcoaceticus* (RAG1)
	Pseudomonas sp., *Candida lipolytica*
Arthrofactin	*Arthrobacter* sp.,
Lichenysin A, Lichenysin B	*Bacillus licheniformis*
Surfactin	*Bacillus subtilis*, *Bacillus pumilus*
Viscosin	*Pseudomonas fluorescens*
Ornithine, lysine peptides	*Thiobacillus thiooxidans*
	Streptomyces sioyaensis
	Gluconobacter cerinus
Phospholipids	*Acinetocbacter* sp.
Sulfonylipids	*T. thiooxidans*
	Corynebacterium alkanolyticum
Fatty acids (Corynomycolic acids, spiculisporic acids, etc.)	*Capnocytophaga* sp.
	Penicillium spiculisporum
	Corynebacterium lepus
	Arthrobacter paraffineus
	Talaramyces trachyspermus
	Norcadia erythropolis
Alasan	*Acinetobacter radioresistens*
Streptofactin	*Streptomyces tendae*
Particulate surfactant (PM)	*Pseudomonas marginalis*
Biosur PM	*Pseudomonas maltophila*

2.6.2 Rhamnolipid

Among biosurfactants, rhamnolipids have been studied more. The microorganism, which produces them, is *Pseudomonas aeruginosa (Mulligan, 2009)*. They decrease the surface tension to 30- 32 mN/m and the critical micellar concentration (CMC) ranges from 5 to 65 mg/L (Rahman and Gakpe, 2008). Rhamnolipids are a part of the glycolipid biosurfactants and they include rhamnose which is the sugar component of the rhamnolipid hydrophilic group (Özdemir *et al.*, 2004). Figure 2-11 shows the structures of rhamnolipids. As illustrated two distinct configurations can be observed: a) one rhamnose attached to β-hydroxydecanoic acid (R1 and R3) and b) two rhamnose linked to β-hydroxydecanoic acid (R2 and R4). The fermentor design, pH, nutrient composition, substrate and temperature affect production and the constitution of rhamnolipids (Mulligan, 2009). Rhamnolipids have the potential to assist the environmental remediation more than synthetic surfactants based on some of their benefits such as high specificity, biodegradability, and biocompatibility (Guo *et al.*, 2009).

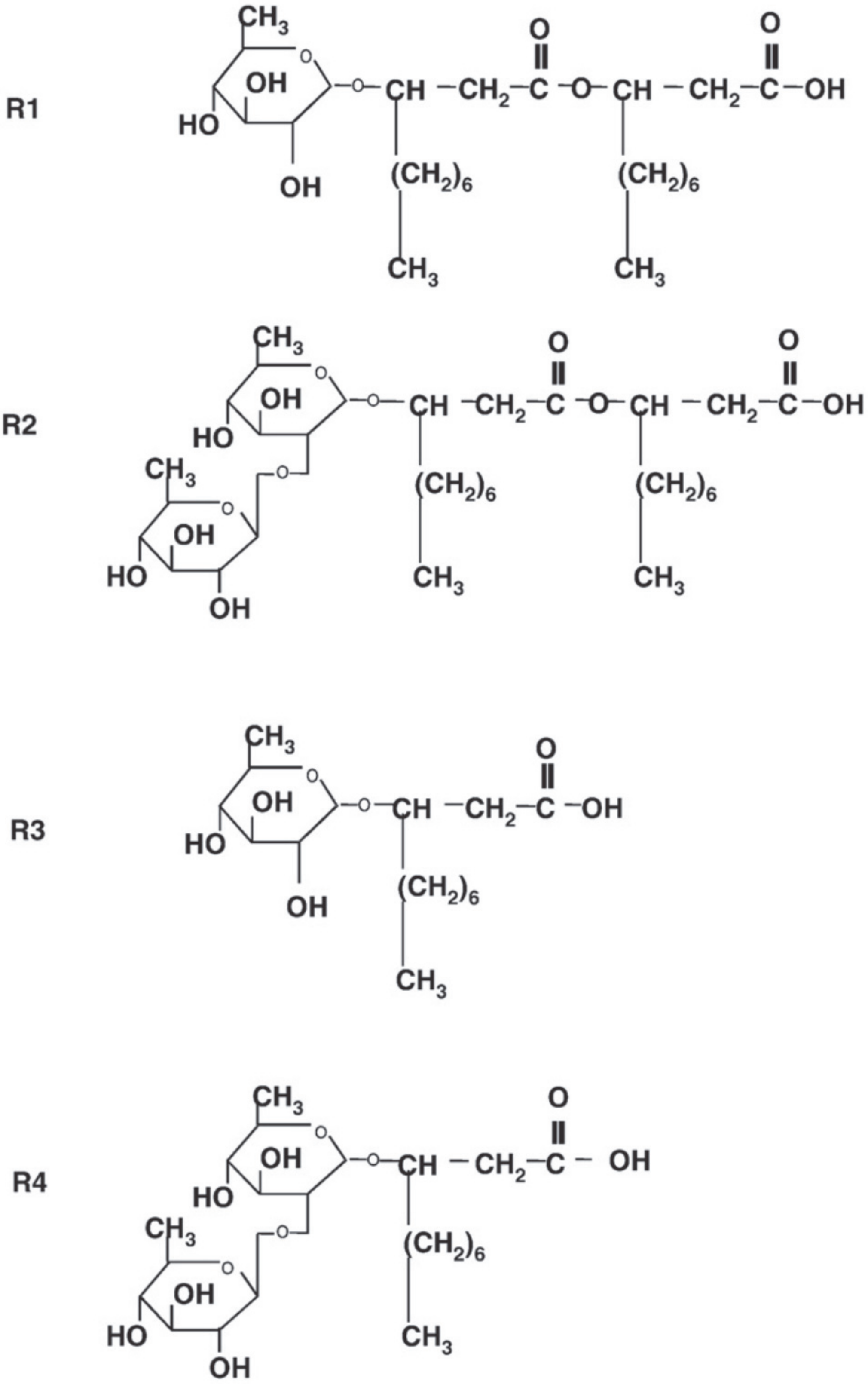


Figure 2-11: Chemical Structure of Rhamnolipids (Mulligan, 2009).

2.7 Micellar Enhanced Ultrafiltration

Micellar enhanced ultrafiltration (MEUF) is a new version of ultrafiltration membrane (Ghosh and Bhattacharya, 2006). The aim in micellar enhanced ultrafiltration is to enlarge the size of pollutant molecules to prevent them from passing through the membrane. This occurs to binding without micelles, which are formed by a suitable surfactant (Deriszadeh *et al.*, 2010). In the MEUF process, surfactants have an opposite charge with the heavy metal ions(Ghosh and Bhattacharya, 2006). When surfactants with a concentration more than critical micelle concentration (CMC) are added to an aqueous solution, they form large amphiphilic aggregate micelles (Khosa *et al.*, 2011). Electrostatic interaction captures heavy metal cations in the external part of the micelles and then the ultrafiltration membrane prevents them from passing through. Those heavy metals which cannot be captured and are free surfactant monomers pass through the ultrafiltration membrane (Landaburu-Aguirre *et al.*, 2010).

MEUF has some advantages such as high removal efficiency, low energy consumption and small space is needed because it has a high packing density (Rahmanian *et al.*, 2011). Like other technologies, MEUF has some drawbacks. For instance, anionic surfactants are costly because of their high CMC and they impose a large operating cost on the process. For solving this problem and economizing the MEUF process, it is better to recover the surfactants (Landaburu-Aguirre *et al.*, 2010).

Generally, the productivity of removing the heavy metals by MEUF depends on some parameters such as the characteristics and concentration ratio of surfactant and metals, pH, flow rate, and membrane pore size (Juang *et al.*, 2010).

As Cr (VI) is much more toxic than Cr (III), it is better to be reduced to Cr (III) which is also an essential trace element for human and animals. On the other hand, Cr (III), in high concentration is also very toxic and often converts to Cr (VI) in wastewater treatment processes and this shows the importance of removing both Cr (III) and Cr (VI) to protect the environment and human health (Konczyk *et al.*, 2010). Based on the reasons mentioned earlier, reduction and micellar enhanced ultrafiltration as the methods for reducing hexavalent chromium to trivalent chromium, and removing trivalent chromium from water and rhamnolipid as the biosurfactant and reducing agent seemed to be good candidates to study the removal of the two forms of chromium as carcinogenic and toxic contaminants from water.

3 Materials and Methods

3.1 Chemicals

The potassium dichromate $(K_2Cr_2O_7)$ 95 % was used as a source of hexavalent chromium in this study. This reagent metal salt was provided by Fisher Scientific Co.

Nitric acid (66-70%) and sodium hydroxide (NaOH) were purchased from Fisher Scientific Co. as an acid and base respectively. For adjusting the pH, HNO_3 (0.5 N) and NaOH (0.5 N) were used.

The used biosurfactant was rhamnolipid (JBR 425) from Jeneil Biosurfactant Co., USA. This biosurfactant was a liquid solution which contained 25% of rhamnolipid. Some of the properties of the rhamnolipid are illustrated in Table 3-1

Table 3-1: Physical and Chemical Properties of JBR 425 (Jeneil Biosurfactant Co., 2007)

Property	Value
Surface Tension	29 mN/m
Interfacial tension	0.3 mN/m
pH	6.5 – 7
Specific Gravity	1.05– 1.06
Odor	Soapy
Appearance	Amber solution
Solubility in Water	Soluble at neutral pH
Suitable Diluents	Water and most common alcohols
Volatility	Not volatile
Stability	Stable at room temperature

3.2 Instruments

3.2.1 Ultrafiltration System

The QuixStand BenchTop System (Figure 3-2) (M series from A/G Technology Corporation) was used for separation of Cr (III) which was attached to the surface of micelle from the solution of chromium-rhamnolipid. The system included a feed reservoir, peristaltic recirculation pump, inlet pressure gauge, hollow fiber cartridge (Xampler cartridge), retentate outlet, outlet pressure gauge, sampling valve, and backpressure valve.

3.2.2 Peristaltic Pump

The peristaltic pump that was included in the ultrafiltration system to pump the fluid was purchased from Watson-Marlow Company (313 S).

3.2.3 Xampler™ Cartridge

The hollow fiber cartridge which was used in QuixStand BenchTop (Ultrafiltration System) was purchased from A/G Technology Corporation. A bundle of polysulfone fibers which are parallel inside a plastic housing forms the cartridge. Molecular Weight Cut-Off (MWCO) is an important parameter in classification of ultrafiltration membranes. The MWCO that was used in the experiments was 10000 MWCO.

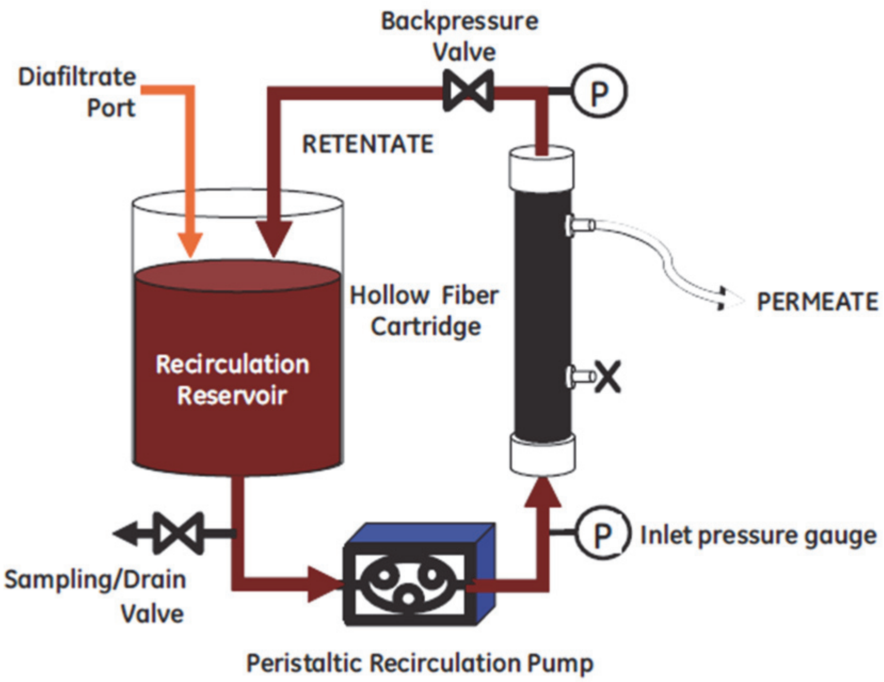


Figure 3-1: QuixStand BenchTop System Flow Diagram (GE Healthcare, 2004)

Figure 3-2: QuixStand BenchTop System (GE Healthcare, 2004)

3.2.4 Miscellaneous Instruments

Additional instruments used in this research are as follows:

- pH meter: The pH was measured by using the AR25 Dual Channel pH/Ion Meter from Fisher Scientific Co.
- Shaker: The used shaker was AROS 160 adjustable reciprocating orbital shaker.
- UV/ VIS: The used spectrometer was Perkin Elmer lambda 40 UV/VIS spectrometer. It characterizes a double-beam and all reflecting optical system.
- ICP-MS: Inductively Coupled Plasma-Mass Spectrometry (Agilent model 7500ce) for measuring the concentration of total chromium.
- Tensiomat 21: The Tensiomat 21 which was purchased from Fisher Scientific Company was utilized for measurement of the apparent surface tension and interfacial tension of liquids.
- Traceable Manometer/Pressure/Vacuum Gauge: The traceable manometer/pressure/vacuum gauge was purchased from Control Company. The device is able to show gauge and differential pressure/vacuum in eleven units and it has a response time of 0.5 seconds. The device has a simple hose fitting that allows the use of hose/tubing with different inside diameters ranging from 1/16 to 3/16 centimeters.

3.3 CMC Determination

There are several methods for measuring the critical micellar concentration of surfactants. Some of these methods are based on surface tension, conductivity, light scattering intensity, fluorescence intensity, NMR and X-ray scattering intensity (Shi *et al.*, 2011). The CMC of rhamnolipid was measured on the basis of the Du Nouy method by plotting surface tension versus biosurfactant concentration. In the Du Nouy ring method, the ring is placed in the solution and then pulled out. At the moment the ring breaks the surface of solution, the number on the dial determines the value of solution's surface tension. Rhamnolipid at various concentrations (0, 25, 50, 75, 100, 500, 1000 mg/L) was prepared and then the surface tension of each sample was measured by using the Surface Tensiomat® 21 from Fisher Scientific Company. The surface tension was drawn versus the concentration of rhamnolipid and then the CMC of rhamnolipid was determined by drawing the crossing point of two tangents of the graph. The curve is illustrated in Figure 4-1 in the next chapter.

3.4 Reduction Experiments

A stock solution of 2000 mg/L of Cr (VI) was prepared by dissolving 5.6577 g of potassium dichromate salt ($K_2Cr_2O_7$) in 1 liter of distilled water. Batch experiments were included of studying the reduction of Cr (VI) by rhamnolipid at different pHs, Cr (VI) and rhamnolipid concentrations. The prepared samples were shaken at 60 rpm for 24 hours to reach the equilibrium and then were centrifuged and examined. The initial and final concentrations of hexavalent chromium were determined by UV/VIS spectrometer based on the colorimetric method for measuring the concentration of Cr (VI) in water

(EPA SM 3500 - Cr D). In this method, 1,5-diphenylcarbazide was added to the samples containing Cr (VI) to reach a reddish purple color and then the amount of absorbance was measured at a visible wavelength of 540 nm and based on the calibration curve which was prepared, the concentration of Cr (VI) in solutions were determined. The equation used to calculate the percentage of hexavalent chromium reduction was:

$$\%Cr\ (VI)_{reduction} = \frac{Cr\ (VI)_{initial} - Cr\ (VI)_{final}}{Cr\ (VI)_{initial}} \times 100\%$$

3.4.1 Study of pH

As pH is a very important factor in reduction of Cr (VI), the effect of different pH values was verified. Precipitation of rhamnolipid occurs at pH 5.5 and therefore the samples were prepared at pH 6, 7, 8, 9 and 10. Each test was in triplicate and the final volume of samples was 50 mL. Samples were shaken for 24 hours. The temperature, hexavalent chromium concentration, and rhamnolipid concentration were fixed at 23℃, 10 mg/L and 0.5% respectively. Adjustment of pH was done by using 0.5 NaOH and 0.5 HNO_3 and the initial and final concentrations of Cr (VI) were measured by UV based on colorimetric method.

3.4.2 Study of pH Without Rhamnolipid

The method in this experiment was identical with what it was done in the test of study of pH in previous section. The difference was not adding the rhamnolipid in the samples which were prepared in 50 mL. They were shaken for 24 hours before measuring the concentration of hexavalent chromium by UV. For adjusting the pH, 0.5 N NaOH and 0.5 N HNO_3 were used.

3.4.3 Study of Rhamnolipid Concentration

Different concentrations of rhamnolipid (0.05%, 0.1%, 0.2%, 0.4%, 0.5%, 1%, 2% and 4%) were prepared to determine the effect of rhamnolipid concentration on the reduction of hexavalent chromium. All samples were prepared at 10 mg/L concentration of Cr (VI) and pH of 6 and 23℃. The ultimate volume of each sample was 50 ml. After 24 hours of shaking, samples were centrifuged and analyzed by UV/VIS. The pH was adjusted by HNO_3 (0.5 N) and NaOH (0.5 N). Each test was in triplicate and the average was shown as the final result. The optimum concentration of rhamnolipid was the one at which the most Cr (VI) reduction was observed.

3.4.4 Optimization of Cr (VI) Concentration

In this experiment, different concentrations of Cr (VI) (10, 50, 100, 200 and 400 mg/L) were used at identical conditions (rhamnolipid concentration = 2%, pH 6 and T = 23 ℃) to determine the best concentration of Cr (VI) for a higher reduction percentage of Cr (VI). For each concentration three samples were prepared. Then rhamnolipid was added and the pH was adjusted by 0.5 N NaOH and 0.5 N HNO_3. The volume of all samples was 50 mL. All the samples were placed in the shaker for 24 hours, then centrifuged and analyzed by UV for measuring the concentration of Cr (VI) after reduction. Obviously, the concentration of sample at which the highest reduction occurred introduced the best concentration of hexavalent chromium.

3.5 Membrane Unit Experiments

These experiments were performed in batch mode. The initial volume of feed solution was 400 mL and the retentate stream was continuously recycling. At the optimized transmembrane pressure, the flux of water was measured before and after the experiment in order to verifying the fouling of the membrane. When the water flux was less than 85-95% of the flux of a new membrane, it was the time to clean the membrane. The process will be explained in the cleaning of ultrafiltration system section.

A stock solution of 2000 mg/L of hexavalent chromium was prepared by dissolving the potassium dichromate salt in distilled water and desired concentrations of Cr (VI) were prepared by dilution of the stock solution using the same water. Various molar solutions of rhamnolipid were prepared by dilution of rhamnolipid JBR 425 (25%) using the distilled water. Trivalent chromium was prepared by reduction of Cr (VI) and the reducing agent was rhamnolipid. The difference between the concentrations of total chromium and hexavalent chromium introduces the concentration of trivalent chromium in the solution after reduction. The amounts of total chromium and hexavalent chromium were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) Agilent model 7500ce at Loyola Campus and UV/VIS respectively. The feed solution included the initial Cr (III) and rhamnolipid in the reservoir was pumped by peristaltic pump into the ultrafiltration membrane and the retentate solution was returned to the feed reservoir after exiting the cartridge. Samples were gathered from the permeate, retentate and feed for measuring the concentration of Cr (III) by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The performance of MEUF system was examined by doing the mass balance. All experiments were done in 23 ℃ and pH 6. The control solutions were metal- free and rhamnolipid free. The flow loop was flushed by passing the distilled water through the system after each experiment.

Each test was repeated three times and the average was used as the final result.

3.5.1 Cleaning the Ultrafiltration Membrane

Cleaning the ultrafiltration system was done in seven steps. First, the retentate should be pumped out. Second, the system was flushed with double distilled water. In third steps, 0.5 N NaOH was recirculated for one hour at 50℃. Then it should be flushed by double distilled water for the second time. In the fifth step, NaOCl was recirculated through the system at 50℃ and pH 10-11 for one hour and flushing the system was done for the last time and in the last step, the collected sample from the permeate was analyzed for residual metal ions (El Zeftawy and Mulligan, 2011).

3.5.2 Study of Transmembrane Pressure (TMP)

For observation of the effect of TMP on the permeate flux, various TMP (40, 70, 100 and 150 kPa) were chosen. This experiment was done at 23 ℃ and pH 6. The feed solution contained trivalent chromium and 0.05% rhamnolipid. The permeate pressure was measured by traceable manometer/pressure/vacuum gauge and the TMP was determined based on the following equation:

$$\text{Transmembrane Pressure} = ((P_{inlet} + P_{outlet})/2) - P_{permeate}$$

Equation 3-1

The permeate flux was calculated by using Equation 3-2

$$\boldsymbol{Flux\left(\frac{L}{m^2.h}\right)=\left[\left.permeate\ flow\left(\frac{mL}{min}\right)\middle/_{Cartridge\ Area\ (m^2)}\right.\right]\times 0.06}$$

Equation 3-2

The cartridge area was 140 Cm^2 and the permeate flow was measured by using the flow meter for the permeate flow in the ultrafiltration system.

3.5.3 Temperature

In this experiment, the effect of temperature on the permeate flux was observed by using different temperatures (20, 25, 35 and 45℃) of the feed solution. The conditions such as room temperature, transmembrane pressure, and pH were constant and the solution included 10 mg/L of hexavalent chromium and 0.05% of rhamnolipid and the concentration of trivalent chromium was 2.6 mg/L. The measured flow rate by flow meter was replaced in Equation 3-2 and the permeate flux was calculated.

3.5.4 Fouling

Fouling plays an important role in the efficiency of the ultrafiltration membrane systems. It reduces the flux by time. Therefore, it was verified in this experiment as follows. The permeate flux was measured at various times (1, 5, 10, 12 and 20 min). The pH, TMP, temperature, pump speed, and concentration were fixed values during the experiment for aqueous solution of chromium-rhamnolipid.

3.5.5 Study of Rhamnolipid Concentration on Cr (III) Rejection

To see the influence of rhamnolipid (Jeneil Biosurfactant Co.) on removal of trivalent chromium in micellar enhanced ultrafiltration system, three different concentrations of rhamnolipid: 265, 530, and 1060 mg/L (0.025, 0.05, and 0.1%) were used at the pH 6, 23℃. For preparation of the trivalent chromium- rhamnolipid solutions, rhamnolipid was added to the 10 mg/L of Cr (VI) in different concentrations. The final volume was 400 mg/L. Each test was performed in triplicate and the samples were shaken for 24 hours and then centrifuged and analyzed. Then the initial concentration of Cr (III) was measured. Final concentration of Cr (III) in permeate flux was determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and UV. Various concentrations of rhamnolipid were prepared from rhamnolipid JBR 425 (25%). The rejection percentage of Cr (III) was calculated by Equation 3-3.

$$\boldsymbol{R}\ (\%) = \mathbf{1} - \left[\frac{\boldsymbol{C_P}}{\boldsymbol{C_F}}\right] \times \mathbf{100}\ \%$$

Equation 3-3

$R = Rejection$

$C_P = Permeate\ concentration\ of\ Cr\ (III)$, mg/L

$C_F = Feed\ concentration\ of\ Cr\ (III)$, mg/L

3.5.6 Rhamnolipid Behavior in Presence of Cr (III)

In this trial, the rejection percentage of rhamnolipid based on Equation 3-3 in the presence of Cr (III) was observed. This percentage illustrated the amount of rhamnolipid micelles which were passing through the membrane during the ultrafiltration of chromium-rhamnolipid solution. In other words, the rejection ratio of rhamnolipid indicates the productivity of the membrane. C_P and C_F are concentrations of rhamnolipid in the permeate and feed solutions respectively. The concentration of rhamnolipid in the permeate was determined by Tensiomat 21 according to the Du Nouy method which was explained in prior sections.

4 Results and Discussion

4.1 Introduction

This chapter includes two parts. In the first part, the results of the reduction of hexavalent chromium to trivalent chromium experiments are demonstrated and discussed and in the second part, the results and discussion of micellar enhanced ultrafiltration are presented.

Some of the experiments in the first part such as effect of the pH, rhamnolipid concentration, and initial concentration of Cr (VI) were done with JBR 425 to compare with the results of Ara (2007) performed with JBR 210.

4.2 Determination of Rhamnolipid Critical Micellar Concentration (CMC)

As it was mentioned in the previous chapter, this CMC was measured by determining the cross point of two tangent lines of the graph in Figure 4-1. In this experiment, the critical micellar concentration (CMC) of rhamnolipid was determined to be 30 mg/L. This CMC is the same as Clifford *et al.* (2007) and Wang and Mulligan (2009) reported for the rhamnolipid. The CMC of rhamnolipid varies from 10 to 230 mg/L.

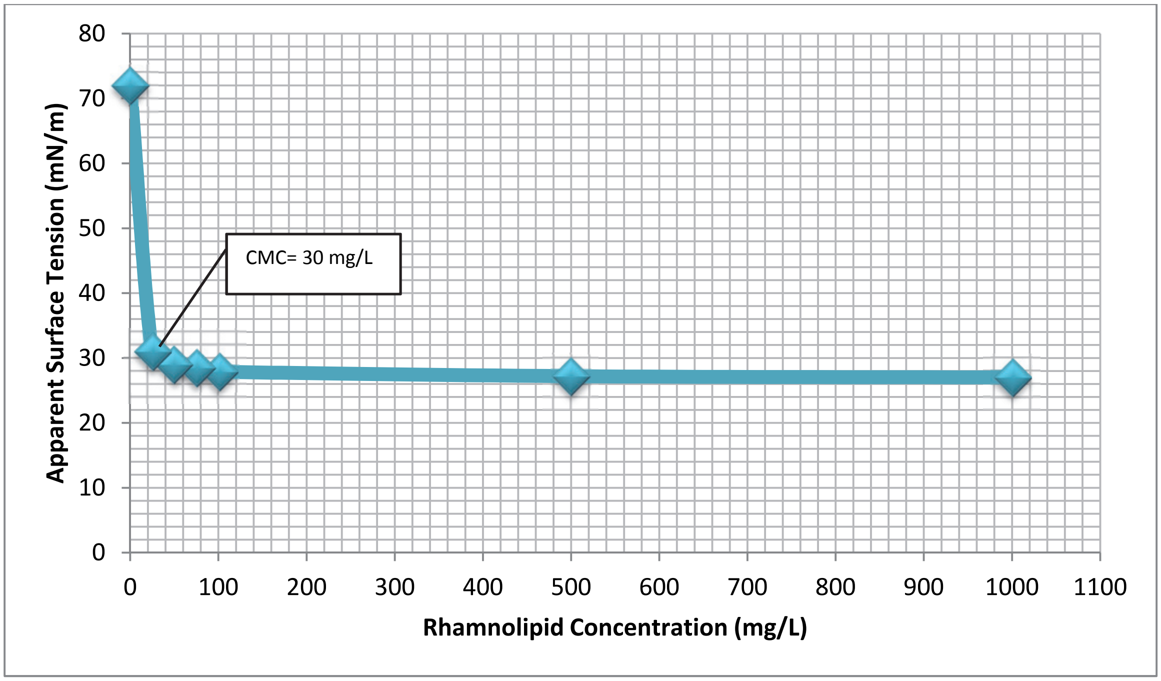


Figure 4-1: CMC Determination of Rhamnolipid

As Figure 4-1 demonstrates, the surface tension depends on the rhamnolipid concentration. When the concentration of rhamnolipid increases from 0 to 50 mg/L, the surface tension suddenly decreases from 72 to 29 mN/m and this high reduction of surface tension occurs merely by the small increase of the rhamnolipid concentration. This trend continues as the concentration of rhamnolipid grows from 50 mg/L to 1000 mg/L, but this time the surface tension lessening from 29 to 27 mN/m happens gradually, while rhamnolipid concentration is rising significantly (Zhang and Miller, 1992).

4.3 Reduction of Hexavalent Chromium to Trivalent Chromium

In this research, rhamnolpid as a reducing agent was used for converting hexavalent to trivalent chromium. Rhamnolipids have a potential to act as an electron donor in the reduction of Cr (VI) to Cr (III). They are a combination of $C_{26}H_{49}O_9$ and $C_{32}H_{58}O_{13}$. The oxygens in the form of carboxyl and phenolic functional groups in the structure of rhamnolipid are involved in the process of chromium reduction (Massara et al, 2007). In the following experiments, the effects of pH, initial concentrations of Cr (VI), and rhamnolipid concentrations on reduction of Cr (VI) to Cr (III) were investigated.

4.3.1 Effect of pH with and without Rhamnolipid

In this study the effect of different pH values (6, 7, 8, 9, and 10) on reduction of hexavalent chromium was evaluated. The experiments were done at room temperature, the concentration of Cr (VI) was 10 mg/L and the concentration of rhamnolipid was 0.5%. The reason for choosing this range of pH was based on the precipitation of rhamnolipid at pH 5.5 (Dahrazma and Mulligan, 2004).

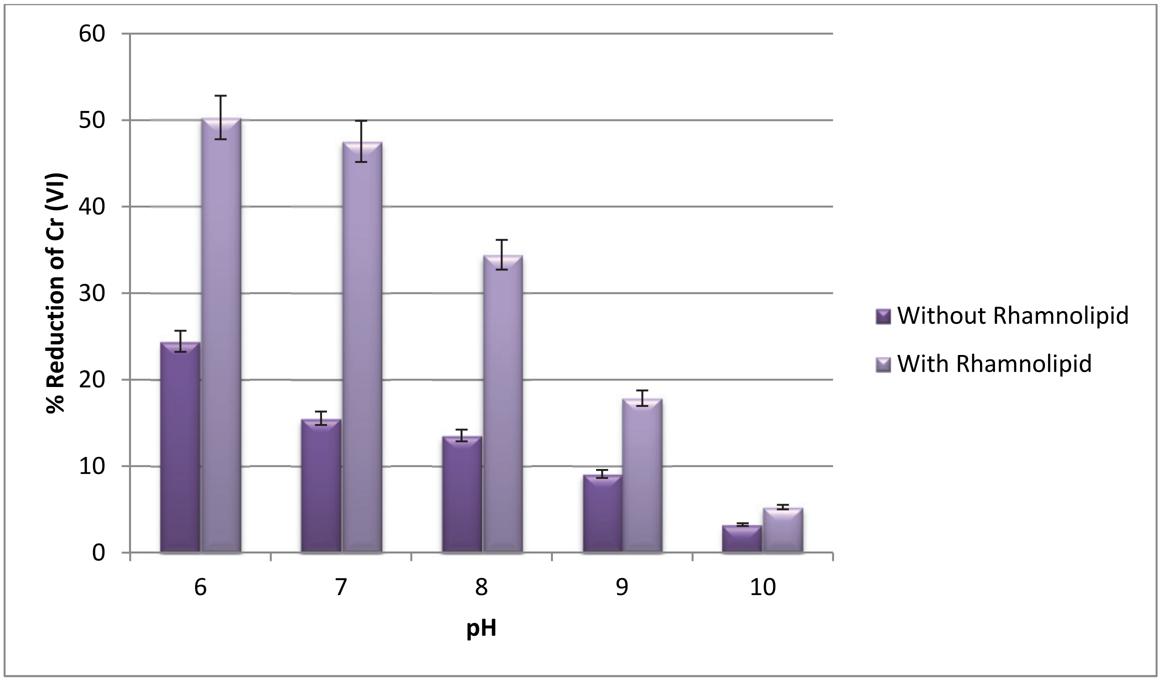


Figure 4-2: Effect of pH on Reduction of Cr (VI) with and without Rhamnolipid

As shown in Figure 4-2, the pH has a significant effect on the reduction of Cr (VI). By increasing the pH, the reduction of hexavalent chromium decreases. In other words, when the pH increases, the concentration of Cr (VI) in the solution increases (Xu *et al.*, 2004). Maximum reduction of Cr (VI) was 50.2% which happened at pH 6 and the reduction reached its minimum amount of 5.2% at pH 10. Two major oxidation states of Cr (VI) at pH 2 to 6 are $HCrO_4^- \ and \ Cr_2O_7^{2-}$. At pH more than 6, CrO_4^{2-} constitutes the main species. Therefore, the mechanism for removal of Cr (VI) at lower pH could be anion exchange and reduction. The reduction of hexavalent chromium decreases at alkaline pH because there is a competition between $CrO_4^{2-} \ and \ OH^-$ ions (Bhaumik *et al.*, 2012). Therefore, the optimized pH for reduction of Cr (VI) is 6.

In this experiment, the effect of pH without rhamnolipid was investigated as well. The test was done at room temperature, and 10 mg/L concentration of Cr (VI). pH was changed from 6 to 10. As Figure 4-2 shows, by increasing the pH, reduction of Cr (VI) decreases. The maximum reduction of hexavalent chromium in the absence of rhamnolipid in the solution was 24.4 % which occurred at pH 6. In Figure 4-2, a comparison between the reduction percentage of hexavalent chromium in two experiments (effect of pH on reduction of Cr (VI) with and without rhamnolipid) has been illustrated. The conditions such as temperature, and concentration of Cr (VI) were the same for both experiments. Figure 4-2 demonstrates a considerable increase in reduction percentage of Cr (VI) when there is rhamnolipid in the solution compared to the control and at increasing the pH, reduction percentage reduces.

The maximum reduction percentage of Cr (VI) occurred at pH 6 in both experiments, but in the first experiment (with rhamnolipid), the highest level of reduction was 50.3% while in the second one (without rhamnolipid), it was 24.4% which is approximately half of the maximum reduction in the first experiment. Figure 4-2 shows how using rhamnolipid is effective in the reduction of hexavalent chromium.

4.3.2 Effect of Rhamnolipid Concentration

In this experiment, reduction of Cr (VI) in presence of different concentrations of rhamnolipid was verified. The concentration of Cr (VI) and the pH were 10 mg/L, and 6 respectively. The test was done at room temperature. As Figure 4-3 shows, the reduction of hexavalent chromium increases when the concentration of rhamnolipid rises until it becomes constant at 2% and 4% of rhamnolipid in the solution.

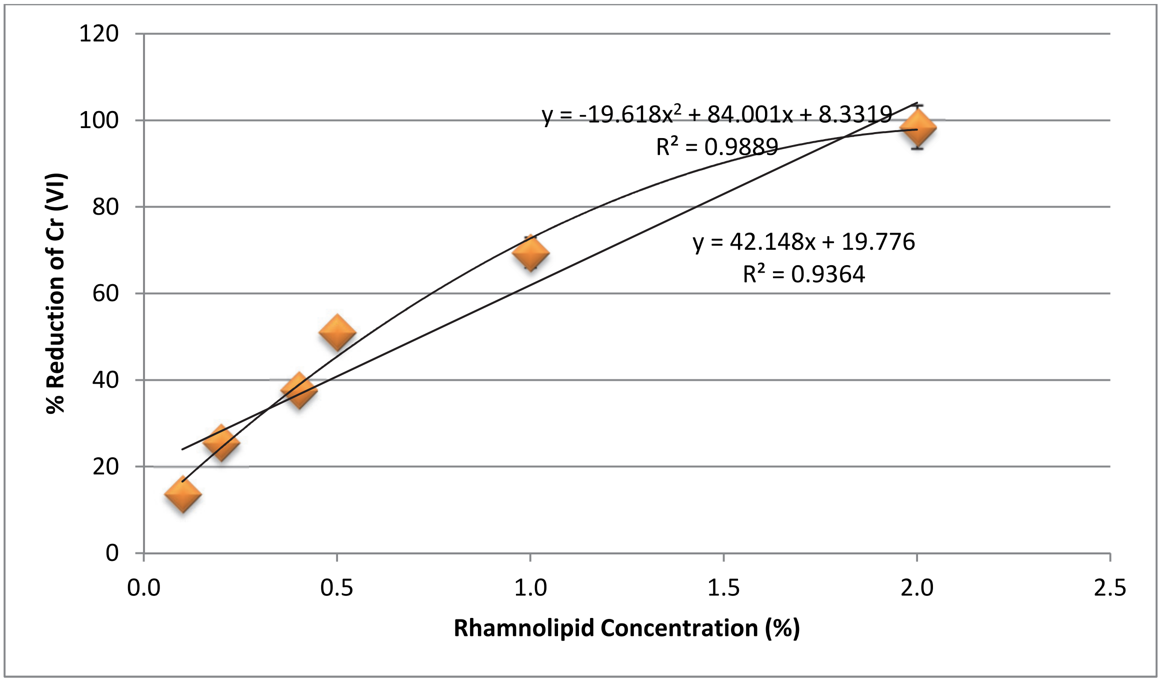


Figure 4-3: Effect of Different Concentrations of Rhamnolipid on Reduction of Cr (VI), pH 6, T= 23℃ and Cr (VI) = 10 mg/L solution

The lowest reduction was 13.8% and happened at 0.1% of rhamnolipid solution and the greatest percentage of Cr (VI) reduction was 98.3% which occurred at 2% rhamnolipid

(Figure 4-3). Therefore, the best concentration of rhamnolipid was 2% which means a rhamnolipid solution of 21200 mg/L is needed to reach the maximum reduction of Cr (VI) in a solution of 10 mg/L and it was determined that molar ratio of rhamnolipid required to reduce Cr (VI) was 189:1. In Figure 4-3, the polynomial second order trendline was selected as the best fit for the values because the coefficient of determination (R^2) for the second order was closer to 1 than that of the linear regression.

4.3.3 Effect of Initial Hexavalent Chromium Concentration

This experiment was performed to observe the effect of various initial concentrations of Cr (VI) on reduction of hexavalent chromium. In this experiment all conditions such as pH, temperature, and rhamnolipid concentration were constant except initial concentration of Cr (VI) which was changed from 10 to 400 mg/L.

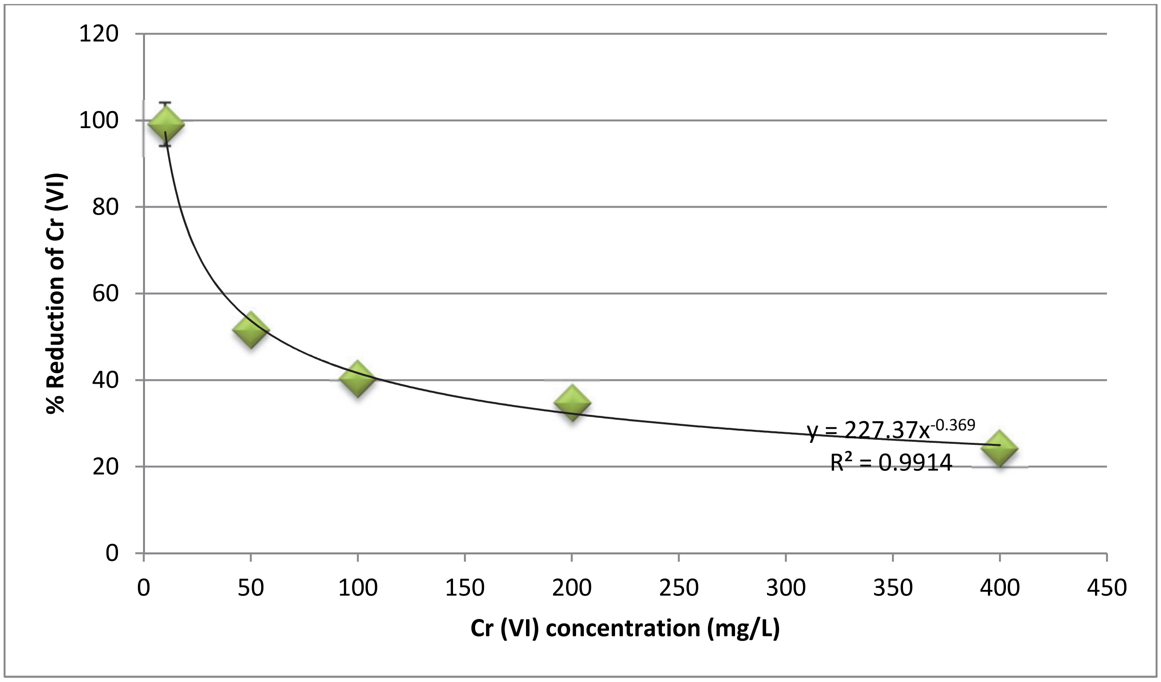


Figure 4-4: Effect of Different Initial Concentrations of Hexavalent Chromium on Reduction of Cr (VI)

The result is shown in Figure 4-4.

When the initial concentration of Cr (VI) increases the percentage reduction of Cr (VI) decreases. The highest level of reduction was 99.1 % at 10 mg/L and the minimum level was 24.3% which occurred at 400 mg/L. The maximum percentage reduction of Cr (VI) occurred at 10 mg/L of initial Cr (VI) and 2% rhamnolipid concentration. The same result was obtained in previous experiment, so this initial concentration of hexavalent chromium was chosen as the best initial concentration of Cr (VI).

4.4 Micellar Enhanced Ultrafiltration

4.4.1 Effect of Transmembrane Pressure on Permeate Flux

In this trial, the effect of different transmembrane pressures (40, 70, 100, and 150 kPa) was studied. The other conditions such as pH, temperature, initial concentration of trivalent chromium and the concentration of rhamnolipid were constant during the experiment. The molecular weight cut off (MWCO) was 10,000.

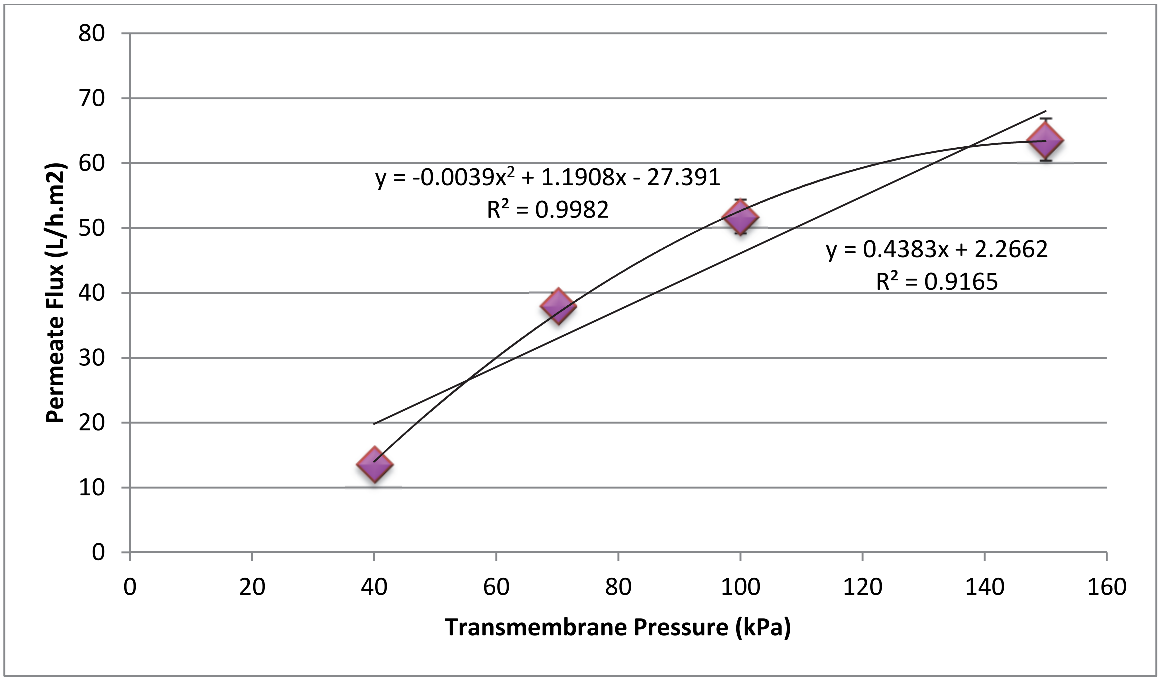


Figure 4-5: Effect of Transmembrane Pressure on Permeate Flux for Chromium-Rhamnolipid Solution, pH 6, Cr (VI) =10 mg/L, Rhamnolipid= 0.05 %

As Figure 4-5 shows, increasing the transmembrane pressure (TMP) has a positive effect on permeate flux which means by raising the TMP, the driving force increases as well, so the flux is heightened. Also, a linear relationship between TMP and flux illustrates that the concentration polarization is insignificant (Landaburu-Aguirre *et al.*, 2010). The lowest flux occurred at TMP= 40 kPa which was 13.6 L/h.m^2 and the highest flux was 63.5 L/h.m^2 at TMP of 150 kPa. For decreasing the operating costs, the lowest transmembrane pressure is desired (Danis and Aydiner, 2009). In Figure 4-5, the best fit was polynomial second order regression because of its R^2 value which was more than the linear trendline.

4.4.2 Effect of Temperature on Permeate Flux

In this experiment, the effect of temperature on flux was observed over a range of 20 ℃ to 45℃. The pH, initial concentration of Cr (III), transmembrane pressure and concentration of rhamnolipid were fixed.

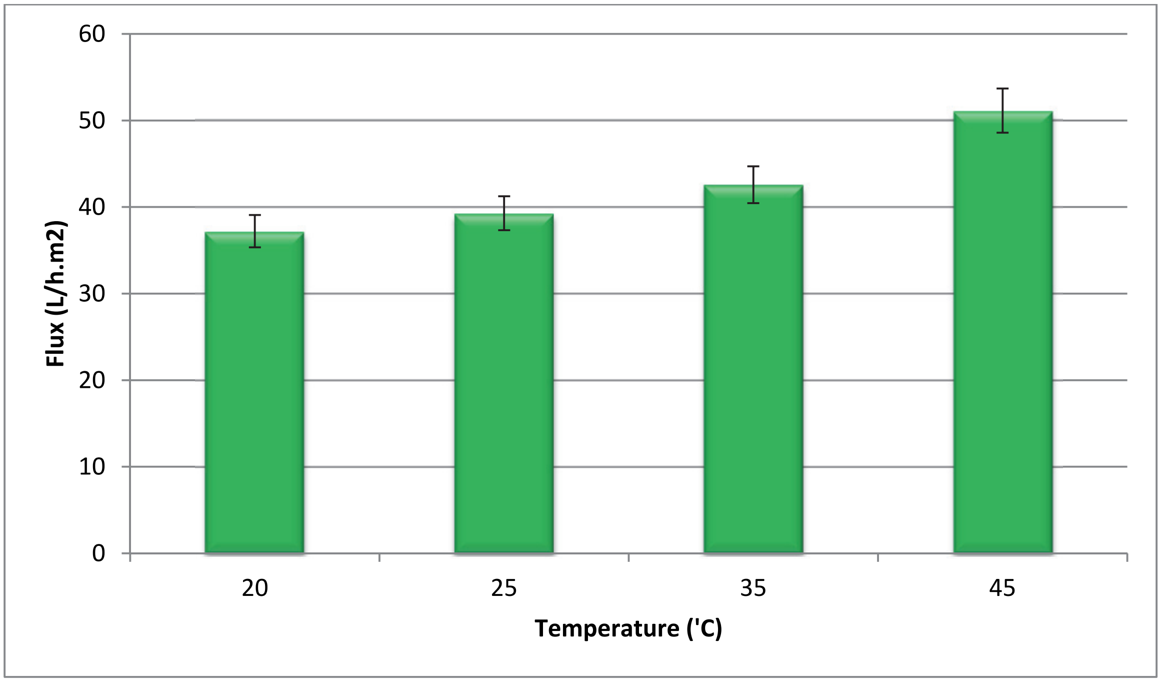


Figure 4-6: Effect of Temperature on Permeate Flux, pH 6, Cr (VI) = 10 mg/L, Rhamnolipid conc. = 0.05 %

As Figure 4-6 indicates, when temperature increases, the flux also increases. Although, the effect of the temperature on the permeate flux is not as significant as the transmembrane pressure effect, its trend is the same. By increasing the temperature, the viscosity of chromium-rhamnolipid solution decreases and this causes the flux to become higher. The maximum level of the flux was 51.1 L/$m^2.h$ at 45 ℃ and the minimum level was 37.2 L/$m^2.h$ at 20℃.

4.4.3 Effect of Fouling on Permeate Flux

In this experiment, the effect of fouling on permeate flux was investigated at different times (2, 5, 10, 12, and 20 min) while the other conditions such as pH, Cr (III) initial concentration, temperature and transmembrane pressure were constant during the test.

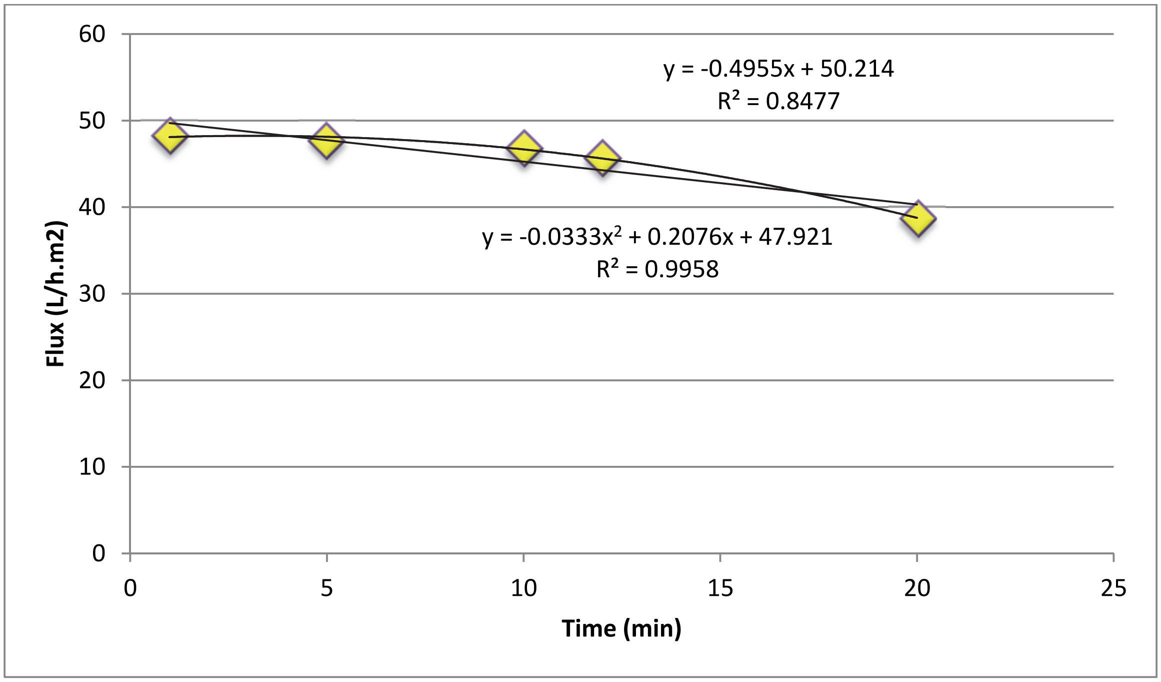


Figure 4-7: Effect of Fouling on Permeate Flux at pH 6, Cr (III) = 2.6 mg/L and Rhamnolipid = 0.05%

As Figure 4-7 shows, fouling is a key parameter in the performance of the micellar enhanced ultrafiltration. As the equations on the Figure 4-7 indicate, R^2 for the linear and polynomial second order regressions were 0.848 and 0.996 respectively. The greater R^2 signified the second order as a better fit for this graph.

4.4.4 Effect of Rhamnolipid Concentration on Cr (III) Rejection

In this trial, the rejection ratio of trivalent chromium at various concentrations of rhamnolipid (265, 530 and 1060 mg/L) was evaluated. The other parameters such as pH, TMP, and temperature were constant during the experiment. The molecular weight cut off (MWCO) of the membrane was 10,000.

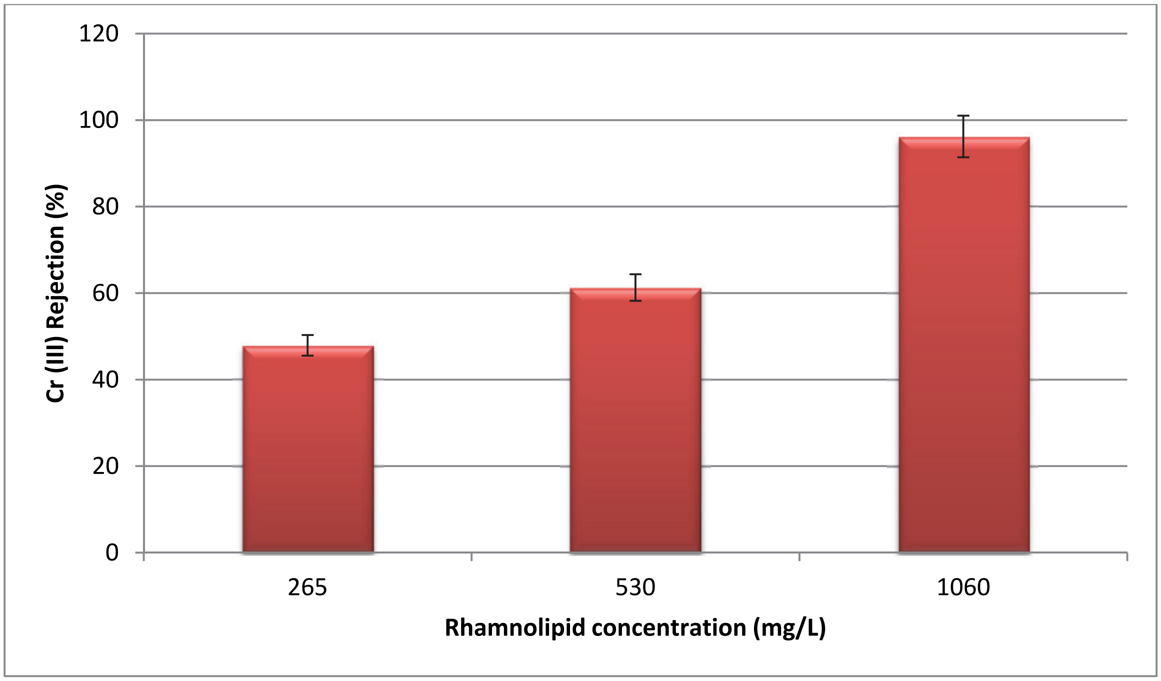


Figure 4-8: Rejection Ratio of Cr (III) Versus Rhamnolipid Concentration

Figure 4-8 illustrates that rejection of trivalent chromium is in direct relation with the concentration of rhamnolipid (JBR 425). This means by increasing the concentration of rhamnolipid from 265 mg/L to 1060 mg/L (0.025% to 0.1 %) the Cr (III) rejection increases as well. When the concentration of rhamnolipid in the feed solution increases, the concentration of micelles in the solution increases too, this increases the removal of Cr (III) ions by micelles. The highest rejection ratio of Cr (III) which was 96.2 % occurred at the rhamnolipid concentration of 1060 mg/L (0.1 %). Therefore, the molar ratio of rhamnolipid to metal was 36:1 to achieve this maximum removal.

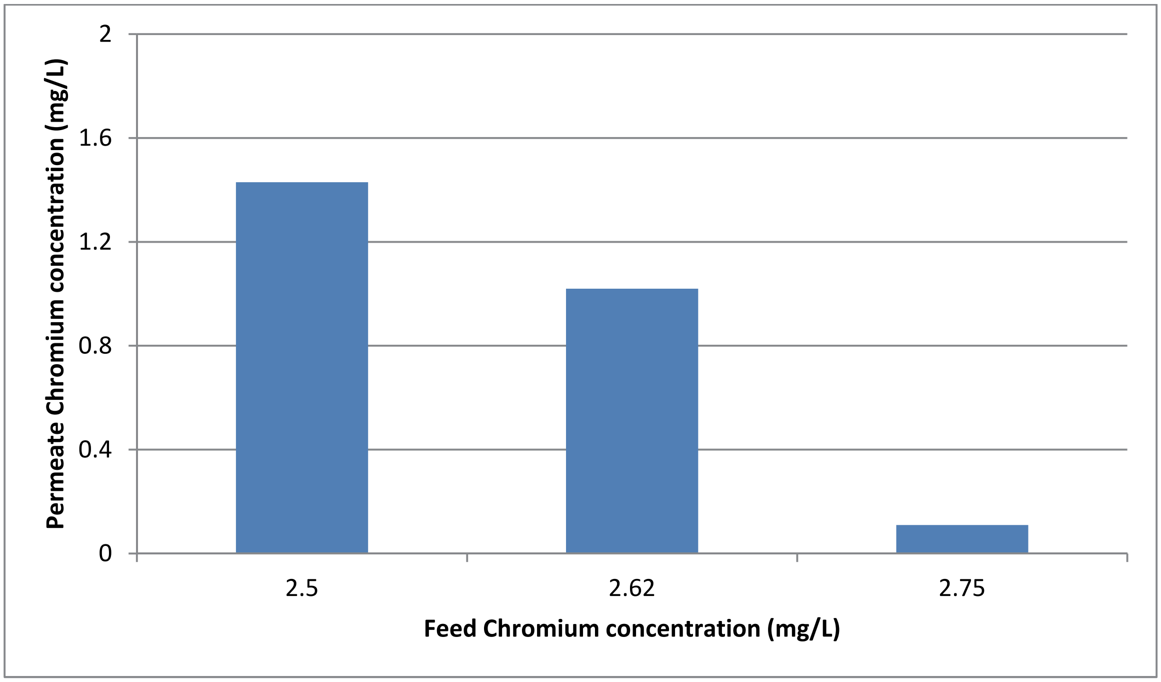


Figure 4-9: Feed Chromium Concentration Versus Permeate Chromium Concentration

Figure 4-9 indicates that the concentration of chromium in the permeate was reduced to below the allowable level of chromium in surface water (2 mg/L) based on EPA (Malaviya and Singh, 2011).

4.4.5 Rhamnolipid Behaviour in Presence of Cr (III)

In this experiment, rhamnolipid at different concentrations (265, 530, 1060 mg/L) was added to the feed solution containing Cr (III) to observe the effect of various concentrations of rhamnolipid on its concentration in the permeate solution. The concentrations were more than CMC of rhamnolipid which was measured before (30 mg/L). Temperature, pH, and the TMP were fixed during the experiments at 23 ℃, 6, and 70 kPa respectively.

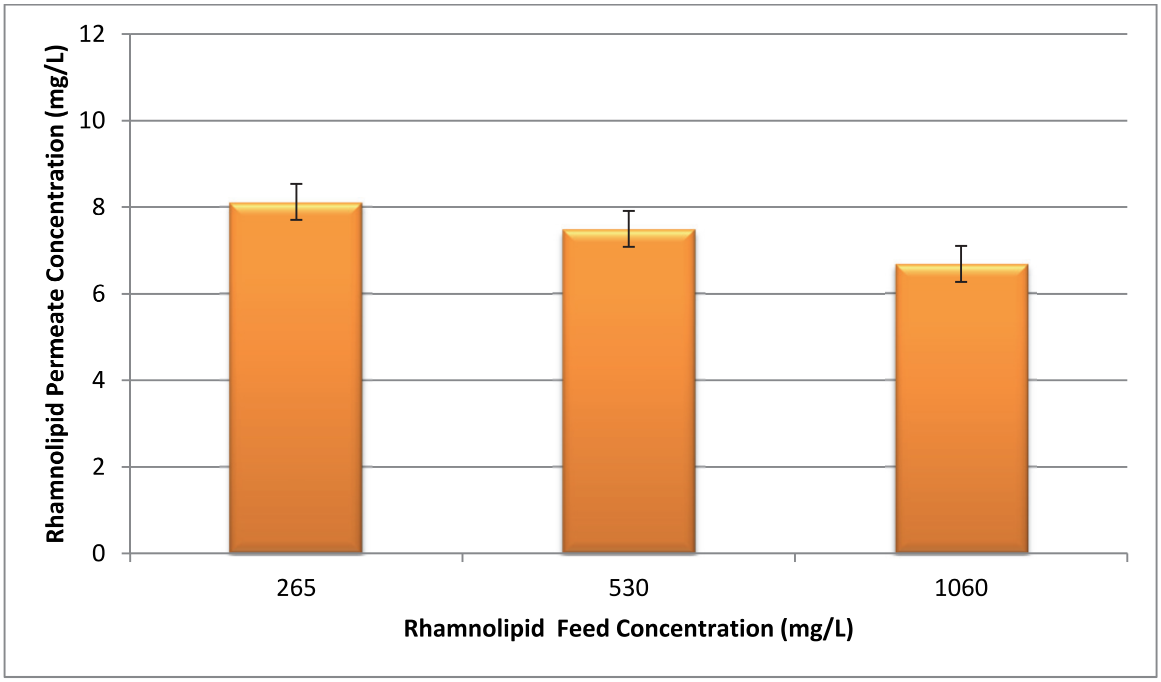


Figure 4-10: Rhamnolipid Permeate Concentration Versus Rhamnolipid Feed Concentration, pH 6, T= 23 ℃, TMP= 70 kPa

Figure 4-10 demonstrates a negative relationship between the rhamnolipid concentrations in the feed and permeate solutions. When the concentration in the feed increases, it declines in the permeate solution. The reason can be explained in this way that as the rhamnolipid concentration increases, more micelles form and just a few free monomers can pass to permeate. At the lowest rhamnolipid feed concentration (265 mg/L), the permeate concentration was 8.1 mg/L and at the highest rhamnolipid feed concentration (1060 mg/L), the permeate was 6.7 mg/L.

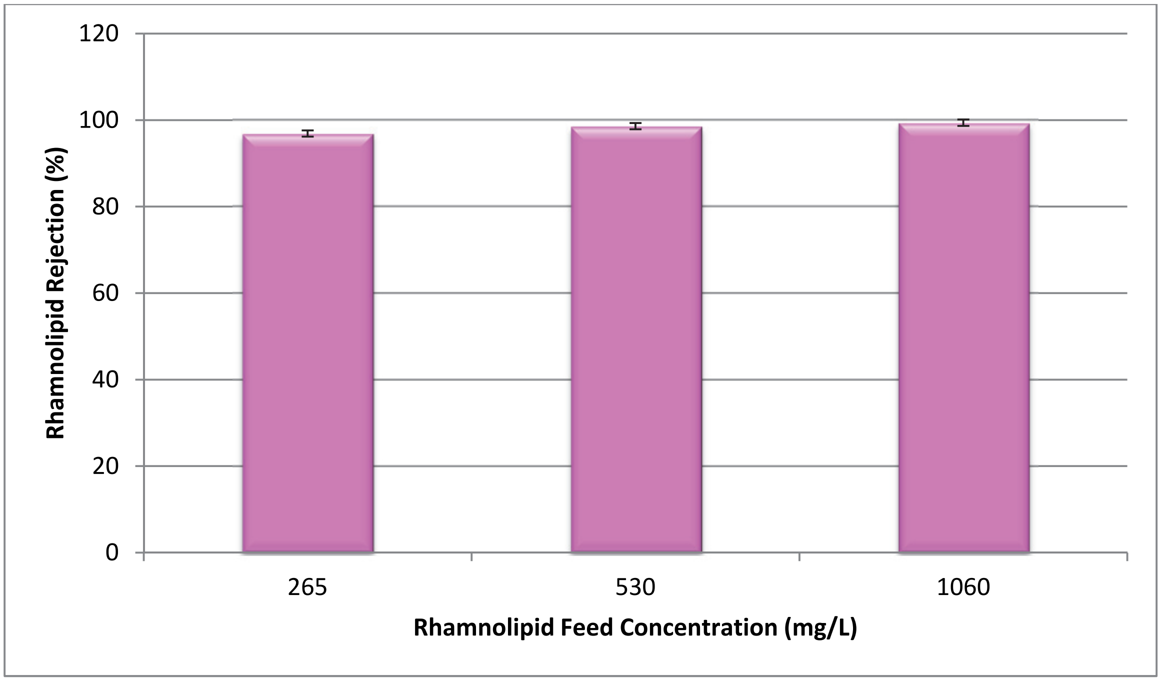


Figure 4-11: Effect of Rhamnolipid Feed Concentration on Rhamnolipid Rejection

As Figure 4-11 shows, the rhamnolipid concentration in permeate is negligible in comparison with its concentration in feed solution which is in agreement with what was explained above. The maximum rhamnolipid rejection ratio was 99.4 % that occurred in rhamnolipid feed concentration of 1060 mg/L. Figure 4-12 illustrates a negative correlation between rhamnolipid concentration and surface tension. As it was mentioned in the literature review, rhamnolipid decreases the surface tension and Figure 4-12 demonstrates it very well. These permeate concentrations are below the CMC which is expected as this mean that the monomers are retained by the membranes in the retentate.

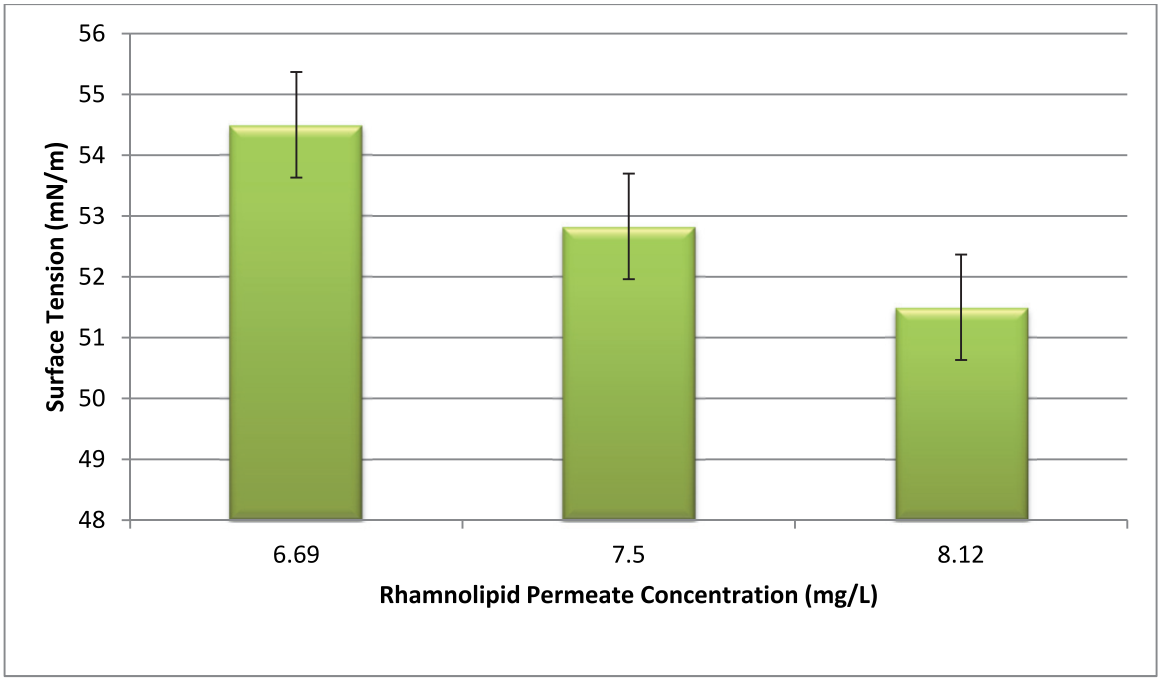


Figure 4-12: Surface Tension Versus Rhamnolipid Concentration

Consequently, Based on the results from this research, it has been observed that rhamnolipid (JBR 425) as a biosurfactant has an extremely good efficiency for removal of chromium as a toxic heavy metal from water by using biosurfactant micellar enhanced ultrafiltration system. These results can be compared to other authors such as El Zeftawy and Mulligan (2011) and Ridha (2010) who have reported similar results for efficiency of rhamnolipid to remove heavy metals. El Zeftawy and Mulligan (2011) achieved more than 99% removal of some heavy metals such as zinc, nickel, and cadmium from water by using rhamnolipid as a biosurfactant in the MEUF system and Ridha (2010) achieved 100% removal for copper from water by using the same method and in this research 96% removal was achieved for chromium.

5 Conclusions

5.1 Summary and Conclusions

The main purpose of this research was to evaluate the efficiency of rhamnolipid for removing hexavalent chromium and trivalent chromium from water. For removing the Cr (VI) and Cr (III), rhamnolipid was used as a reducing agent and a biosurfactant in micellar enhanced ultrafiltration (MEUF) system in this research respectively.

For reduction of Cr (VI), several factors such as pH, initial concentration of hexavalent chromium, rhamnolipid concentration were examined to find the best condition for each factor.

Rhamnolipid has a significant role in removing trivalent chromium by MEUF system, when it is used at a concentration more than its critical micellar concentration. The trivalent chromium ions were attached to hydrophilic parts of rhamnolipid. The aggregates could not pass through the membrane because they were bigger than pore sizes of the hollow fiber membrane filter while clean water with very low amount of rhamnolipid and chromium were passing through the membrane. In this part of the research, the influence of some of the operating factors such as transmembrane pressure (TMP), temperature, fouling, and rhamnolipid concentration on the performance of MEUF system was investigated. Also, the behaviour of rhamnolipid in the presence of trivalent chromium was observed.

Based on the experimental results, following conclusions were obtained from this work:

- The parameters such as pH, initial concentration of hexavalent chromium, and rhamnolipid concentration had various effects on the percentage of hexavalent chromium reduction. Initial concentration of Cr (VI) and pH by decreasing and rhamnolipid concentration by increasing had a significant effect on reduction of Cr (VI). Initial concentration of Cr (VI) = 10 mg/L, pH 6 and concentration of rhamnolipid= 2% were selected as the best conditions for reduction of Cr (VI) by rhamnolipid.

- Temperature and transmembrane pressure as the operating factors played important roles in the micellar enhanced ultrafiltration system process. By increasing both, the flux increased. However, the influence of transmembrane pressure was more than the effect of temperature on the flux.

- The concentration of rhamnolipid in presence of Cr (III) in the feed solution had a meaningful influence on the percentage of rhamnolipid rejection and concentration of rhamnolipid in permeate. Increasing the concentration of rhamnolipid in the feed solution raised the rejection percentage of rhamnolipid. However, the concentration of rhamnolipid in the permeate remained constant at all feed concentrations.

- Rhamnolipid as a biosurfactant in micellar enhanced ultrafiltration system was very effective for removing trivalent chromium from water.

5.2 Recommendations for Future Studies

- Evaluate the effect of rhamnolipid on reduction and removal of hexavalent chromium and trivalent chromium respectively from actual contaminated water and wastewater.

- Examine the influence of other biosurfactants and a mixture of them on removing Cr and Cr (III) by reduction and MEUF system.

- Determine the effect of other components such as Ca, Mg, Fe, and organic matter on the removal of chromium by using reduction and MEUF system.

- Determine fouling mechanisms in the removal of chromium by MEUF system and investigate a way to reduce it.

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