Simultaneous Removal of Benzene and Copper from Water and Wastewater Using Micellar-Enhanced Ultrafiltration

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ABSTRACT

Simultaneous Removal of Benzene and Copper from Water and Wastewater Using Micellar-Enhanced Ultrafiltration

Zaid Ahmed Mohammed Ridha

To remove metal ions and/or organic molecules from aqueous solutions is a difficulty commonly encountered in the treatment of contaminated water. Traditional ultrafiltration is usually used to separate the high molecular weight molecules and is ineffective in removing heavy metal ions or organic molecules with small molecular weights. Micellar-enhanced ultrafiltration (MEUF) is an effective technique to remove contaminants that traditional ultrafiltration cannot remove. Micellar-enhanced ultrafiltration makes use of the micellar properties of surfactant solutions to remove dissolved ions and/or organics from aqueous streams. Chemical surfactants have proven effective. However compared to biosurfactants they are toxic and create a secondary problem since part of the surfactant monomers frequently leak through the pores of membrane filters. This study is an attempt to examine the effect of rhamnolipid biosurfactant, JBR 425, on contaminant removal from aqueous solutions.

The required quantity of rhamnolipid to remove the copper ions as a heavy metal pollutant and benzene molecules as an organic pollutant separately has been determined for different concentrations of pollutants. This quantity, the molar ratio

(MR), was 6.25 to obtain a 100% rejection for the copper ions and 1.33 to obtain the same rejection of benzene molecules. When copper and benzene were mixed, these molar ratios have been either improved as in benzene molar ratio which was decreased from 1.33 to 0.56 or remained the same as in copper molar ratio but in all cases rhamnolipid JBR 425 proved of excellent efficiency in the removal of contaminants and a rejection of 100% has been obtained for copper and benzene either separately or simultaneously which is the objective of this study.

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CHAPTER ONE

INTRODUCTION

1.1 GENERAL REMARKS

One of the most considerable environmental problems in the world is water pollution [60]. This serious problem which threatens one of the main important sources of life, not only for human beings but also for the whole ecosystem, has been discussed in detail and many solutions have been applied to solve this important issue. Identifying the pollutants or contaminants which caused this significant problem is part of the solution; the other main part is to determine the treatment method. With focusing more on the solution part, these two parts have been discussed in this study specifically for benzene as an organic pollutant and copper as a heavy metal pollutant since they have been considered to be part of the water pollution problem as will be explained later in this chapter and the next one, the Literature Review chapter.

According to the National Pollutant Release Inventory-1999, the total releases of benzene from facilities that reported the largest on-site releases are 1,523.061 tonnes [15]. Benzene is widely used in industries and its releases result in quantifiable concentrations in a variety of media to which humans and other organisms may be exposed. The most important source of human exposure to the benzene in Canada is ambient and indoor air, food, and drinking water. Benzene has been revealed to cause cancer. It can cause undesirable effects at any level of exposure, so for this reason benzene is a "non-threshold toxicant", therefore, according to the Canadian Environmental Protection Act, benzene is believed to be "toxic" [20].

Copper is very abundant in the earth's crust and has very important properties in the same time. Therefore it is one of the major metals in most industries approximately. Because of this wide availability in nature and industry, the copper and its compounds can enter the water bodies and share in the water pollution problem [29]. The Canadian total releases of copper and its compounds are 1,265.328 tonnes as documented in National Pollutant Release Inventory-1999; this is only for the facilities that considered producing the largest on-site releases [15].

Generally the removal of contaminants or hazardous compounds from aqueous streams by conventional methods is not economical in the cases of huge volumes of dilute wastewaters that must be handled. Some existing methods of separating soluble compounds from a stream usually involve a phase change, as in distillation only, or distillation preceded by extraction. a number of treatment methods, such as adsorption, chemical precipitation, or oxidation and ion exchange, need a physicochemical treatment or pretreatment and are no longer environmentally acceptable due to the low level of pollutants or contaminants allowed in wastewater discharges. The high cost of precipitating and complexing agents and the probability of not separating all of the contaminants that need to be removed make this choice also not efficient [24].

To remove different organic and inorganic pollutants from aqueous solutions, micellar-enhanced ultrafiltration (MEUF) has been used. It has been found to be a capable method of removing low levels of pollutants like organic compounds and heavy metal ions [60].

Micellar-enhanced ultrafiltration (MEUF), a membrane separation process utilises surface active agents to form micelles that capture the contaminants to enhance the filtration process, has the capability to remove the organics and heavy metal ions either separately or simultaneously. This capability is not the only reason to select MEUF as a process to remove the contaminants.

The energy consumption of micellar-enhanced ultrafiltration is considered to be very low compared to the above conventional methods since the required energy is only for pumping water through the membrane filter and for the separation processes such as filtering and precipitation that are needed for polishing the permeate or surfactant recovery from retentate. For this economical reason besides its efficiency, the micellar-enhanced ultrafiltration (MEUF) could be an alternative of the high energy consumption techniques. The surfactant molecules that do not participate in micelle formation represent a disadvantage since these molecules can leak throughout the filter membrane into the flux of permeate [48]. To overcome this problem of secondary pollution, rhamnolipid has been utilised as a biological surfactant, (biosurfactant), instead of chemical surfactants in this research because of its biodegradability and low toxicity.

1.2 OBJECTIVE OF THIS RESEARCH

The utilization of surfactants obtained by chemical synthesis to remove the contaminants from aqueous solutions will solve a problem but it will create a new one since the chemical surfactant is toxic and non-biodegradable. To solve these two problems together, biodegradable surfactants (biosurfactants) have been used as an environmentally acceptable alternative for chemical surfactants. Therefore, the general objective of this research is to investigate and determine the ability of rhamnolipid biosurfactant (JBR425) to remove organic molecules and heavy metal ions either separately or simultaneously and to determine what the efficiency of that removal is.

The specific objectives of this research are to:

1. Determine the molar ratio (MR) of rhamnolipid biosurfactant to copper ions, as heavy metal contaminants, that reject 100% of the copper ions.

2. Determine the molar ratio (MR) of rhamnolipid biosurfactant to benzene molecules, as organic contaminants, that reject 100% of the benzene molecules.
3. Investigate the effect of presence of benzene on the 100% rejection molar ratio of rhamnolipid to copper.
4. Investigate the effect of presence of copper on the 100% rejection molar ratio of rhamnolipid to benzene.

1.3 ORGANIZATION OF THIS THESIS

This thesis consists of five chapters, a list of references, and appendices. The necessary theoretical background of micellar-enhanced ultrafiltration and the main related subjects have been discussed in Chapter two such as the important membrane filtration processes, the surfactants, and the micelle mechanisms of the contaminants removal. Chapter three includes the chemicals, methods, and the experimental design. In Chapter four, the results of conducted experiments are presented and discussed. The conclusions of this research and recommendations for future work are summarized in Chapter five. References are listed at the end of this thesis.

CHAPTER TWO

BACKGROUND AND LITERATURE REVIEW

2.1 INTRODUCTION

This background and literature review chapter reviews the current literature on the potential of rhamnolipid efficiency to remove simultaneously benzene and copper from aqueous streams and micellar-enhanced ultrafiltration system used for this reason. To facilitate the understanding of this study including this literature review, background knowledge on other surfactants and filtration systems is presented as well.

2.2 BENZENE

In 1825 Michael Faraday was the first to isolate the benzene from the liquid condensed by compressing oil gas [29]. All 12 atoms of benzene, C_6H_6, lie in a single plane Figure 2.1. Benzene is one of the natural petroleum components. However, it represents a small amount in most crude oils (less than 1.0% by weight). According to the Environmental Protection Agency (EPA) classification, benzene is a hazardous waste and under Section 11 of the Canadian Environmental Protection Act it is considered to be "toxic" [29], [20].

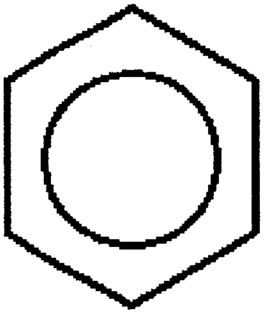


Figure 2.1 Benzene, C_6H_6, adapted from Kirk-Othmer Encyclopaedia [29]

2.2.1 IDENTITY, STRUCTURE, PHYSICAL AND CHEMICAL PROPERTIES

Benzene is a monocyclic, organic compound with the molecular formula C_6H_6 and a molecular weight of 78.11 g/mole. Benzene synonyms are benzol, carbon oil, coal naphtha and others. Benzene (CAS registry number 71-43-2) is a volatile, flammable, colorless liquid at room temperature with aromatic odour and it is readily miscible in many organic solvents like alcohol, chloroform, acetone and ether [29], [20]. The main physical and chemical properties have been summarized in Table 2.1.

2.2.2 PRODUCTION AND USES

Benzene is a natural component of petroleum. In gasoline, benzene acts as an octane-enhancer and an anti-knock agent. An estimated 35 000 megalitres of gasoline were consumed in Canada in 1989 (Priority Substances List Assessment Report, Benzene, 1993). An estimated 540,000 tonnes of benzene are present in the gasoline sold annually in Canada; most of this benzene is burned during normal engine operation. The total yearly consumption of benzene in Canada, including both

Table 2.1 Benzene's most important physical and chemical properties, adapted from Environment Canada, Environmental Protection Service, Hemond and Fechner-Levy [41], [14], [23].

PROPERTY	**VALUE**
MELTING POINT	5.53 °C
BOILING POINT	80.1 at 101.3 kPa
FLASH POINT	-11 °C
HENRY'S LAW CONSTANT	0.24
DENSITY	873.7 kg/m^3
WATER SOLUBILITY	820 – 2167 mg/l at 25 °C
VAPOUR PRESSURE	10.1 – 13.2 kPa at 25 °C
Log Kow	1.56 – 2.69
HEAT OF COMBUSTION	41.8 kJ/g at 25 °C

isolated benzene and benzene as a component of gasoline, is therefore estimated to be 1,362,000 tonnes. In Canada in 1990, 765,000 tonnes of isolated (purified) benzene were produced, 131,000 tonnes were imported while 74,000 tonnes of these were exported, leads to a domestic use for the rest quantity of isolated benzene (Priority Substances List Assessment Report, Benzene, 1993). In Canada, most isolated benzene is produced from petroleum sources. Commercially benzene can be produced from natural gas condensates, petroleum, or coal [20]. Benzene is used in a very wide sector of industries like oils, greases, resins, inks, paints, and motor fuels, a fat solvent, also in the manufacture of plastics, synthetic rubber, textiles, detergents, explosives, packing materials, pharmaceuticals, disinfectants, and pesticides. In Canada, benzene is used mainly for the production of ethylbenzene, styrene, cumene, cyclohexane, and maleic anhydride [5].

2.2.3 NATURAL AND ANTHROPOGENIC SOURCES AND RELEASES

Benzene exists in nature at low concentrations and is a crude oil component. One of the main sources of benzene for water and soil are petroleum spills and seepage. For groundwater, benzene enters from rocks. Forest fires, volcanoes considered to be important sources for air and the volatile chemicals from plants too. The emissions from natural sources is believed to be generally low in comparison with anthropogenic sources, however the levels of these emissions are unknown. Other sources of benzene to the environment include the use, production, storage, emissions from fuel combustion, and transportation of isolated benzene, crude oil, and gasoline.

In 1985, according to the estimations 34,150 tonnes of benzene were released into the Canadian atmosphere (Priority Substances List Assessment Report, Benzene, 1993). Surface water contamination could result from spills of petroleum and chemical products besides the industrial and municipal effluents. It is estimated that every year in Canada, 34,000 tonnes of benzene are released into the atmosphere, 1000 tonnes into water, and 200 tonnes onto soil [20]. The National Pollutant Release Inventory-1995 shows that benzene is one of the 25 highest releases by weight through Canada [5].

2.2.4 ENVIRONMENTAL FATE

In soil, benzene biodegrades mainly under aerobic conditions. In surface water, it rapidly volatilizes to the air, biodegrades with a half-life of a few days to weeks, or reacts with hydroxyl radicals with a half-life of several weeks to months. In air, it reacts with hydroxyl radicals, with a half-life of about 5 days [62].

2.2.5 CANADIAN ENVIRONMENTAL LEVELS AND DRINKING WATER GUIDELINE

According to 586 samples of ambient air surveyed between 1988 and 1990, the mean concentrations of benzene were range from 1.2 to 14.6 $\mu g/m^3$ in ten Canadian cities. 41.9 $\mu g/m^3$ was the maximum 24-hour average concentration and 4.4 $\mu g/m^3$ the overall mean concentration [41]. Surface water concentrations of benzene in general are low. Non-detectable to 5 µg/L are the concentrations documented in Canadian water quality guidelines (CCREM ,1987) for several locations in the St- Lawrence River and Ontario [41], [5]. Normally, the concentrations of benzene were in the range of 50–200 µg/L. The maximum contaminant concentration of 500 µg/L [41]. Benzene levels were approximately below the detection limits (2 µg /kg dry soil) in two-thirds of the soil samples. Soil samples concentrations collected from a Port Credit petroleum plant and a refinery in Oakville, Ontario were less than 0.002 to 0.16 µg /kg dry soil [41]. The maximum acceptable concentration (MAC) for benzene in drinking water is 0.005 mg/L (5 µg/L) [17].

2.2.6 EFFECTS ON HUMANS

Death may be caused by acute exposure to 65 g/m^3 of benzene. Acute exposure primarily affects the central nervous system at high concentrations of benzene. High benzene concentrations (325 mg/m^3) may ultimately result in leukaemia [62].

2.3 COPPER

Early humans used copper as one of the first metals they discovered and knew. About 8500 B.C. was the earliest use of copper. The records indicate that this was in northern Iraq. Copper has an average estimated concentration of 55 mg/kg in the earth's crust which is one of the most available metals. Copper is a preferred metal for conductors and especially for electrical wires [29].

For adults, the dose between 4 and 400 mg of copper (II) ion per kg of body weight is considered to be the acute lethal dose, based on suicide cases and data from accidental ingestion. Copper ions, at lower doses, can cause symptoms like vomiting, headache, and diarrhoea [62].

2.3.1 IDENTITY, STRUCTURE, PHYSICAL AND CHEMICAL PROPERTIES

Copper (CAS registry number 7440-50-8), has the symbol Cu and the atomic number 29. Absorption caused by optical transitions in copper structure give its distinguishing red color. Copper forms monovalent and divalent cations, cuprous and cupric respectively. It is a transition metal and shows stability in its metallic state. ^{63}Cu (69.2 % abundance) and ^{65}Cu (30.8% abundance) are the two stable isotopes. General copper compounds are copper (II) acetate monohydrate, copper (II) chloride, copper (II) nitrate trihydrate, copper (II) oxide, and copper (II) sulphate pentahydrate [29], [62], and [21].

2.3.2 PRODUCTION AND USES

Copper as a metal is ductile and has a good electrical and thermal conductivity. Copper is used to make pipes, valves, electrical wiring, and building materials. It is used in alloys like bronze and brass and also in the coatings. Food additives are one of the copper compound uses and they can be part of animal feeds and fertilizers. Compounds of copper are used in algaecides, insecticides, wood preservatives, petroleum refining, and in electroplating [62].

2.3.3 NATURAL AND ANTHROPOGENIC SOURCES AND RELEASES

Natural Flux to Atmosphere and Oceans

Copper enters the natural environment since it is abundant in the earth's crust by different mechanisms like volcanic dust, ashes, and by riverbed erosion [29].

Table 2.2 Pure copper physical properties, adapted from Kirk-Othmer Encyclopaedia [29].

Property	**Value**
atomic weight	63.546
atomic volume, cm^3/mol	7.11
mass numbers, stable isotopes	63 (69.1%), 65 (30.9%)
oxidation states	1, 2, 3
density, g/m^3	8.95285 (pure, single crystal) 8.94 (nominal)
thermal conductivity, W/(m)(K)	394
electrical resistivity at 208C, nΩ_m	16.70
melting point	1358.03 K (1084.88^{0}C)
heat of fusion, kJ/kg	212
boiling point	2868 K (2,595^{0}C)
surface tension, mN/m	1300 (99.99% Cu, 1084^{0}C, vacuum)

Mining operations of copper have all the time been faced with the problem of large solid-waste disposal. Wastes of course contain small copper concentrations [29]. Introduction of the metal to freshwater and saltwater bodies by rainwater runoff is the main concern because aquatic life may be harmfully affected. Many sources can supply copper to rainwater runoff which enters water bodies through the breakdown of copper-based antifouling paints, chemicals, wood preservatives, landfills as seepage, or through the use of copper algaecides in lakes and ponds [29].

Anthropogenic Sources and Releases

In 2007, the Canadian total on-site releases of copper were 801 tonnes and the total disposals were 2541 tonnes [63].

2.3.4 ENVIRONMENTAL FATE

In water, elemental copper fate is complex and affected by many factors such as pH and dissolved O_2. Copper surface oxidation produces copper (I) oxide or hydroxide. Mainly, copper (I) ion is consequently oxidized to copper (II) ion. The copper (II) ion is the common oxidation state in pure water. Removing dissolved copper ions from solution has to be done with precipitation or sorption to organic solids, clays, and minerals. Clay materials strongly adsorb copper depending on pH values. Collected copper from wastewater during treatment is in the sludge. Copper removal from the atmosphere is by rain, snow, gravitational settling, and dry disposition [62].

2.3.5 LEVELS IN THE CANADIAN ENVIRONMENT

The average daily exposure for copper in Canada has been reported in Table 2.3.

Table 2.3 Average values of the daily exposures, Adapted from Health Canada website [22].

Route	Concentration (mg/day)	% of total	mg/kg body weight/day
Food	2.200	89.14	0.0314
Water	0.264	10.70	0.00377
Air	0.00070–0.004	0.16	0.00001–0.00006
Total	**2.468***	**100.00**	**0.0352***

(* Maximum exposure assumed to be through air.)

2.3.6 EFFECTS ON HUMANS, ACUTE EXPOSURE

Based on data obtained from accidental ingestion and suicide cases, adults acute lethal dose is 4 - 400 mg of copper(II) ion per kg of body weight. human beings ingesting high doses of copper could have many symptoms like gastrointestinal bleeding, haematuria, intravascular haemolysis, hepatocellular toxicity. Copper ions may cause symptoms, at lower doses, typical of food poisoning such as diarrhoea, headache, and vomiting. After 15–60 minutes of exposure, symptoms usually appear. Children could be affected with lower levels depending on some studies [62].

2.4 MEMBRANE SEPARATION PROCESSES

According to many factors like membranes driving forces or areas of application, membrane separation processes can be very different from each other. The main membrane separation processes have been summarized in Table 2.4 with their operating principles and applications [57].

Table 2.4 Membrane separation processes, their driving force, and applications. Adapted from Ullmann's Encyclopaedia [57].

Separation Process	Membrane type used	Applied driving force	Applications
Microfiltration	symmetric porous membrane, pore radius 0.1–10 μm	hydrostatic pressure, 0.05 – 0.2 MPa	water purification, sterilization
Ultrafiltration	asymmetric porous membranes, pore radius 2 – 10 nm	hydrostatic pressure, 0.1 – 0.5 MPa	separation of molecular mixtures
Reverse osmosis	asymmetric skin-type solution-diffusion membrane	hydrostatic pressure, 1 – 10 MPa	sea- and brackish water desalination
Dialysis	symmetric porous membrane	concentration gradient	artificial kidney
Electrodialysis	symmetric ion-exchange membrane	electrical potential	water desalination

2.4.1 REVERSE OSMOSIS

To separate low molecular mass compounds, particles, and macromolecules from a solvent, generally water, reverse osmosis is considered a very suitable technique. Feed solutions frequently have a considerable osmotic pressure that should be overcome by applied hydrostatic pressure. Solutions osmotic pressure holding low molecular mass solutes can be rather high even with low solute concentrations. The difference of hydrostatic pressure is the driving force in this process. The structure of the membrane is asymmetric. The membrane side which faces the feed solution has a dense barrier layer [57].

2.4.2 ULTRAFILTRATION

Macromolecules are the retained components by an ultrafiltration separation process with membranes of asymmetrical structure mostly and skin layer pores of 2 – 10 nm in diameter. Pressure gradient is the driving force and convective flux passing through pores is dominating the mass transport. The separation in ultrafiltration depends on the difference of hydrostatic pressure and the asymmetric porous membrane with small pores compared to membranes of the microfiltration process. The retained components are of molecular weight between 5000 and several million Daltons [57].

2.4.3 MICROFILTRATION

When the required particles to be separated from a solvent have a diameter range of 0.1 - 10 μm, the microfiltration then is the suitable process to separate these particles by a mechanism that is derived from a sieving effect. The applied hydrostatic pressure differences range is 0.05 – 0.2 MPa and the pressure gradient is the driving force for the mass to transport across a membrane with a symmetric porous structure [57].

2.4.4 DIALYSIS

When a specific solute is transferred through a membrane to a receiving or stripping solution by the influence of the concentration gradient, this is called dialysis. Compound separation depends on diffusivity differences in the matrix of the used membrane [57].

2.5 CLASSIFICATION OF FILTERS

2.5.1 DEPTH FILTERS

Depth filters are filters where the particle removal or filtration occurs inside the depths of the material matrix of the filter. This matrix is composed of randomly oriented fibres or beads. These filters are used in dead-end filtration [7].

2.5.2 SCREEN FILTERS

Screen filters have the capability of retaining the particles on their surfaces. These filters have a structure which is in general more rigid, continuous, uniform, and with a defined pore size [7].

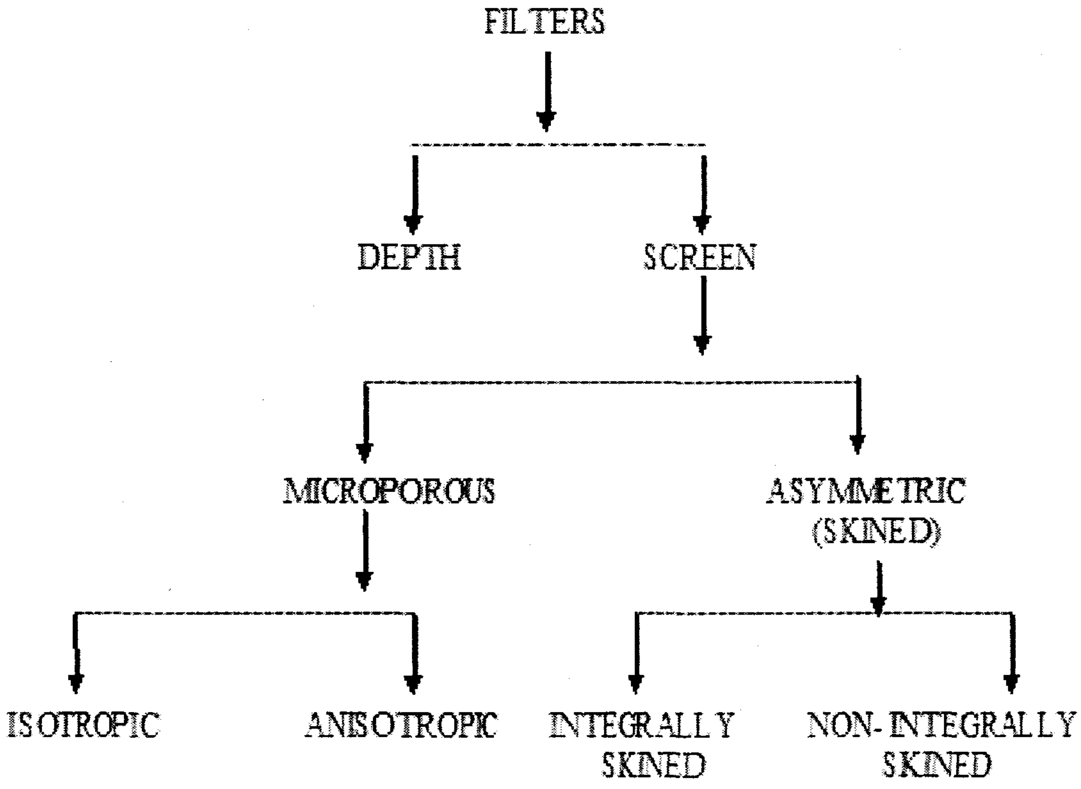


Figure 2.2 Filter classification. Adapted from Cheryan [7].

2.6 MEMBRANE CLASSIFICATIONS

According to the ultrastructure, as in Figure 2.2, screen filters are classified as asymmetric and microporous which are subdivided in to isotropic (uniform pore size throughout the membrane body) and anisotropic (non-uniform size of the pore on membrane surfaces). Asymmetric membranes which can be called skinned membranes can be subdivided in to integrally skinned and non- integrally skinned [7].

2.6.1 CONVENTIONAL MODULES OF ULTRAFILTRATION

One of the important requirements of modules is to be removed and replaced with simple procedures since the membranes have short operation life time. Another important factor is the way that these modules control the feed fluid flow turbulent flow is the main operational flow that used for the most devices utilize cross-flow membrane, so the conduit diameter should not subjected to a sudden contraction or expansion in order to get a low energy consumption design. These contractions and expansions have very less importance in laminar flow modules than the limiting factor in this kind of flow which is the smallest passage diameter in which fluid has to flow [43]. Table 2.5 shows the main modules of ultrafiltration with their advantages and disadvantages. The other filtration technologies where these modules are used as shown below are MF (microfiltration), UF (ultrafiltration), NF (nanofiltration), and RO (reverse osmosis).

Table 2.5 Main modules of ultrafiltration with their advantages and disadvantages. a: microfiltration; b: ultrafiltration; c: nanofiltration; d: reverse osmosis. Adapted from Zeftawy [13] and Cheryan [8].

The Module	Advantages	Disadvantages	Technology
Hollow Fiber	Backflush, very compact, low capital cost	Limited choices, not recommended for viscous systems, easy to be fouled	MF [a], UF [b], NF [c], RO [d]
Tubular	Toleration of high suspended solids feed, easy to clean with mechanical ways	High energy, high capital cost, large space, high hold-up	MF, UF, NF, RO
Spiral Wound	Compact system, low capital cost, many sizes	No backflush, possibility of dead spots	UF, NF, RO
Flat Plate (Plate-and-Frame)	Many choices, Low energy	Expensive, Consume time to replace	MF, UF, RO

2.7 CROSS-FLOW AND DEAD END FILTRATION

The definition of filtration is the separation of components, two or more, from a stream of fluid [8]. As illustrated in Figure 2.3, filtration equipment can be operated in two modes. The first one is the dead-end filtration where the feed solution is pumped towards the filter directly resulting in one stream leaving the membrane which is usually called the permeate. The second mode is the cross-flow filtration where the feed solution is pumped tangentially to the surface of used membrane resulting in two streams, the permeate and the retentate. Cross-flow could be used when easy recovery of solids is required since it decreases the build up layer on the surface of the membrane [7].

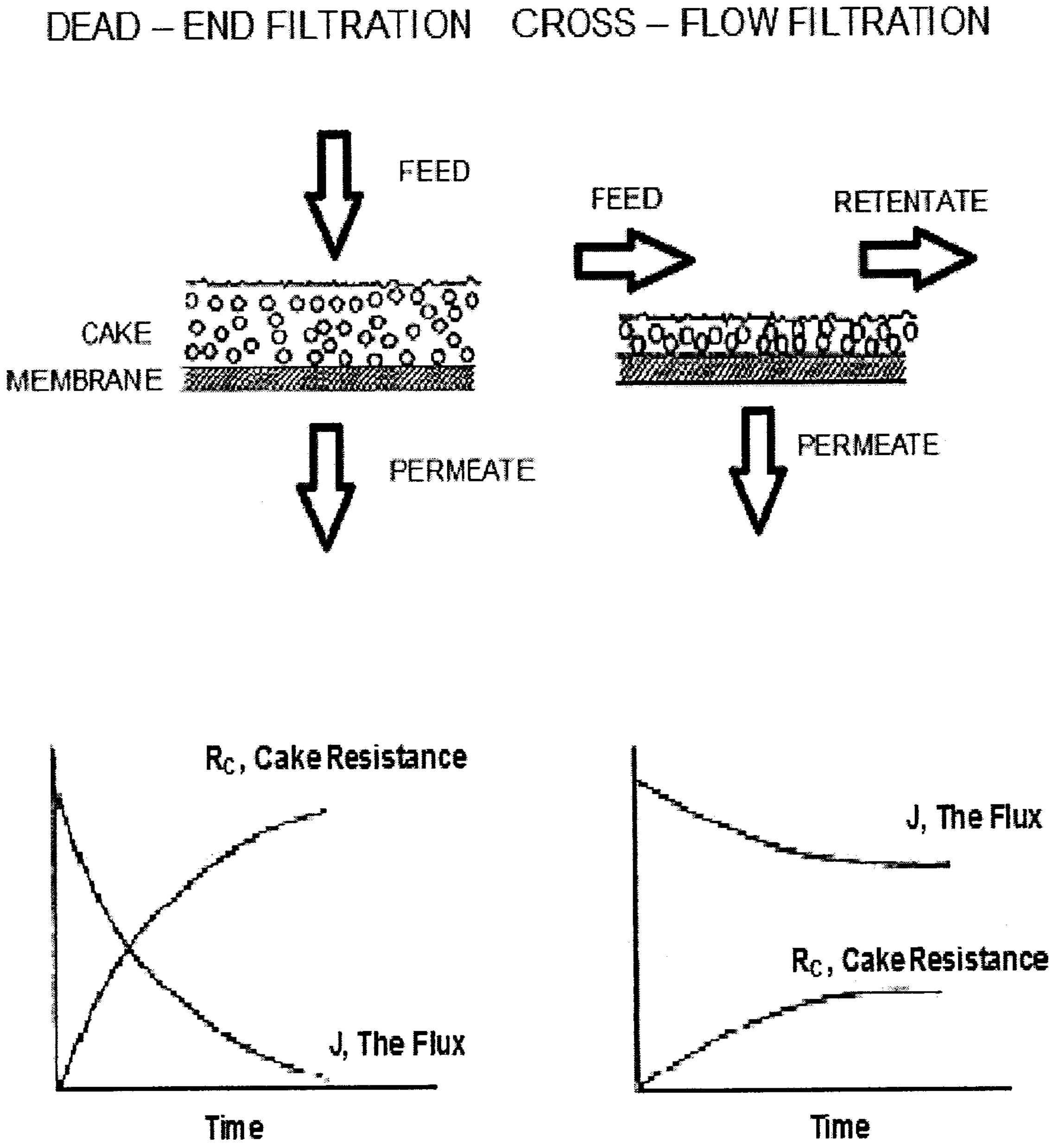


Figure 2.3 Dead-end (conventional) and cross-flow filtration. Adapted from Cheryan [7].

2.8 MICELLAR ENHANCED ULTRAFILTRATION (MEUF)

To separate high molecular weight molecules, traditional ultrafiltration could be one of the recommended choices. However separation of small molecular weight molecules such as metal ions or organic solutes with the same way is not effective. When a surfactant is added at higher than its critical micelle concentration (cmc) to a polluted water, the surfactant starts to form large amphiphilic aggregates (micelles). These micelles are capable of attracting metal ions on their surfaces and solubilizing organic molecules in their interiors.

If this solution of polluted water and surfactant is passed through a membrane with pores smaller than micelles volume then this filtration is called the micellar-enhanced ultrafiltration (MEUF), as shown in Figures 2.4 and 2.5, and the permeate will be a clean water with very low concentrations of surfactant monomers and unbound organic molecules or metal ions [53].

There are a lot of potential applications for an improved, separation process of low energy to remove dissolved metals or organics from water in present industries. Such applications may include toxic metal separation from or valuable metal concentration from dilute streams industrial wastewater streams [18].

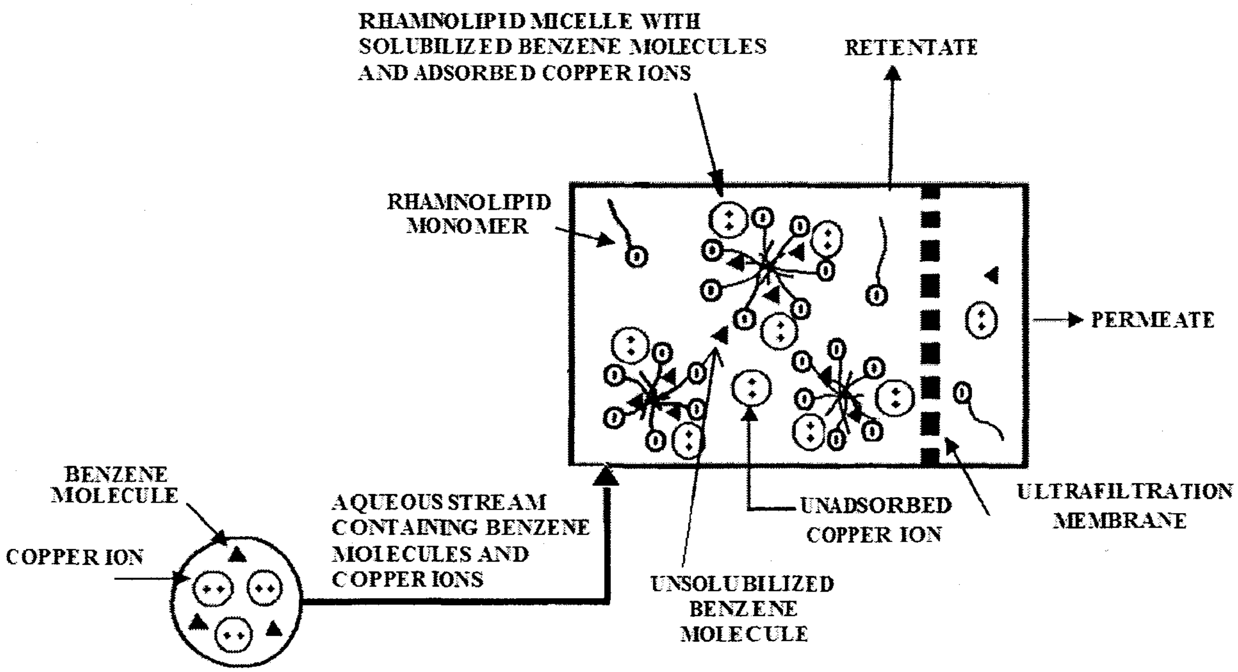


Figure 2.4 Simultaneous removal of Cu (II) ions and benzene molecules from aqueous solutions utilizing Micellar-Enhanced Ultrafiltration (MEUF system). Adapted from Misra et al. [36].

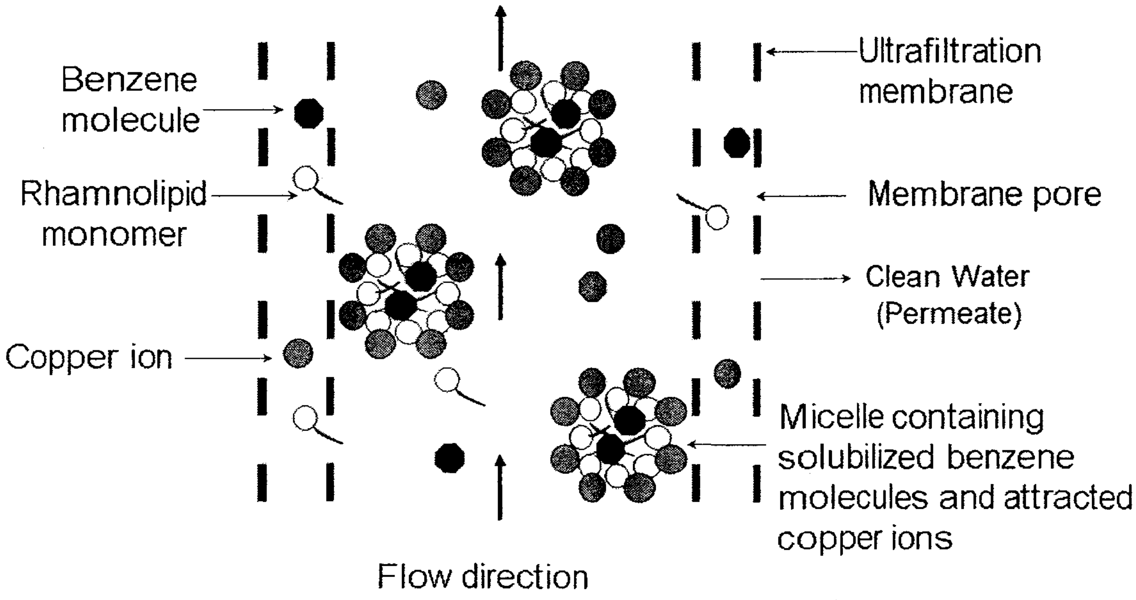


Figure 2.5 Simultaneous removal of Cu (II) ions and benzene molecules from aqueous solutions utilizing Micellar-Enhanced Ultrafiltration (inside the membrane).

2.8.1 CRITICAL MICELLE CONCENTRATION (CMC)

When surfactant solution remain below a critical value of concentration (CMC) as shown below in Figure 2.6, then surfactant molecules will continue to be mainly in a single monomer state. At the CMC or higher values the single molecules start to form the micelles. As shown in Figure 2.7, the hydrophilic heads are aligned at the micelle surface and exposed to the aqueous phase while the hydrophobic tails are gathered inside the micelle [51]. Micelles are in dynamic equilibrium of association-disassociation with monomers in the solution which represents the difference between micelles and other colloids [37]. In general, micelles are spherical for many common ionic surfactants in the absence of electrolyte and concentrations ranging from the cmc to a minimum of 10 times the cmc [9]. Micelles consist of monomers that average 30-200 monomers [50].

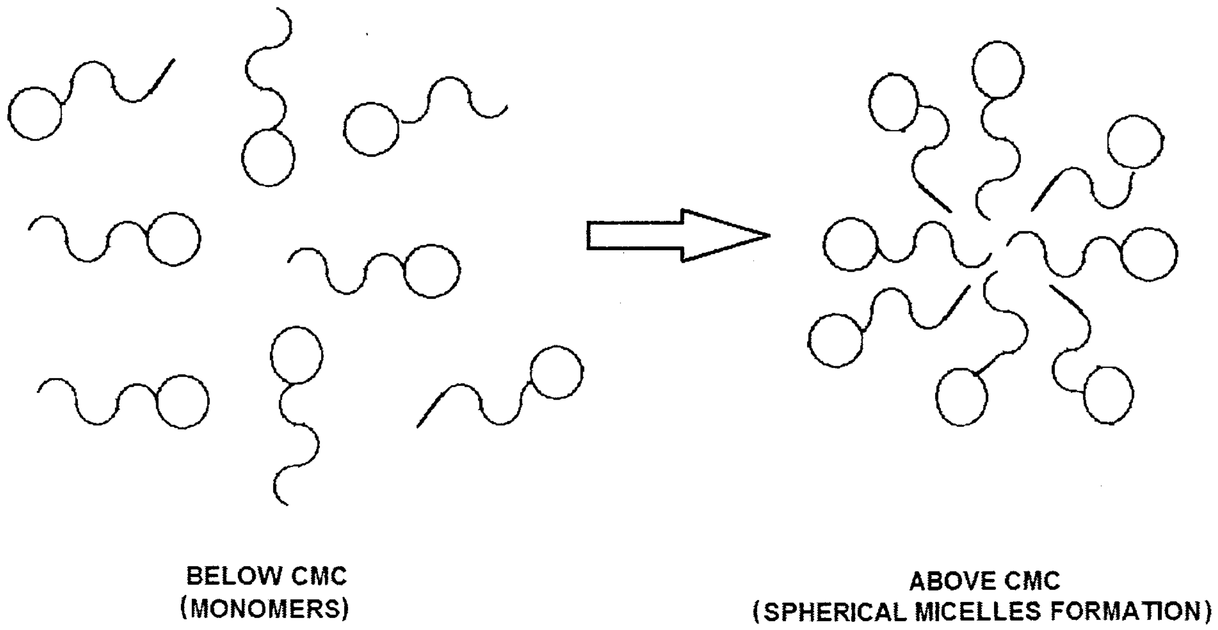


Figure 2.6 Surfactant below and above cmc (micelle formation). Adapted from Hudson [25].

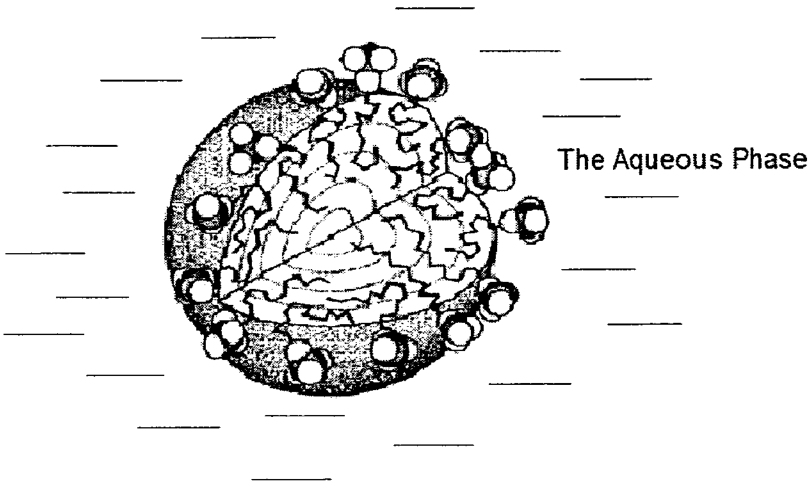


Figure 2.7 Micelle in aqueous solution. Hydrophobic tails are gathered inside the micelle and hydrophilic heads are exposed to the aqueous phase. Adapted from Tadros [54].

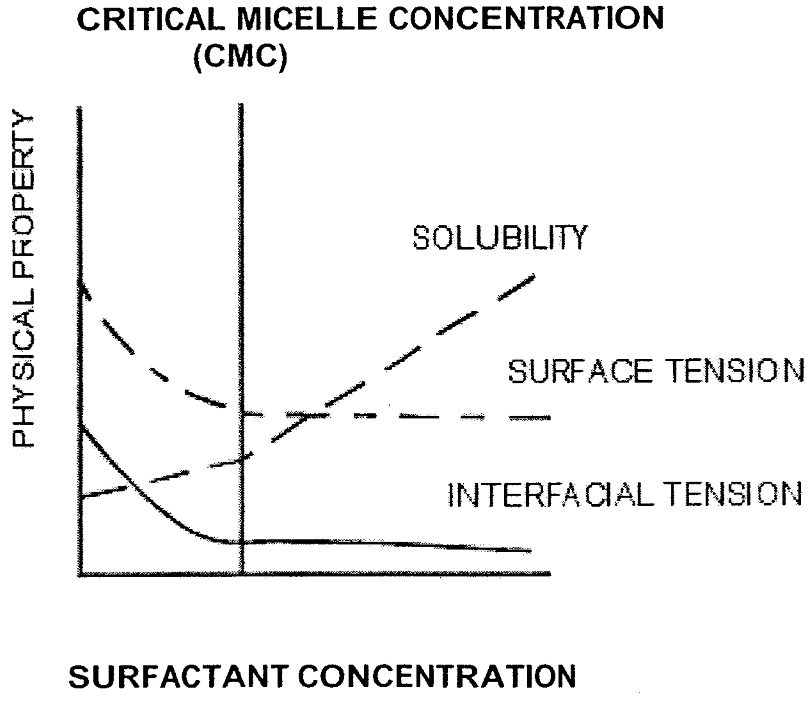


Figure 2.8 Solubilization, surface tension, and interfacial tension versus the concentration of surfactant. Adapted from Mulligan [38].

2.8.2 CONCENTRATION POLARIZATION

Because of the build up effect of retained compounds in membrane separation processes, near the membrane interface, a gradient of concentration usually occurs. The concentration polarization is the name of this effect. Increasing the flux of permeate results in an increase in the concentration polarization which leads to the reduction of permeation driving force and eventually leads to low selectivity of separation and lower flux [4].

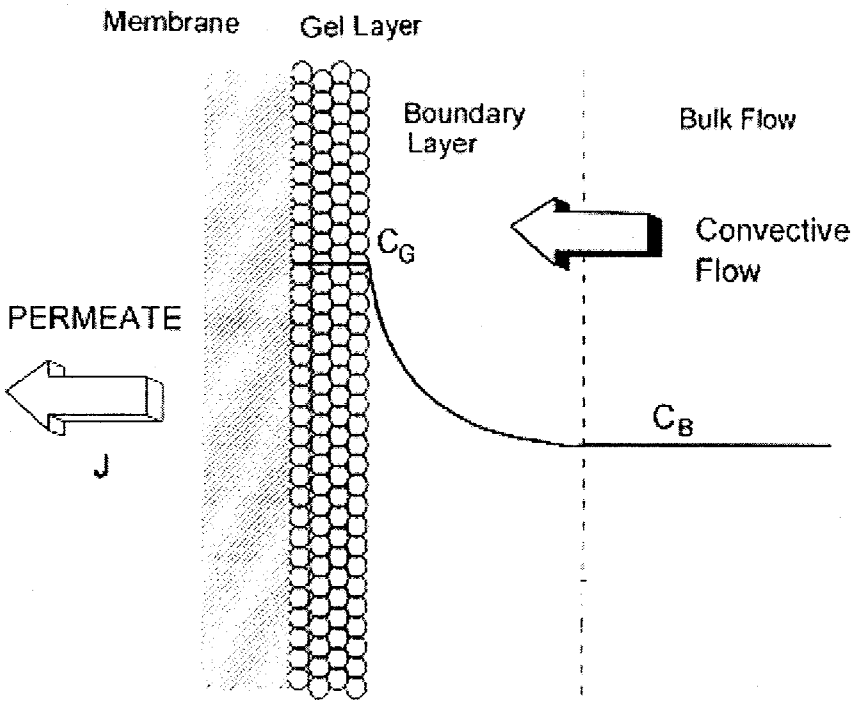


Figure 2.9 Concentration polarization of macromolecular solutes and colloidal, showing the build up of the polarized (gel) layer and associated boundary layer. Adapted from Cheryan [7].

2.8.3 FOULING

Fouling is the irreversible flux declination with operation time; this occurs because of specific interactions of the feed solutes with the membrane, and hence it is considered the restrictive factor of membrane technology. Flux occurs when other operation parameters like pressure, temperature, flow rate, and feed concentration are remaining constant. Usually flux declination occurs rapidly in the first few minutes followed by a more gradual decline [7].

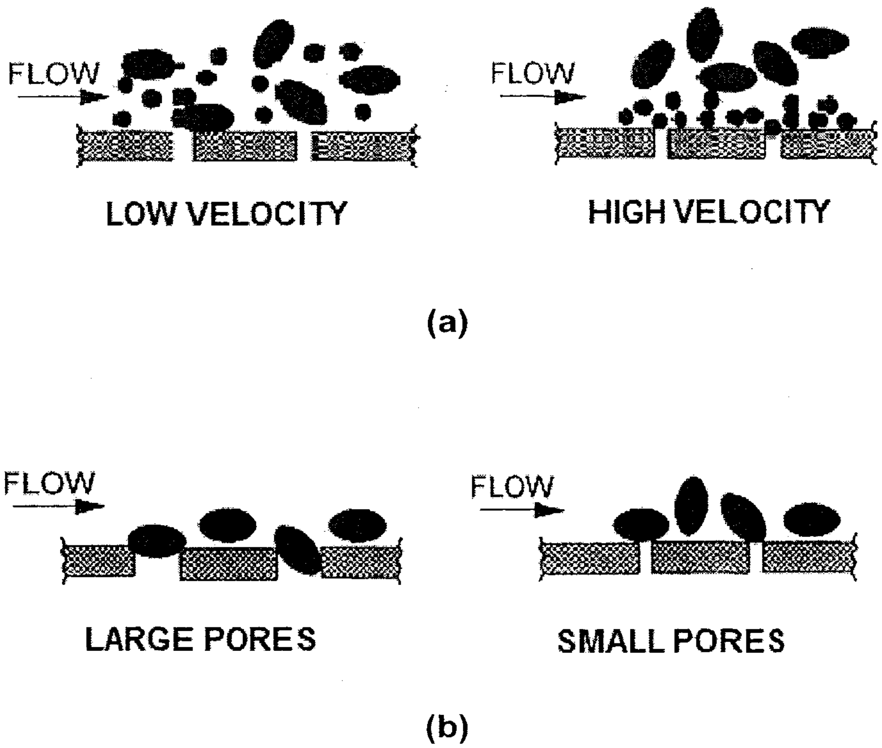


Figure 2.10 a. Fouling by mixed size particulates. At high velocity, larger particles are subjected to comparatively greater lift velocities which give smaller particles a higher probability to foul the membrane. b. Fouling by particulates, effect of pore size. Adapted from Cheryan [7].

2.9 SURFACTANTS

Surface active agents are chemical compounds and they are composed of a polar or ionic portion (the head-group) and a linear or branched hydrocarbon portion in their most general structure as in Figure 2.11 [55]. Other references define the surfactants as follows: A surface active amphiphile (molecules with hydrophilic "water-loving" and hydrophobic "water-hating" parts) that aggregates in solvents like water to form micelles or other different microstructures [40], [32]. Surfactants reduce the system free energy, at an interface, by replacing the higher energy bulk molecules [38], [39].

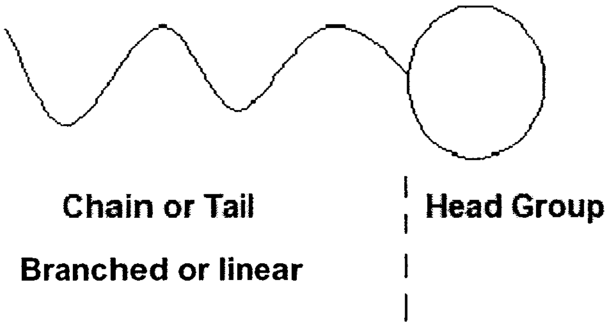


Figure 2.11 Surfactant monomer, the building unit of the micelle, adapted from Tadros [55] and Myers [40].

2.9.1 GENERAL CLASSIFICATION OF SURFACTANTS

The classification generally used is depending on the head-group nature as illustrated in Figure 2.12 [55]. Cationic surfactants contain a positive charge on the molecule surface- active portion [40]. Anionic surfactants possess a negative charge on the molecule surface-active portion [40] and nonionic surfactants do not have any electrical charge [40]. When the functional group of an amphiphilic compound, depending on the pH, has the ability to carry both cationic and anionic charges then the surfactant is amphoteric. If amphiphiles demonstrate cationic and anionic behaviour independent of the pH then the surfactant is zwitter-ionic [16].

2.10 BIOSURFACTANTS

The biosurfactants are produced either on the surfaces of microbial cell or excreted extracellularly. The biosurfactants have both moieties, hydrophilic and hydrophobic. Compared to the chemical surfactants, the biosurfactants have more advantages like the high selectivity at extreme temperatures and pH, higher biodegradability, and lower toxicity. Some biosurfactants have low CMC in addition to the high surface activities the reasons that make these biosurfactants are promising as a substitutes for the synthetic surfactants [56]. Inexpensive raw materials can be used to produce biosurfactants. These materials are available in big quantities. For the interest of bulk production, biosurfactant can be produced from industrial wastes as well as their by-products [56]. Biosurfactants have been used in many industrial applications such as petroleum, environmental, food, biological, and agricultural industries [30].

2.10.1 CLASSIFICATION OF BIOSURFACTANTS

Biosurfactant classification is based mainly on the categorization of their microbial origin and their chemical composition [12].

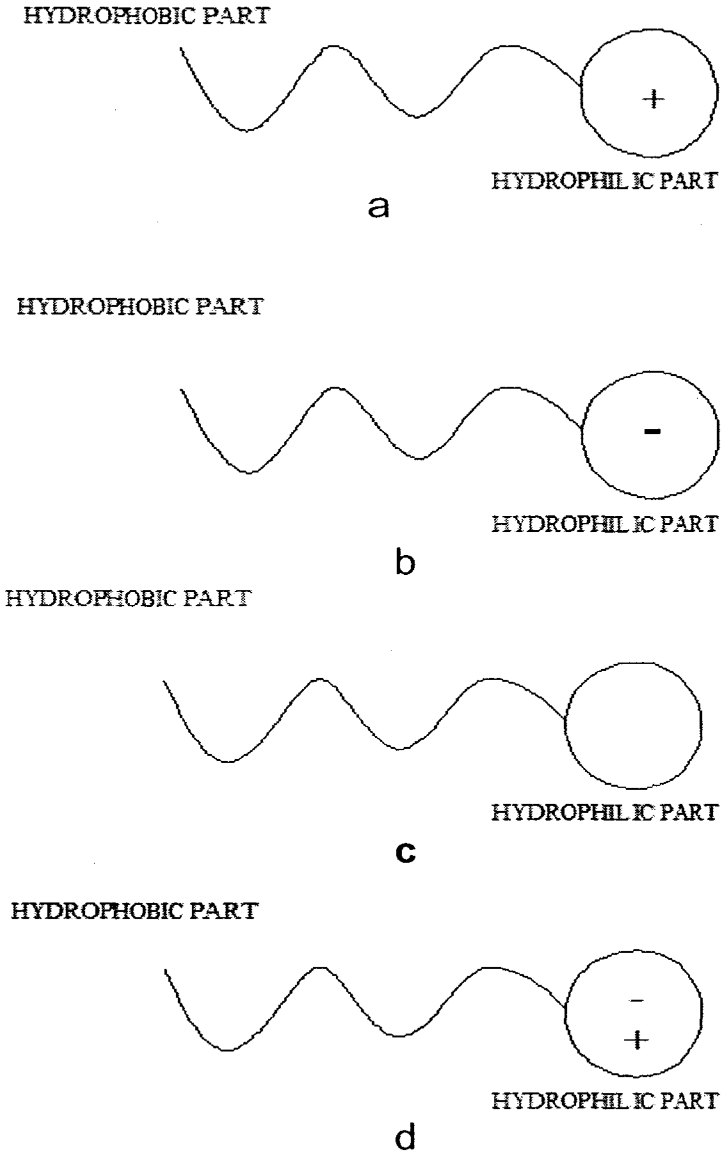


Figure 2.12 Surfactant monomer hydrophilic and hydrophobic parts and their classification according to the head-group charge. (a) Cationic surfactant monomer, (b) anionic surfactant monomer, (c) nonionic surfactant monomer, and (d) amphoteric and zwitterionic surfactant monomer, adapted from Tadros [55].

Table 2.6 Main biosurfactants classified according to chemical composition. Adapted from Kosaric [31].

1. Glycolipids	**4. Polymeric Surfactants**
Trehalose mycolates	Lipoheteropolysaccharide
Trehalose esters	Heteropolysaccharide
Mycolates of mono-, di-,and trisaccharide	Polysaccharide protein
Rhamnolipids	Mannoprotein
Sophorolipids	Carbohydrate protein
2. Phospholipids and Fatty Acids	Mannanlipid complex
Phospholipids and fatty acids	Mannose/erythrose lipid
Phospholipids	Carbohydrate protein-lipid complex
3. Lipopeptides and Lipoproteins	**5. Particulate Biosurfactants**
Gramicidens	Membrane vesicles
Polymyxins	Fimbriae
Ornithine lipid	Whole cells
Cerilipin	
Lysinlipid	
Surfactin. Subtilysin	
Peptide lipid	

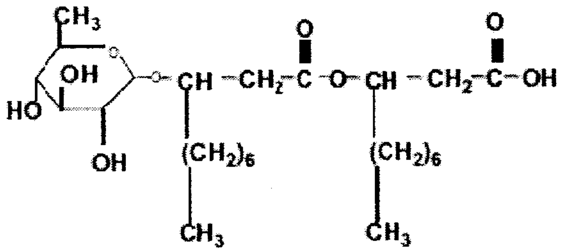
2.10.2 RHAMNOLIPIDS

The rhamnolipid biosurfactants produced by *Pseudomonas* species, when grown on different carbon substrates, have shown surface active properties. *Pseudomonas aeruginosa* has the ability to produce four different rhamnolipids. These rhamnolipids are composed of one or two L-rhamnose units and one or two units of ß-hydroxydecanoic acid. Two of the rhamnolipids, RL1 and RL3, are the principal products of *Pseudomonas aeruginosa* while RL2 and RL4 could be biosynthesized only when certain cultivation conditions are available [56]. Rhamnolipids (R1-R4) are anionic biosurfactants. The interfacial tension against n-hexadecane can be lowered to about 1 mN/m and surface tension to 25 - 30 mN/m depending on the salt concentration and pH when pure rhamnolipids from *Pseudomonas spp.* are utilized [31]. Figure 2.13 illustrates the structures of R1 to R4 mentioned above. Recent studies showed that there are seven rhamnolipid homologues that have been identified. These biosurfactants are capable of lowering the water surface tension to 29 mN/m [33]. At pH values above 4.0, rhamnolipid molecules show anionic behaviour [42].

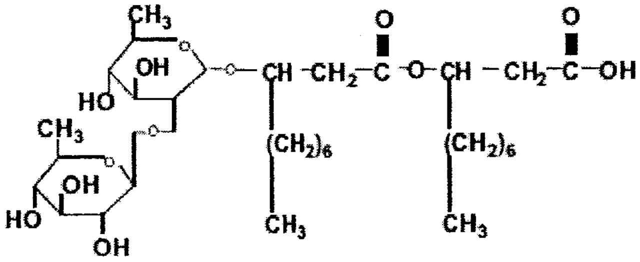
2.10.3 ENVIRONMENTAL APPLICATIONS OF RHAMNOLIPID

BIODEGRADATION OF PETROLEUM HYDROCARBONS

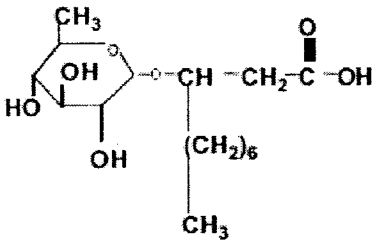
Rhamnolipid can enhance the biodegradation when is added to hexadecane, octadecane, phenanthrene, and n-paraffin in liquid systems, as well as the hexadecane, pristine, tetradecane, creosote and hydrocarbon mixtures in soils [38].



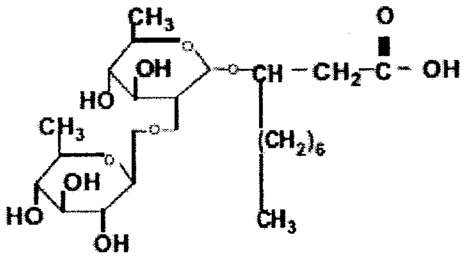
R1



R2



R3



R4

Figure 2.13 Four different rhamnolipid structures produced by *P. aeruginosa*. Adapted from Mulligan [38].

REMOVAL OF HEAVY METALS

Rhamnolipid capability to remove metals like copper, cadmium, and zinc from soil and ions is caused by its anionic nature. Rhamnolipid to metal molar ratio for copper is 2.31, for cadmium is 1.91, and for zinc is 1.58 [33].

BIODEGRADATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

Rhamnolipids in a bioslurry were more effective than SDS, a chemical surfactant, up to five times as they could improve the four-ring PAH solubilization more than three-ring PAHs significantly [38].

DISPERSING OIL IN CONTAMINATED WATER

Since they are less toxic and persistent than synthetic surfactants, rhamnolipid can be useful for oil spills. A new development is the feasibility of rhamnolipid biosurfactants for dispersing oil slicks [38], [10]. Rhamnolipids biosurfactant are efficient for heavy metal and hydrocarbon removal and could also be efficient for the removal of mixed contaminants, metals and hydrocarbons. However, large scale studies have not been performed [38].

The current study is an application of the mixed contaminant removal from simulated polluted water samples with copper ions and benzene molecules using rhamnolipid biosurfactant. Ultrafiltration with a hollow fiber membrane was used to perform this separation process.

CHAPTER THREE

MATERIALS AND METHODS

3.1 INTRODUCTION

The main objective of this research is to determine the efficiency of rhamnolipid biosurfactant (JBR 425) to remove both the heavy metal, copper in this case, and organic pollutant, benzene in this case, simultaneously. This chapter includes the experimental preparation including materials and methods, rhamnolipid characterization, and experimental design. The experiments were divided into three groups. Rhamnolipid characterization was done to obtain the critical micelle concentration for the rhamnolipid surfactant. The first group is to determine the effect of the operation factors. The second one is to determine the molar ratios that achieve 100% rejection for each pollutant, and the fourth group is to evaluate the efficiency of the rhamnolipid biosurfactant to achieve the main objective of this research which is the simultaneous removal of both, the copper ions and benzene molecules.

3.2 CHEMICALS AND BIOSURFACTANT

3.2.1 COPPER

A copper reference standard solution, (a solution of copper nitrate and every 1 ml = 1 mg of copper), from Fisher Scientific was used to prepare the Atomic Absorption standard solutions and to be diluted in different concentrations with distilled water to prepare the artificially contaminated water samples with Cu^{+2} ions.

3.2.2 BENZENE

Benzene of purity more than 99% from Fisher Scientific was used for preparing the artificially contaminated water samples with benzene molecules at different concentrations and also for preparing the standard solutions to establish the calibration curve of the high performance liquid chromatography (HPLC).

3.2.3 ACIDS AND BASES

Concentrated nitric acid (67-70 %) from Fisher Scientific was used to adjust the pH of the artificial contaminated water samples and to prepare the standard solution (the blank) of the atomic absorption spectroscopy. Sodium hydroxide (0.5N) from Fisher Scientific was used as well to adjust the pH of the artificially contaminated water samples.

3.2.4 RHAMNOLIPID BIOSURFACTANT, JBR 425

The biosurfactant JBR 425 is produced from centrifuged and sterilized fermentation broth that has had all protein removed. JBR 425 is an aqueous solution of rhamnolipids with concentration of 25%, (the used batch is 26%). The two main rhamnolipids R1, ($C_{26}H_{48}O_9$, CAS Registry Number 37134–61-5), and R2, ($C_{32}H_{58}O_{13}$, CAS Registry Number 4348–76-9), are present. The chemical composition of the rhamnolipids are glycosides of rhamnose and β-hydroxydecanoic acid [26].

Table 3.1 Physical properties of rhamnolipid biosurfactant, JBR 425, adapted from Jeneil Biosurfactant Co. [26].

PARAMETER	VALUE
SPECIFIC GRAVITY	1.05 – 1.06
pH*	6.5 – 7.0
ODOR	SOAPY
APPEARANCE	AMBER SOLUTION
WATER SOLUBILITY	SOLUBLE AT NEUTRAL PH
SUITABLE DILUENTS	WATER AND MOST COMMON ALCOHOLS
SURFACE TENSION	29 mN/m
INTERFACIAL TENSION	0.3 mN/m
VOLATILITY	NOT VOLATILE
STABILITY	STABLE AT ROOM TEMPERATURE

* : pH 6.57 for the used batch

3.3 EQUIPMENT USED

3.3.1 QUIXSTAND ™ BENCHTOP SYSTEM (ULTRAFILTRATION SYSTEM)

The MEUF (micellar-enhanced ultrafiltration) system, as shown in Figure 3.1, was used to separate the copper ions which were adsorbed on the micelle surface and the benzene molecules which were solubilized inside the micelle from the aqueous solutions of copper-rhamnolipid, benzene-rhamnolipid, and copper-benzene-rhamnolipid solutions. The Quixstand ™ Benchtop System 'M' Series from A/G Technology Corporation was used to conduct the micellar-enhanced ultrafiltration separation experiments. The system consisted of the feed reservoir, peristaltic pump (Watson-Marlow ® 313 S), inlet pressure gauge, Xampler ™ cartridge (hollow fiber cartridge), outlet pressure gauge, and back pressure control valve.

3.3.2 PERISTALTIC PUMP

The peristaltic pump (Watson-Marlow ® 313 S) is from Watson-Marlow and for the pump to be controlled as a simple dosing pump, then the Single / Continuous / Repeat slider switch should be set to Single or Repeat. When the slider switch set on Continuous, the way that pump was used during the experiments, the timing functions are cancelled and the pump operates as a manual control variable speed unit through knobs front panel control [59].

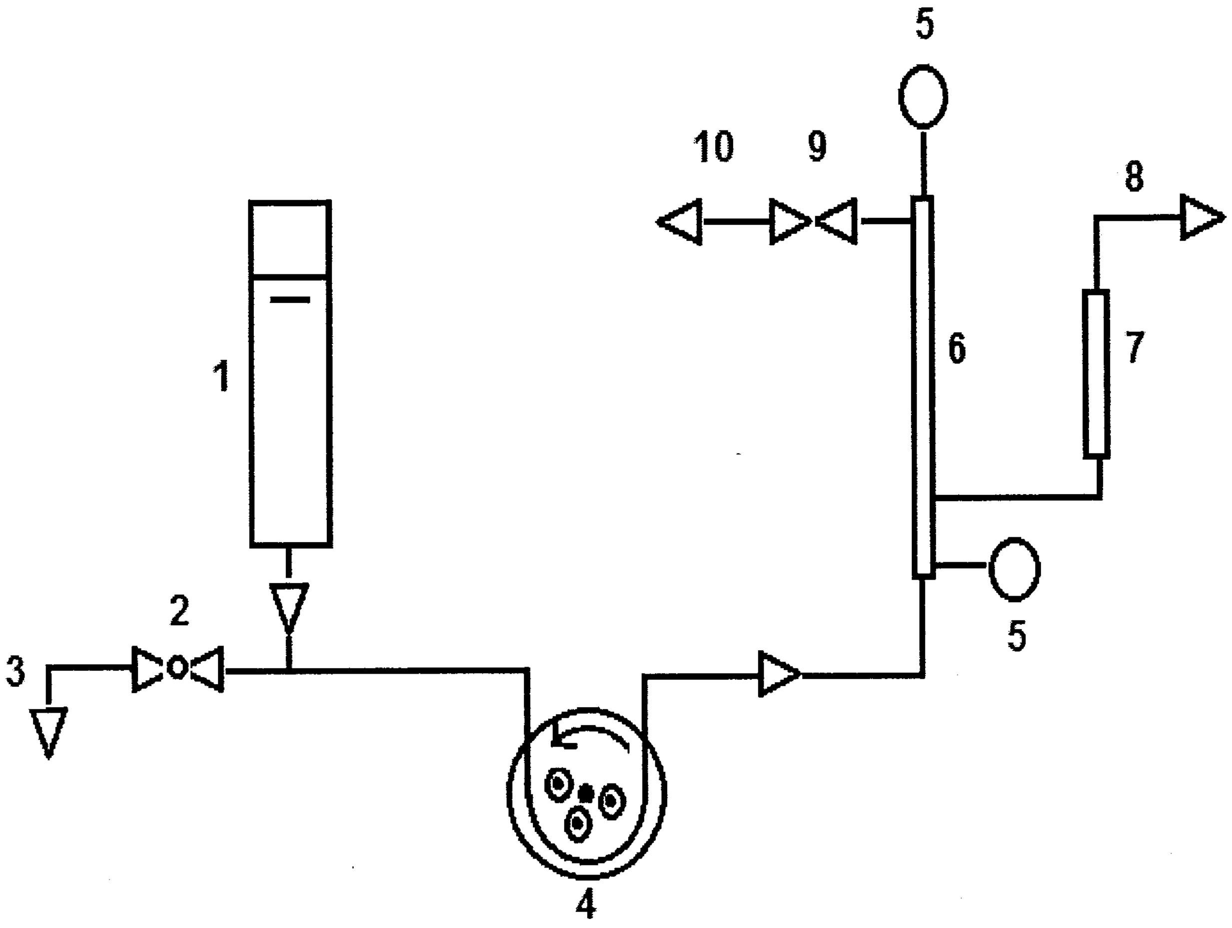


Figure 3.1 Flow diagram of the micellar enhanced ultrafiltration system, adapted from A/G Technology Corporation [1].

(1) Feed reservoir;	(2) Sampling/Drain ball valve;
(3) Feed sampling stream;	(4) Peristaltic pump;
(5) Pressure gauge	(6) Membrane cartridge;
(7) Flow meter;	(8) Permeate stream;
(9) Backpressure control valve;	(10) Retentate stream

3.3.3 XAMPLER™ CARTRIDGE

The hollow fiber cartridge from A/G Technology Corporation was used in the ultrafiltration system. This cartridge represents the membrane filter and each one contains a bundle of polysulfone fibres or tubules potted in parallel within a plastic housing. Ultrafiltration membranes are classified according to their Nominal Molecular Weight Cut-Off (NMWC). Table 3.2 shows the used Xampler ™ cartridge's main characteristics [1].

Table 3.2 Main characteristics of the Xampler ™ cartridge, adapted from A/G Technology Corporation [1].

Nominal Molecular Weight Cut-Off (NMWC)	5000
Cartridge Membrane Area (cm^2)	140
Nominal Fiber ID (mm)	0.5
Nominal Number of Fibres	30
Transmembrane Pressure (10 - 25 ^0C)	344.7 (kPa)
Nominal Flow Path Length	30 cm
Nominal Housing Identifier	3M
pH Range	2-13

3.4 RHAMNOLIPID CHARACTERIZATION AND EXPERIMENTAL DESIGN

3.4.1 RHAMNOLIPID CHARACTERIZATION: DETERMINATION OF RHAMNOLIPID CRITICAL MICELLE CONCENTRATION (CMC)

The ability of rhamnolipid biosurfactant to adsorb or solubilize contaminants starts when the micelles begin to be formed which means that the solution is at its critical micelle concentration (CMC). To determine the concentration, two methods were chosen, the first one was the Du Nouy method and the second one was the conductivity method.

DU NOUY METHOD

In this method the Surface Tensiomat® 21 from Fisher Scientific was used. Aqueous solutions of rhamnolipid with different concentrations (0, 25, 50, 100, 500, 1000 mg/l), were prepared to measure the surface tension and determine the CMC, the point where the rhamnolipid concentration–surface tension values illustrates a sudden change over a narrow range of rhamnolipid concentrations. The Surface Tensiomat® 21 shows the apparent surface tension, P, which could be converted, to the absolute surface tension, S [19].

$$S = P \times F \quad (3.1)$$

Where,

S = absolute surface tension

P = apparent surface tension as indicated by the dial reading

F = correction factor obtained from correction factor chart

CONDUCTIVITY METHOD

In this method the conductivity of aqueous solutions of rhamnolipid with different concentrations, (0, 5, 10, 25, 29.5, 50, 100, 500, 1000 mg/l), were taken [11]. The CMC value was determined where the concentration–conductivity curve demonstrates an abrupt change over a short range of rhamnolipid concentrations. The conductivity meter used was from HACH of the brand HQ 30d.

3.4.2 EXPERIMENTS OF GROUP ONE: EFFECT OF OPERATION PARAMETERS ON FLUX

TRANSMEMBRANE PRESSURE

This experiment was conducted at room temperature, 22^0C, by feeding the membrane filter with the same distilled water at different transmembrane pressures, 40, 73, and 104 (kPa) through the peristaltic pump to see the effect of this factor on flux.

$$\text{Transmembrane Pressure} = \left((P_{\text{inlet}} + P_{\text{outlet}})/2 \right) - P_{\text{permeate}} \qquad (3.2)$$

The flux was calculated by measuring the flow rate by using the flow meter connected to the permeate stream then substituting the measured values in the flux equations 3.3 or 3.4 to obtain the fluxes [58], [1].

$$J = Q_p / A_{system} \qquad (3.3)$$

Where,

J = Flux (L / m^2.h)

Q_p = Permeate Flow (L / h)

A_{system} = Surface area of the membrane system (m^2)

Or,

$$\text{Flux } (L / m^2.h) = (\text{Permeate Flow } (ml / min) / \text{Cartridge Area } (m^2)) \times 0.06 \qquad (3.4)$$

Then correcting these values to the standard temperature, 25^0C, by applying the equation 3.5

$$\text{Temperature Corrected Flux} = (\text{Flux})_{T2} \times (T1/T2) \qquad (3.5)$$

Where,

T1 = Reference Temperature (^0F)

T2 = Actual Temperature (^0F)

TEMPERATURE

Experiments were performed to observe the effect of temperature variance on flux at room temperature, 22^0C, by feeding the membrane filter through the peristaltic pump with distilled water at different temperatures, 24^0C, 38^0C, and 53^0C and the same transmembrane pressure. The flux was calculated by measuring the flow rate using the flow meter connected to the permeate stream then substituting the measured values in the flux equation 3.4 to obtain the fluxes.

PUMP SPEED

To see the effect of this factor on flux and transmembrane pressure, feeding the membrane filter with the same aqueous copper-rhamnolipid solution at different pump speeds was carried out. More details will be discussed in Chapter 4. This experiment was conducted at room temperature, 22^0C.

FOULING

Since fouling is the decline of flux with time, an experiment to examine this important factor was performed at room temperature, 22^0C, by measuring the flux at different times keeping all other factors, transmembrane pressure, temperature, concentration, and pump speed constant for the aqueous copper-rhamnolipid solution.

EFFECT OF pH

All the experiments were conducted at the pH range of 6.81 to 7.11 since the morphology of rhamnolipid is a pH function and this range of pH keep rhamnolipid biosurfactant structure in micelle form, which was required to achieve the research objective, also rhamnolipid solution surface tension is highly affected by pH changes. Decreasing pH from 7.0 to 5.0 is increasing the surface tension from 30 to more than 40 mN/m [18], [64]. The other reason is to prevent the precipitation of positively charged copper ions because the dirhamnolipid, the second major component of the used rhamnolipid, is neutral for more than 98% of its molecules at pH 4.0, while the same percentage is of negative charge when pH value is 7.4 [47]. Sodium hydroxide was used to adjust the pH.

3.4.3 EXPERIMENTS OF GROUP TWO: FINDING THE MOLAR RATIO, MR, FOR THE 100% REJECTION AND INVESTIGATING THE RHAMNOLIPID BEHAVIOUR IN THE PRESENCE OF COPPER AND BENZENE

The formation of rhamnolipid micelles is not the only factor that determines the ability of rhamnolipid biosurfactant to separate contaminants from their aqueous solutions. Also the molar ratio, MR, of the biosurfactant to the contaminant which means in this case the quantity of rhamnolipid in moles to the number of either copper or benzene moles in one litre of aqueous solution can also be used.

When a micellar-enhanced ultrafiltration operation is applied to a contaminated solution with a particular substance (organic, heavy metal, or both), a biosurfactant has to be added to the same solution to enhance the ultrafiltration operation, as explained in the previous chapter, at a specific molar ratio, MR. The MR with 0% of that contaminated substance in the permeate stream or 100% in the retentate stream, which can be called also the rejection, R, will considered to be the 100% Rejection MR [35].

$$R = 1 - (C_p / C_f) \quad (3.6)$$

Where,

R = Rejection; C_p = Permeate Concentration; C_f = Feed Concentration

Three groups of experiments were performed to reach the 100% rejection MR for three concentrations of copper. The mean of three replicates for each concentration were taken. For benzene, also three groups of experiments were done to reach the 100 % Rejection MR, that was done for two concentrations. The mean of two replicates for each concentration were taken.

Since no enough studies indicating the molar ratio of rhamnolipid/benzene 100% rejection, a molar ratio of a chemical compound approximately similar to the benzene composition (styrene) were used as a starting point. The starting point for the molar ratio of rhamnolipid/copper 100% rejection was the values obtained from other studies had similar conditions approximately.

A range of concentrations higher than drinking water guidelines of the maximum acceptable concentration for benzene, 5 µg/L, and copper, 1.0 mg/L, were used when they added as pollutants [17].

Equation (3.6) was used also to calculate the rejection percentage of the rhamnolipid that retained by the membrane filter which indicates the membrane efficiency in preventing the rhamnolipid micelles from going out with the permeate flux as well as the rhamnolipid efficiency to form the needed micelles for contaminant removal.

The Tensiomat® 21 was used to determine the rhamnolipid concentration in the permeate, C_p , by the Du Nouy method as explained previously in this chapter. Two readings for the permeate were taken in each experiment. C_f represents the rhamnolipid feed concentration.

RHAMNOLIPID TO COPPER MOLAR RATIO FOR 100% REJECTION

For copper, three solutions of different concentrations, (3.1, 6.4, and 9.6 mg/l), were prepared at the same MR, 5.41. The sample of permeate flux for each solution was analyzed by the atomic absorption spectroscopy to determine the presence of copper ions. For each experiment the feed sample was analyzed as well to determine the concentrations. Three samples of each feed and permeate were analyzed to determine the copper concentration. The rhamnolipid concentration in the permeate, C_p , for the above experiment was determined by applying the Du Nouy method using the Tensiomat® 21. Two readings of the permeate surface tension were taken. C_f represents the rhamnolipid feed concentration, and then the rhamnolipid rejection was determined by applying equation (3.6).

To reach the 100% rejection MR, the same procedures were repeated. The three aqueous solutions of copper-rhamnolipid, (3.1, 6.4, and 9.6 mg/l), were used but this time at MR = 6.25. The atomic absorption spectroscopy showed the absence of copper ions in the permeate samples. At MR = 6.25, 100% rejection was obtained.

ANALYSIS WITH ATOMIC ABSORPTION SPECTROSCOPY

The aqueous solution samples that were contaminated with copper ions, Cu^{+2}, were analyzed by AAnalyst 100 Atomic Absorption Spectrometer from Perkin Elmer using the Hollow Cathode Lamp from SCP Science at the wavelength 324.8 nm to determine the copper concentrations in the feed and permeate samples [45].

RHAMNOLIPID TO BENZENE MOLAR RATIO FOR 100% REJECTION

Two aqueous solutions of benzene-rhamnolipid were prepared at concentrations of 190 mg/l and 264 mg/l benzene with MR = 0.77 for both. Two samples of the feed were analyzed by the High Performance Liquid Chromatography to evaluate of the concentrations the feed and the permeate samples of the benzene. For the above experiment, the rhamnolipid concentration in the permeate, C_{p}, was determined by applying the Du Nouy method using the Tensiomat® 21. Two readings of the permeate surface tension were taken. C_f represents the rhamnolipid feed concentration, and then the rhamnolipid rejection was determined by applying equation (3.6).

Another two aqueous solutions of benzene-rhamnolipid were prepared at concentrations of 63 mg/l and 129 mg/l benzene. As the expected molar ratio should be higher, a MR = 1.33 was used. The HPLC results showed that MR = 1.33 is the 100% rejection MR. There was no benzene in the permeate samples.

ANALYSIS WITH HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

The aqueous solution samples that contaminated with benzene molecules were analyzed by two HPLCs, System Gold High Performance Liquid Chromatography from Beckman Coulter, Inc. and Agilent 7500 ICP – MS from Agilent Technologies [3], [2].

The connected column to the HPLCs was a SUPELCOSIL ™ LC – 8 from Supelco / Sigma-Aldrich Co. and was operated by the classic reversed phase mechanism, mobile phase 60:40 - methanol: water, detection: UV 254 nm, and flow rate of 1 ml/min [52].

3.4.4 EXPERIMENTS OF GROUP THREE: THE EVALUATION OF RHAMNOLIPID CAPABILITY TO SEPARATE COPPER IONS AND BENZENE MOLECULES SIMULTANEOUSLY

The evaluation of rhamnolipid capability to remove both copper ions and benzene molecules simultaneously required preparing two subgroups of experiments with two objectives, primary and secondary. The primary objective was to observe the effect of the added contaminant on the 100% rejection molar ratio of the other one which means finding the effect of the added contaminants on the capability of the same rhamnolipid quantity required to achieve 100% rejection for the main contaminant. That was repeated at two different concentrations of the main contaminant. The secondary objective was to see how the molar ratio for the added contaminant was affected as well.

To achieve the primary objective of the first subgroup, a certain weight of benzene, 90 mg, was added to two copper aqueous solutions for the 100% rejection molar ratio of 6.25. The copper concentrations for the first and second solutions were 6.2 and 8.3 mg/l, respectively. The effect of benzene on the 100% Rejection MR for copper was examined by analyzing the copper ion content of the permeate samples. The presence of copper ions indicates the negative effect of benzene presence and vice versa. The benzene presence in the permeate samples was analyzed as well as a secondary objective for the same experiment to check the effect of copper concentration on the removal of benzene molecules. Depending on the percentage of benzene, the simultaneous removal efficiency was determined. The lower the percentage of benzene, the higher the simultaneous removal efficiency is.

The primary objective of the second subgroup was to investigate the effect of added copper on the 100% Rejection MR of benzene. To evaluate the capability of rhamnolipid biosurfactant to remove the benzene molecules and copper ions simultaneously, a certain weight of copper (8.3 mg) was added to two benzene aqueous solutions of 100% rejection molecular ratio which was equal to 1.33. The benzene concentrations for the first and second solutions were 43.7 and 63 mg/l respectively.

The effect of copper presence on the 100% Rejection MR for benzene was examined by analyzing the benzene content of the permeate samples. The presence of benzene molecules indicates the negative effect of copper presence and vice versa. The secondary objective of the same experiment was to check the effect of benzene on the removal of added copper ions. That was done by analyzing the copper concentration in the permeate samples. Depending on the percentage of copper rejection, the simultaneous removal efficiency has been determined. The higher the percentage of copper rejection, the higher the simultaneous removal efficiency.

Did you do with 0 mg/L copper (Table 3.3) or 0 mg/L benzene (Table 3.4)? If so add

Table 3.3 Experimental design of group three experiments. Benzene effect on copper molar ratio of 100% rejection (MR=6.25).

Copper Concentration (mg/l)	Benzene Concentration (mg/l)	Rhamnolipid/Cu Molar Ratio
8.3	90	6.25
6.2	90	6.25

Table 3.4 Experimental design of group three experiments. Copper effect on benzene molar ratio of 100% rejection.

Benzene Concentration (mg/l)	Copper Concentration (mg/l)	Rhamnolipid/Cu Molar Ratio
63	8.3	0.77

43.7	8.3	0.77

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 GENERAL REMARKS

The main objective of this research was to determine the efficiency of rhamnolipid biosurfactant (JBR 425^{TM}) to remove simultaneously the benzene molecules by solubilization and the copper ions by adsorption as explained in Chapter 2. To achieve and evaluate this objective, cross-flow micellar-enhanced ultrafiltration experiments were planned, designed, and conducted. Characterization of the rhamnolipid and three groups of experiments were conducted to determine the efficiency of rhamnolipid simultaneous removal of copper and benzene. The second group consisted of two experiments. The first one was prepared to find the copper molar ratio (MR) which is the number of rhamnolipid moles that is required to remove completely a one mole of copper ions from contaminated aqueous solution (100% rejection). The second one was performed to find out the rhamnolipid to benzene molar ratio (MR) of 100% rejection in the same way. The third group also consisted of two experiments. The first one was prepared to investigate the effect of benzene molecules presence on the 100% rejection molar ratio (MR) of copper. This means the effect of benzene on the capability of rhamnolipid micelles to adsorb 100% of copper ions from the contaminated aqueous solution by passing it with rhamnolipid biosurfactant through the filter membrane in the ultrafiltration system. A flow meter was connected to the permeate stream of the ultrafiltration system to control the optimum flux. Filtered samples were collected to evaluate the contamination level (concentrations of copper, benzene, or both of them) by analyzing these samples with the atomic absorption spectroscopy for copper or HPLC for benzene. The second group was accomplished to investigate the effect of copper ion presence on the 100% rejection of benzene.

4.2 CHARACTERIZATION OF RHAMNOLIPID: DETERMINATION OF RHAMNOLIPID CRITICAL MICELLE CONCENTRATION (CMC)

4.2.1 DU NOUY METHOD

As a requirement for selecting the concentration of a biosurfactant to achieve its optimal performance is to know the CMC value of this surfactant. Thus, to determine the amount of rhamnolipid biosurfactant required for contaminant removal, the CMC was obtained from the relationship of rhamnolipid concentrations and surface tension by measuring surface tension of various dilution solutions. The results in Figure 4.1 showed that the apparent surface tension values, the Surface Tensiomat® 21 dial readings of samples from the rhamnolipid dilution solutions, decreased from 75.3 to 31.4 mN/m with an increase in the rhamnolipid concentration from 0 to 50 mg/l, and beyond that an increase in rhamnolipid concentration had a very small effect on surface tension. The absolute surface tension values, the dial readings multiplied by the correction factor, as explained in Chapter three, decreased from 63 to 26.2 mN/m.

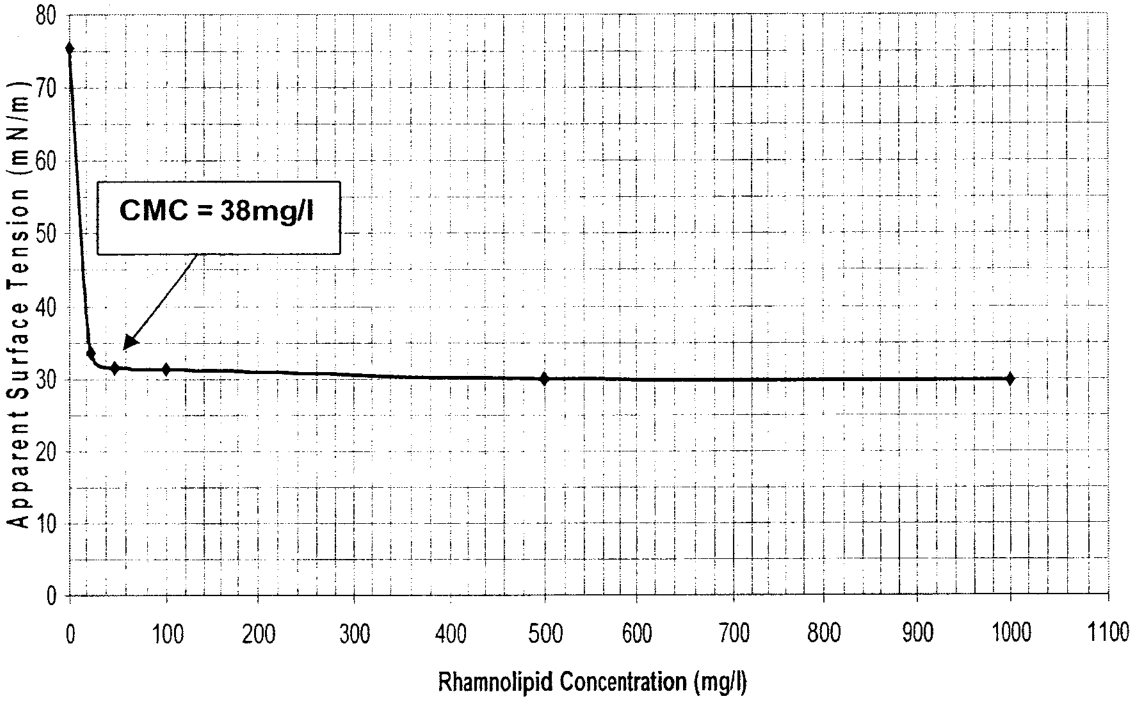


Figure 4.1 Absolute surface tension of different rhamnolipid solutions by Du Nouy method to find the critical micelle concentration (cmc).

The results as represented in Figure 4.1 shows that a low rhamnolipid concentration (≤ 25 mg/l) has a significant effect on the surface tension, while high concentrations (≥ 50 mg/l) have a negligible effect. The critical micelle concentration (CMC) of rhamnolipid biosurfactant was determined as 38 mg/l using the curve of rhamnolipid concentration versus surface tension as shown in

Figure 4.1. This result is close to the CMC value reported by Zhang and Miller which was equal to 40 mg/l [64].

4.2.2 Electrical Conductivity Method

The electrical conductivity was used as another way to determine the value of critical micelle concentration (CMC) by measuring the conductivities of different rhamnolipid aqueous solutions at different concentrations by using the conductivity meter HQ 30d from HACH. The critical micelle concentration (CMC) calculated by this way was equal to 38 mg/l as shown in Figure 4.2 which is the same value that has been obtained from the surface tension versus concentration graph. The intersection of linear slopes in the conductivity versus surfactant concentration graph represents the critical micelle concentration (CMC).

The conductivity in this research was used as an indicator for the solution's equilibrium state during and after the mixing the components of the artificially contaminated water samples. If there is no more change in the conductivity it means the solution reached at ambient conditions its equilibrium state [44].

4.3 EXPERIMENTS OF GROUP ONE: THE EFFECT OF OPERATION PARAMETERS ON FLUX

Many experiments have been performed to understand the effects of the main operation parameters on the ultrafiltration system as well as on the rhamnolipid-copper and rhamnolipid-benzene aqueous solutions. The parameters were transmembrane pressure, temperature, pump speed fouling, and the concentration. Knowing these parameters assisted in determining the optimum running conditions and understanding many details of the micellar-enhanced ultrafiltration process.

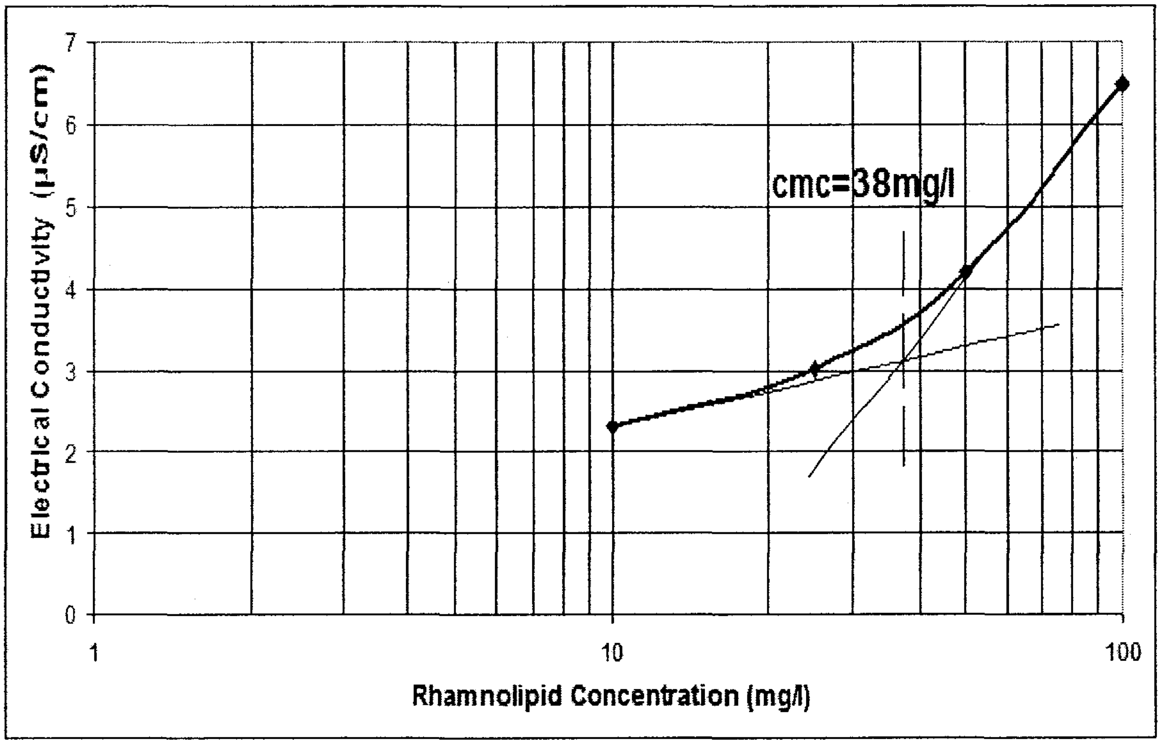


Figure 4.2 Rhamnolipid solution conductivity at different concentrations to determine the critical micelle concentration (cmc) by the electrical conductivity method.

4.3.1 TRANSMEMBRANE PRESSURE (TMP)

Water flux increased linearly with the transmembrane pressure as illustrated in Figure 4.3. Compared to the temperature, the transmembrane pressure has a very significant effect on the process and this is clear according to the flux values in both cases.

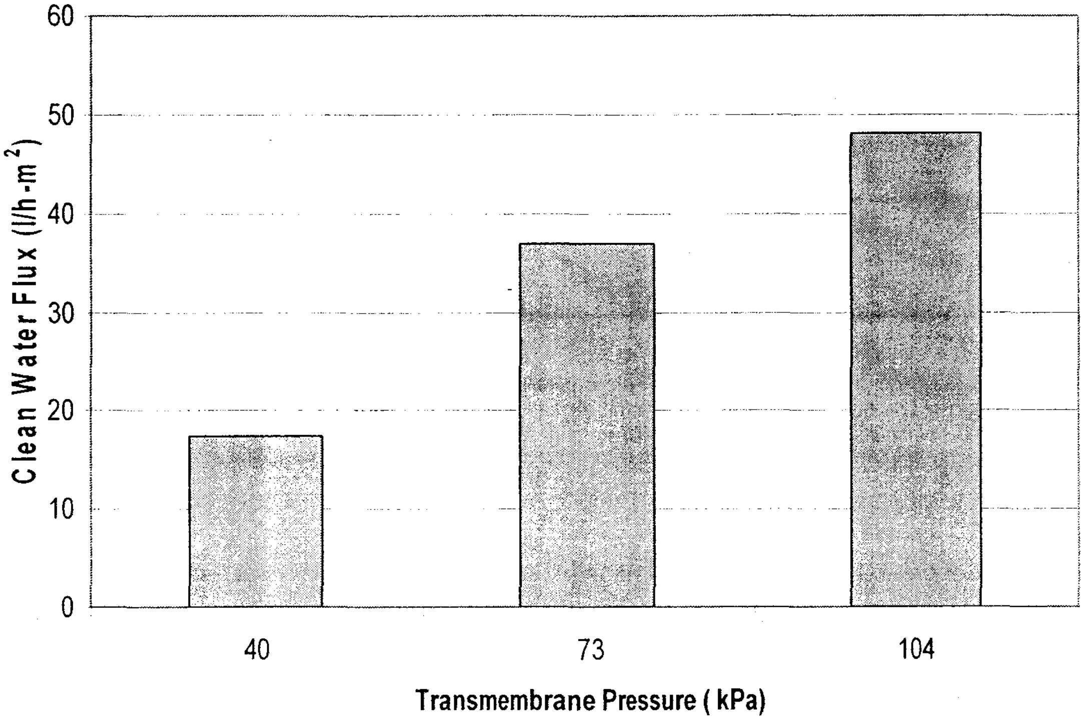


Figure 4.3 Effect of transmembrane pressure on clean water flux.

4.3.2 TEMPERATURE

The temperature effect on the flux was less than that of transmembrane pressure as explained previously. However it behaves in the same way, increasing the temperature increased the clean water flux since increasing the temperature will decrease water viscosity and increase molecules energy and passing through membrane pores. Figure 4.4 shows the temperature-flux linear relationship. The degree of process flux improvement is less predictable than with clean water since both a gel layer and a fouling layer on the membrane surface contribute to flux resistance [1].

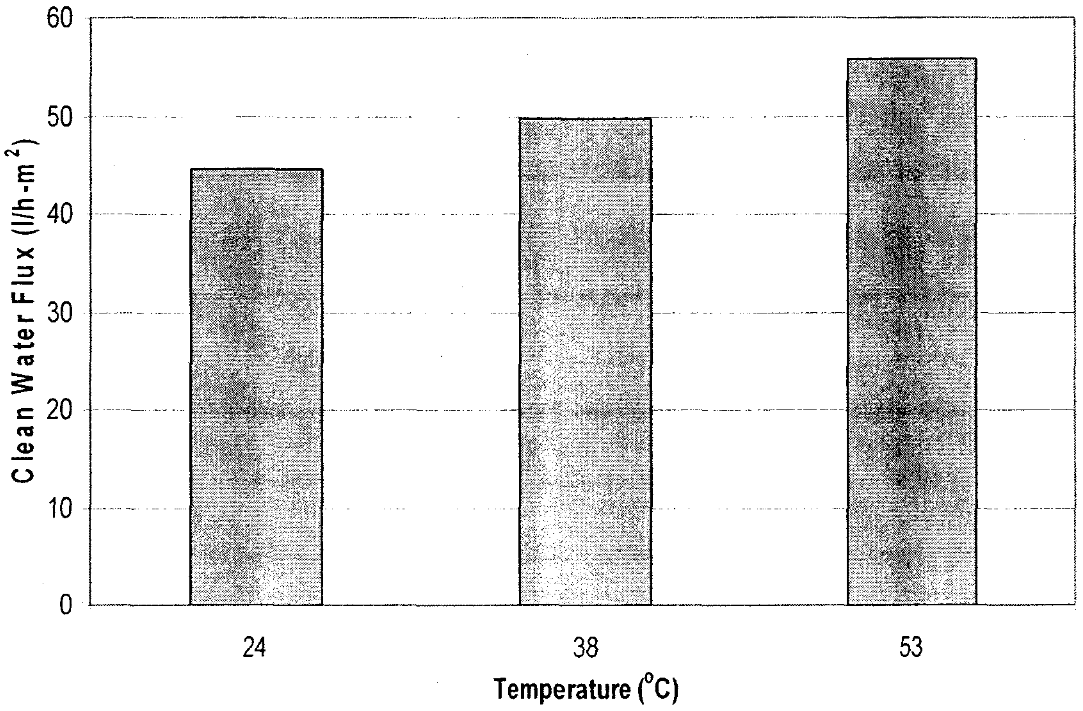


Figure 4.4 Effect of temperature on clean water flux.

4.3.3 PUMP SPEED

Increasing the peristaltic pump speed of ultrafiltration system keeping the temperature and solution concentrations constant increased the flow rate of the pump and eventually the flux. The transmembrane pressure increased as well. However the effect on the transmembrane pressure as illustrated in Figure 4.6 was higher than that of the flux as shown in Figure 4.5. Having a high flux is an important objective of the micellar-enhanced ultrafiltration process but this has to be balanced with fouling, the most dominant factor of the process since increasing the speed will increase the possibility of the membrane pore blockage.

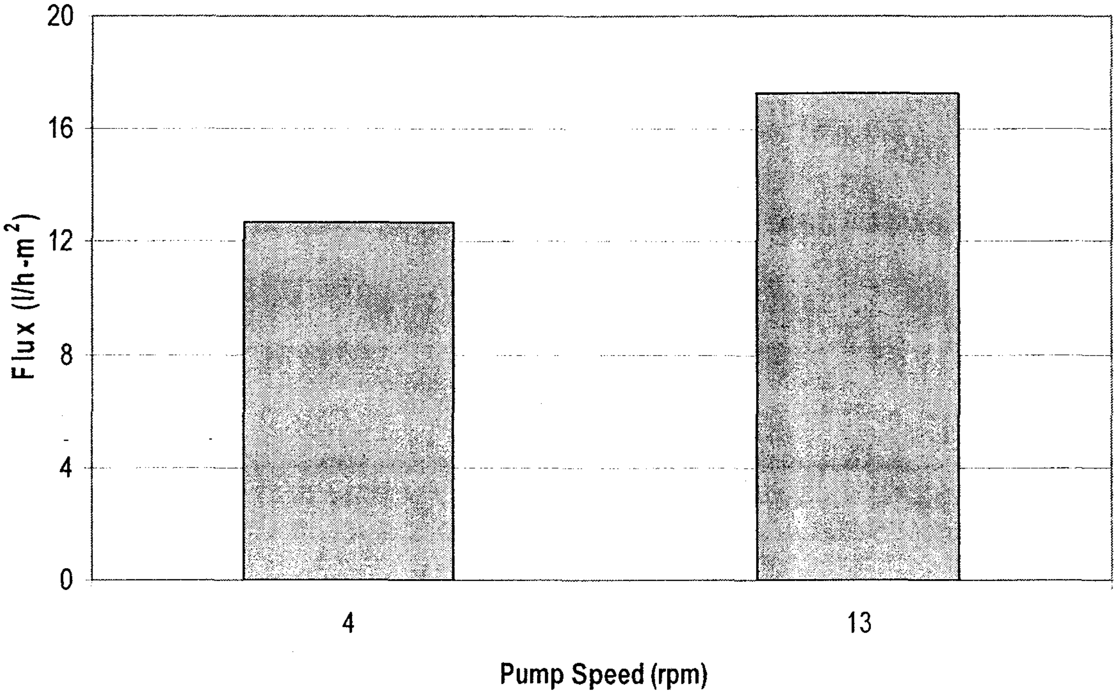


Figure 4.5 Effect of pump speed on flux at constant temperature and solution concentration (476.7 mg/l rhamnolipid and 9.6 mg/l Cu).

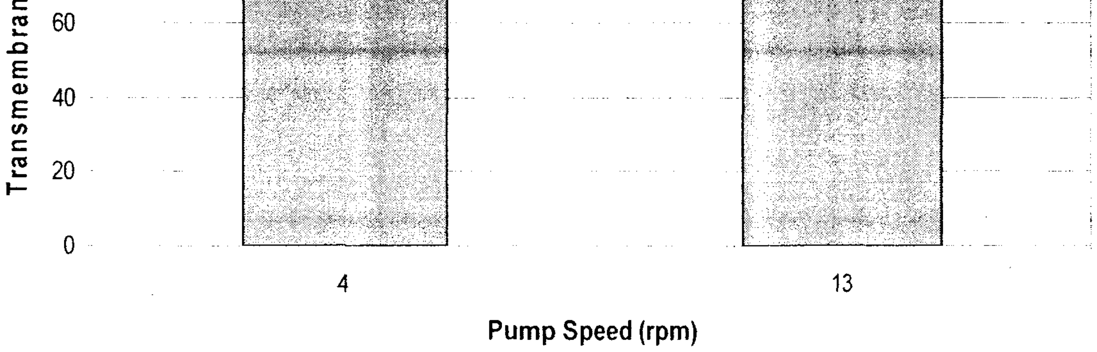


Figure 4.6 Effect of pump speed on transmembrane pressure at constant temperature and solution concentration (476.7 mg/l rhamnolipid and 9.6 mg/l Cu).

4.3.4 FOULING

As explained in the literature review chapter, membrane fouling is the limiting factor in ultrafiltration process. Figure 4.7 shows that within ten minutes of filtration, the flux declined by 42.1% (from 21.4 to 12.4 l/h-m^2). The temperature, solution concentrations, and pump speed were constant during the experiment with a negligible difference in the transmembrane pressure.

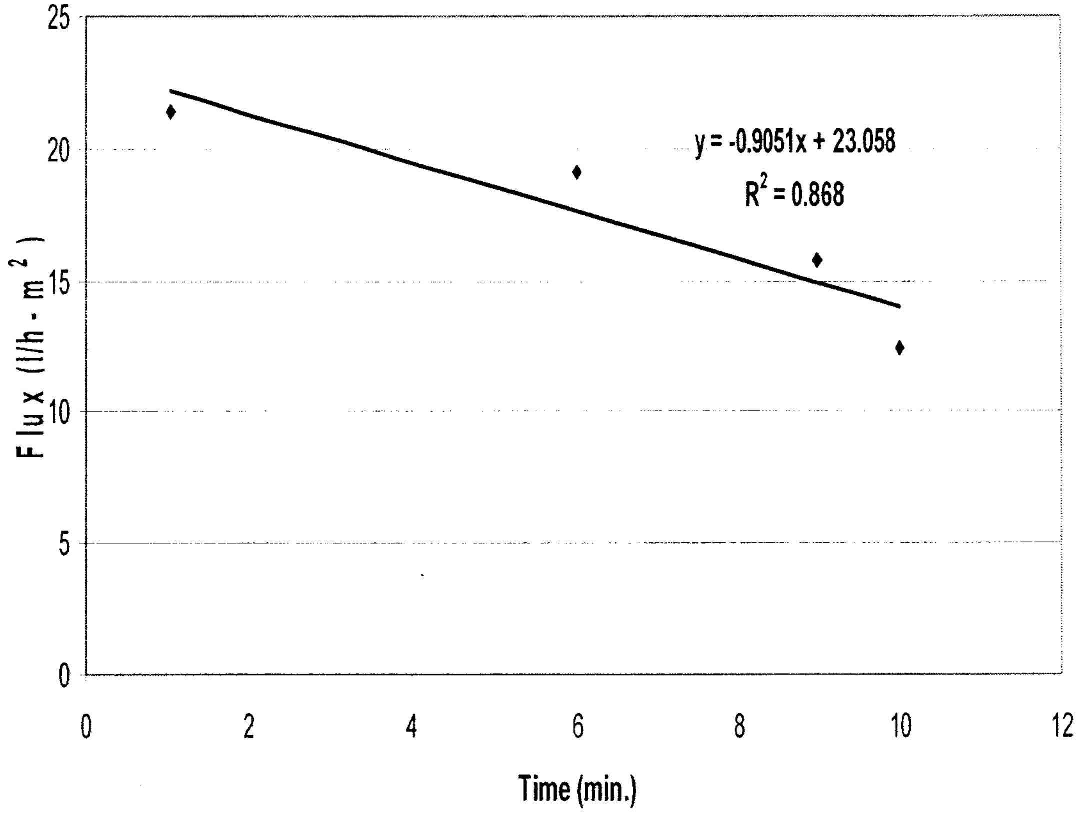


Figure 4.7 Decline of flux with time while keeping temperature, solution concentrations (6.4mg/l Cu and 317.8 mg/l rhamnolipid), and pump speed constant.

4.3.5 CONCENTRATION EFFECTS

Increasing the rhamnolipid - copper concentration increased the transmembrane pressure and decreased the flux at the same temperature (22^0C) and pump speed. Figures 4.8 and 4.9 show the different effects of increasing concentration. When the experiment was conducted at low rhamnolipid and copper concentrations (158.9 mg/l and 3.1 mg/l) respectively, a high flux (23.1 l/h-m^2) and low transmembrane pressure (61 kPa) were obtained.

Doubling the rhamnolipid concentration to 317.8 mg/l and copper to 6.4 mg/l had very little effect on the TMP which increased from 61 to 66 kPa only while the flux was decreased significantly from 23.1 to 17.3 l/h-m^2. The same effects were observed at higher concentrations for the aqueous solutions of rhamnolipid (476.7 mg/l) and copper (9.6 mg/l) on TMP where the increase was by 24% comparing to the first TMP value while the decline of the flux was less by 45%. Increasing the concentrations means more available rhamnolipid molecules, either in micelle form or as monomers, and more copper ions that have been adsorbed by the rhamnolipid micelles or free in the solution.

Therefore these results were expected since these molecules and ions have a higher possibility to interact with the internal membrane surface and eventually the opportunity to block the membrane pores. Increasing the concentration could be considered as another example of the fouling effect.

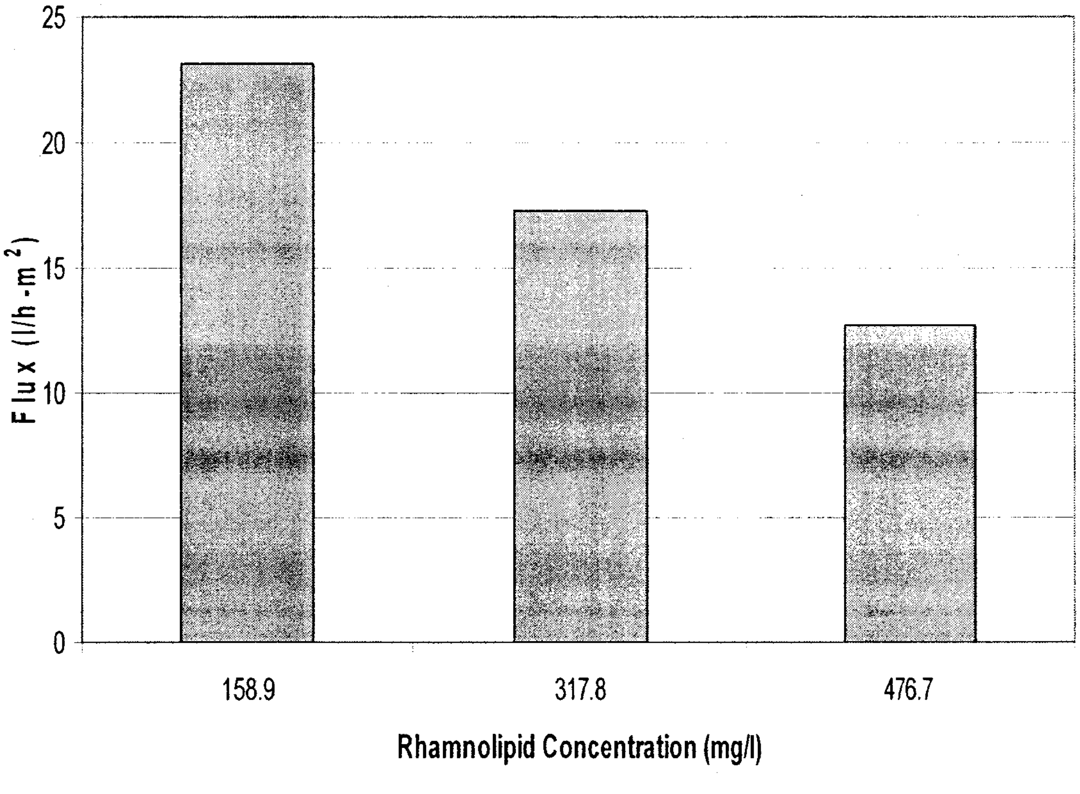


Figure 4.8 Effect of rhamnolipid concentration in rhamnolipid-copper solution on the flux.

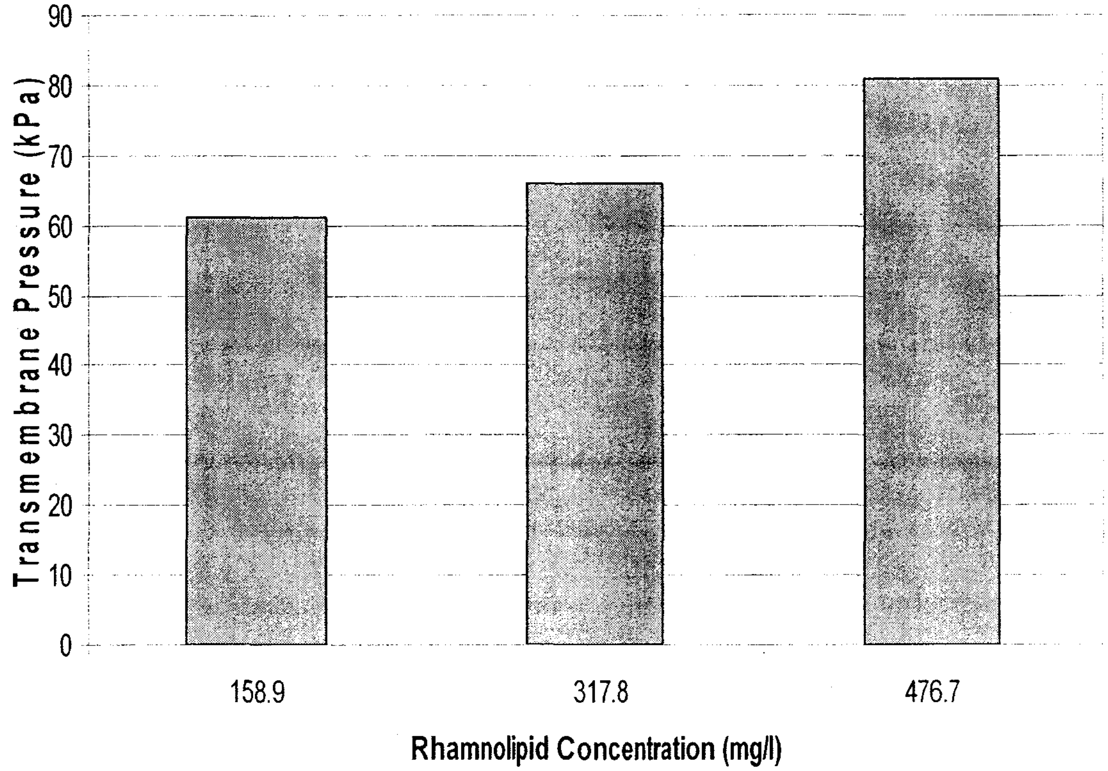


Figure 4.9 Effect of rhamnolipid concentration in rhamnolipid-copper solution on transmembrane pressure.

4.4 EXPERIMENTS OF GROUP TWO: DETERMINING THE MOLAR RATIO, MR, FOR THE 100% REJECTION AND INVESTIGATING THE RHAMNOLIPID BEHAVIOUR IN THE PRESENCE OF COPPER AND BENZENE

4.4.1 DETERMINING THE MR FOR COPPER

Three rhamnolipid-copper aqueous solutions at different concentrations were prepared at the same MR, 5.41 as shown in Figure 4.10 to determine if this

MR will achieve the 100% rejection. The sample of permeate flux for each of 3.1, 6.4, and 9.6 mg/l solutions was analyzed by the atomic absorption spectroscopy and indicate the presence of copper at concentrations of 0.8, 0.7, and 0.7 mg/l respectively.

For each experiment the feed sample was analyzed as well to determine the concentrations. Three samples of each feed and permeate were analyzed then the mean value were taken to determine the copper concentrations.

To reach the 100% rejection MR, the same procedures were repeated and three aqueous solutions of rhamnolipid-copper at concentrations of 3.1, 6.4, and 9.6 mg/l as shown in Figure 4.11 were used but this time at higher MR of 6.25. It was shown that at MR = 6.25 100% rejection molar ratio was achieved.

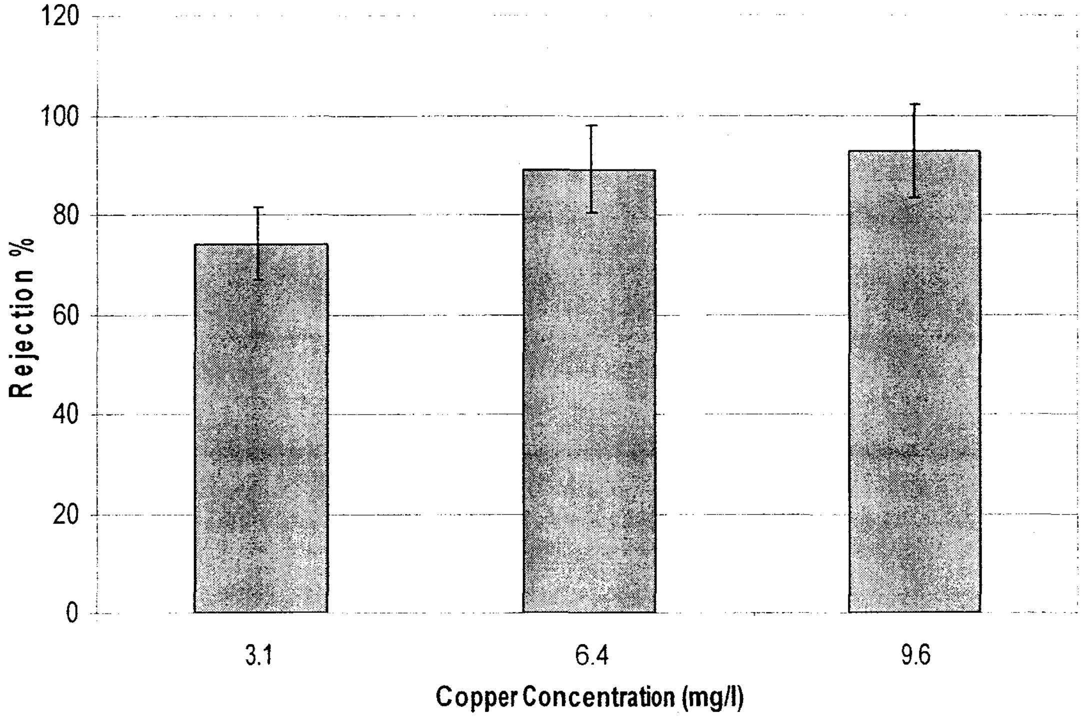


Figure 4.10 Rejection of rhamnolipid-copper solution at molar ratio = 5.41.

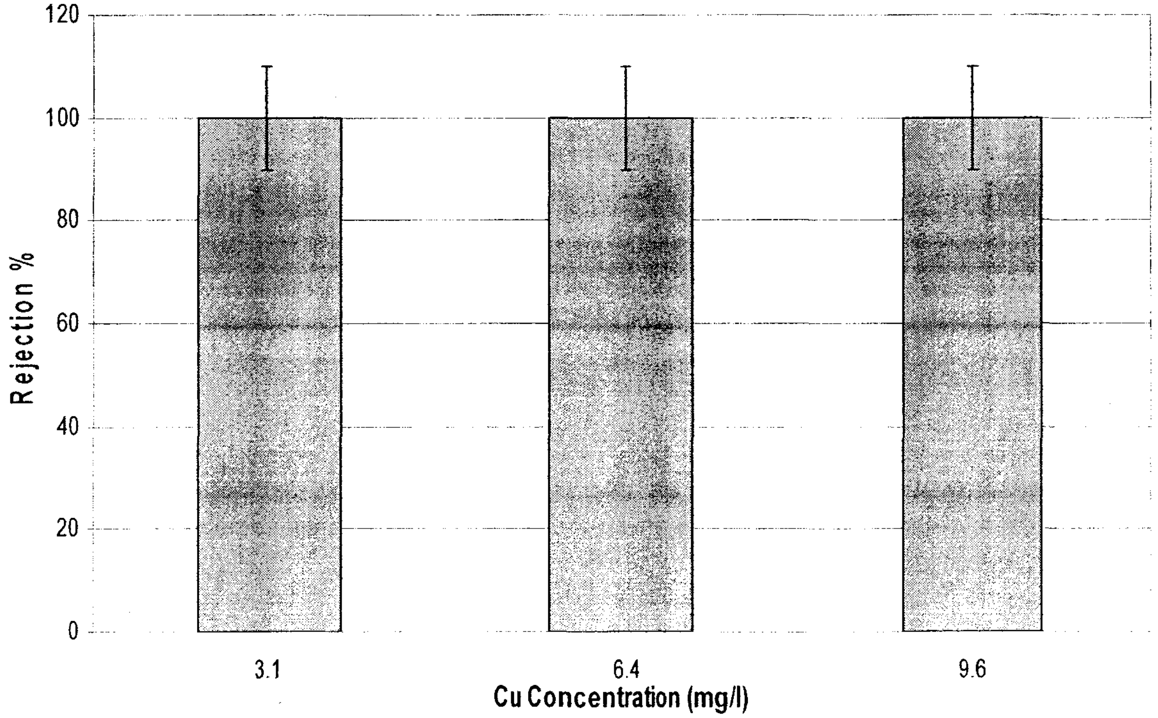


Figure 4.11 Rejection of rhamnolipid-copper solution at molar ratio = 6.25.

4.4.2 DETERMINATION OF THE MR FOR BENZENE

Two rhamnolipid-benzene aqueous solutions were prepared at concentrations of 190 mg/l and 264 mg/l benzene with MR equals to 0.77 for both as shown in Figure 4.12. Two samples of the feed and permeate samples were analyzed by HPLC and the mean value was taken to determine the concentrations. The analysis of the permeate samples confirmed the presence of the benzene. For 190 mg/l of benzene which had been added to make the rhamnolipid – benzene aqueous feed solution, the permeate concentration was 8.2 mg/l. The feed concentration then increased to 264 mg/l, the permeate concentration increased as well to 26 mg/l. Another two aqueous solutions of benzene and rhamnolipid were prepared at concentrations of 63 mg/l and 129 mg/l benzene. The expected molar ratio should be higher and therefore MR = 1.33 was used. The HPLC results showed that MR which equals to 1.33 is the 100% rejection MR for the above benzene two concentrations as shown in Figure 4.13. There was no benzene in the permeate samples.

4.4.3 RHAMNOLIPID BEHAVIOR IN THE PRESENCE OF COPPER

When rhamnolipid biosurfactant was added to copper aqueous solutions at concentrations higher than its CMC (38 mg/l), the micelles start to form and try to bind the copper ions. Figure 4.14 illustrates the results of experiments that were conducted for two reasons, the first one was to investigate the relationship between the rhamnolipid feed and permeate concentrations with values higher than the CMC in the presence of copper ions and the second one was to determine the effect of increasing the rhamnolipid feed concentration on the rhamnolipid permeate.

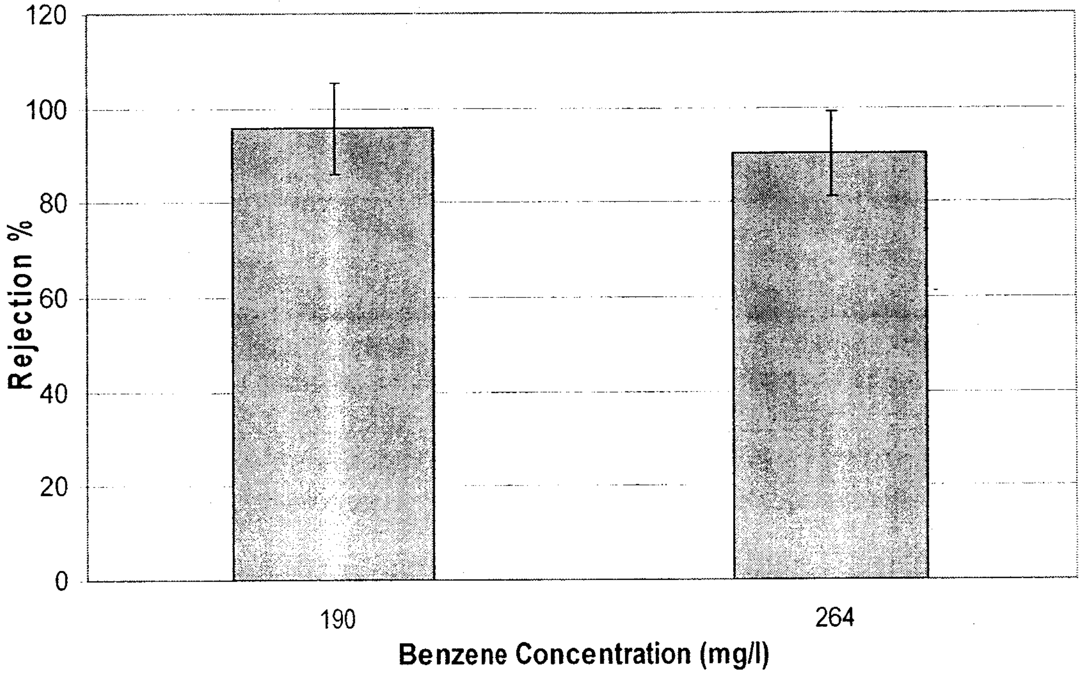


Figure 4.12 Rejection of rhamnolipid-benzene solution at molar ratio = 0.77.

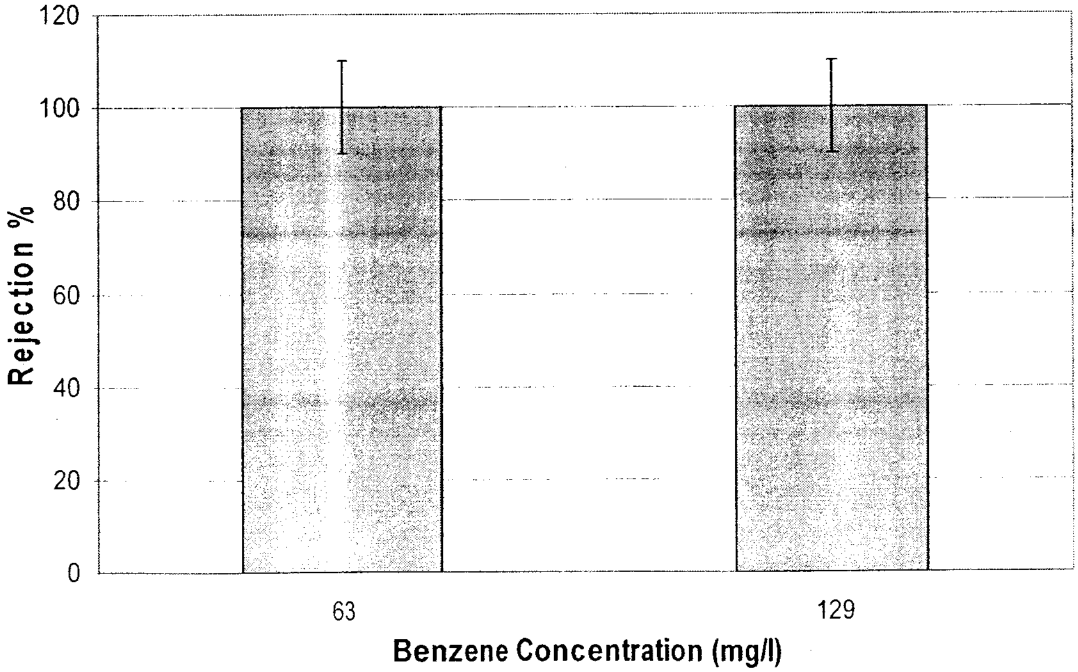


Figure 4.13 Rejection of rhamnolipid-benzene solution at molar ratio = 1.33.

Figure 4.14 shows that rhamnolipid permeate concentration values were very little in general regardless of the feed concentrations. For 159 mg/l of rhamnolipid which has been added to prepare rhamnolipid – copper aqueous feed solution, the permeate concentration was negligible (0.31 mg/l). The feed concentration then doubled to 317.8 mg/l. However, the permeate concentration decreased to 0.29 mg/l. These results were expected since the added rhamnolipid concentrations were more than four times the CMC which means that most of the added rhamnolipid monomers have been transformed into micelles and only a few monomers that remained free passed throughout the membrane filter pores to the permeate stream.

The economical aspect is a limiting point in using the rhamnolipid biosurfactant. Therefore, it is very important to reuse the rhamnolipid which means a high rejection has to be achieved. The low CMC is another important factor which could be included in the economical factor too since less biosurfactant is required to reach the CMC. In order to complete the evaluation of rhamnolipid efficiency by taking the economical aspect in consideration in addition to the contaminant removal, the concentrations of rhamnolipid biosurfactant in the feed and permeate streams needed to be determined as explained in Chapter three to determine the rhamnolipid efficiency by applying equation 3.6. That was done by using a surface tension-concentration curve to find the rhamnolipid concentrations of permeates of the 5.41 molar ratio. Since all the other conditions were approximately the same as for the 6.25 molar ratio, rhamnolipid efficiency procedures was done only for 5.41 MR. Figure 4.15 demonstrates the results of rhamnolipid rejection which indicated the high efficiency of biosurfactant JBR 425 used in the above experiments. Increasing the rhamnolipid concentration from 158.9 to 317.8 mg/l resulted in an increase in the rejection percentage from 99.8 to 99.91%. This was in agreement with the previous results of Figure 4.14 since the highest rejection means the lowest rhamnolipid in the permeate and retention of all the micelles by the membrane filter. Figure 4.16 illustrates the results of surface tension of rhamnolipid permeates which was compatible with the results mentioned above. As explained in the literature review chapter, the high surface tension is an indication of the low rhamnolipid concentration. Therefore the permeates of 99.9% and 99.8% rejections had a surface tension of 62.5 mN/m which is very near to the clean water surface tension (62.9 mN/m).

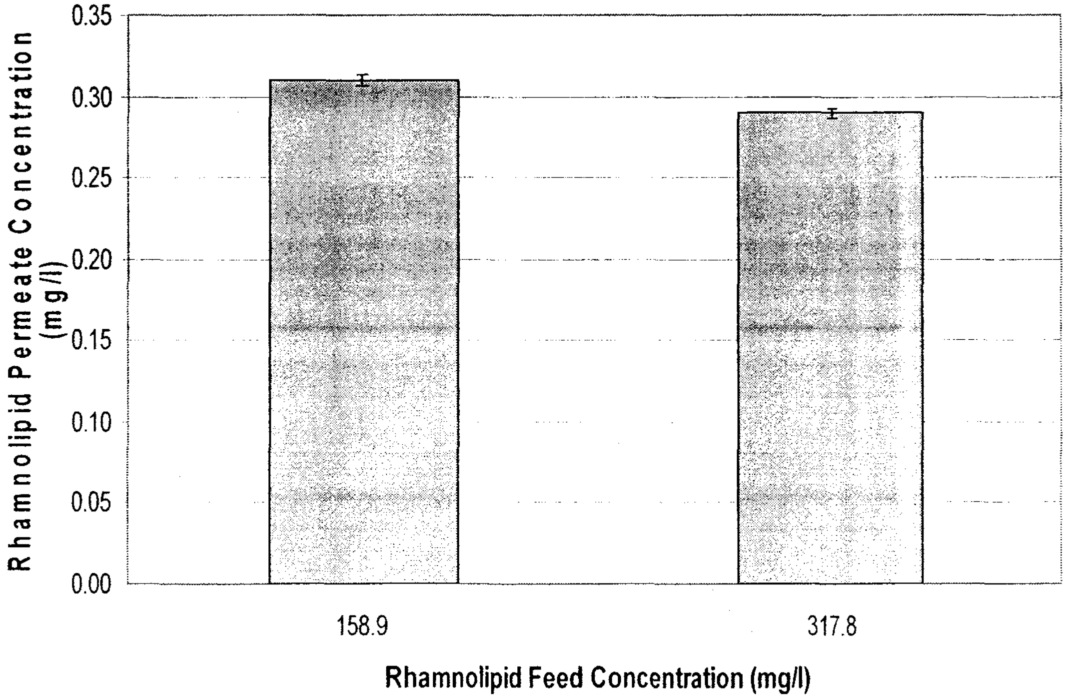


Figure 4.14 Permeate rhamnolipid versus feed rhamnolipid concentrations.

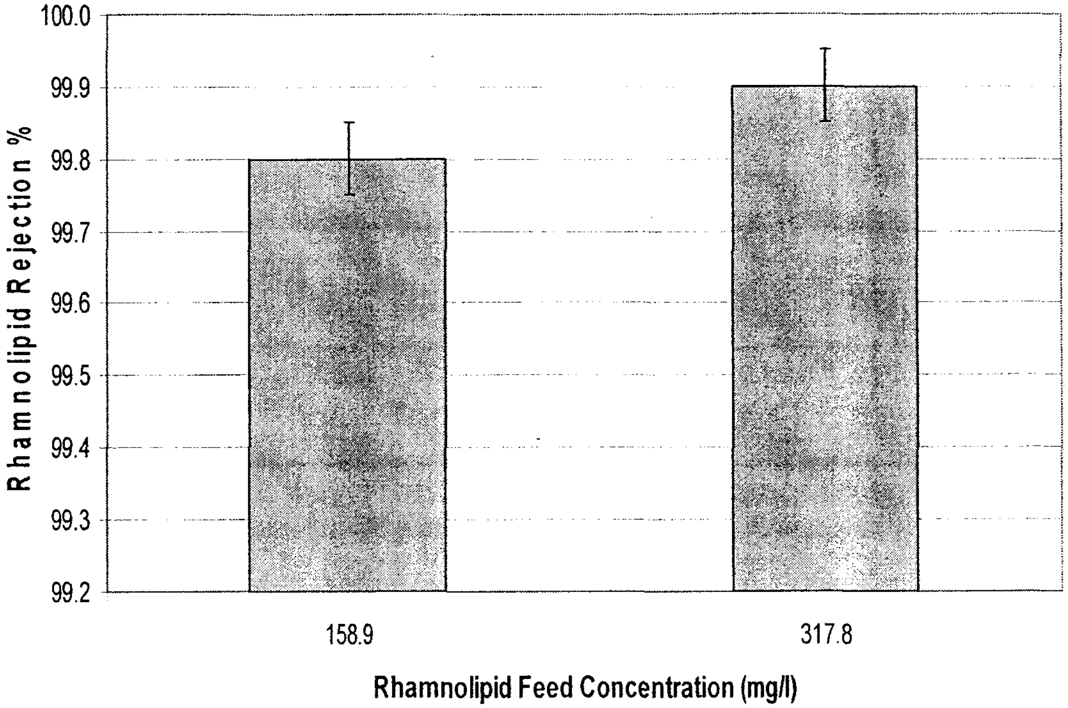


Figure 4.15 Rejection percentage of two rhamnolipid feed solutions.

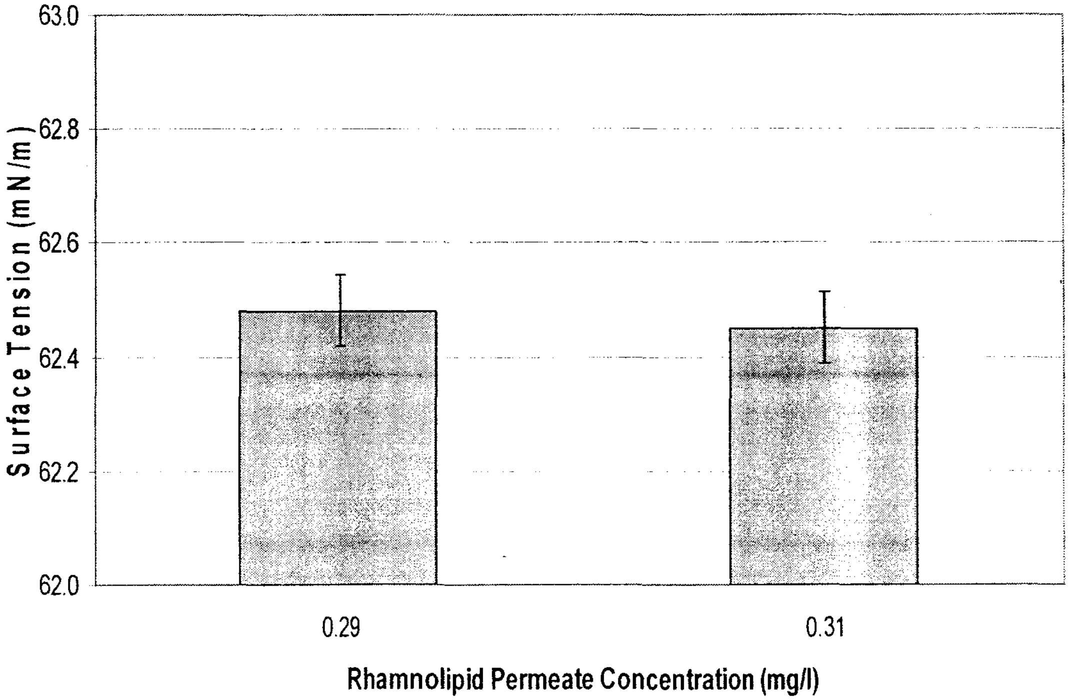


Figure 4.16 Surface tension of rhamnolipid permeates.

4.4.4 RHAMNOLIPID BEHAVIOR IN THE PRESENCE OF BENZENE

When rhamnolipid biosurfactant was added to benzene aqueous solutions at concentrations higher than its CMC (38 mg/l), the micelles start to solubilize the benzene molecules. Figure 4.17 illustrates the results of experiments that have been conducted for two reasons. The first one was to investigate the relationship between the rhamnolipid feed and permeate concentrations with values higher than CMC in the presence of benzene molecules and the second one was to determine the effect of increasing the rhamnolipid feed concentration on the rhamnolipid permeate. Figure 4.18 showed that rhamnolipid permeate concentration values were minimal in general regardless the feed concentration. For 1080 mg/l of rhamnolipid which was added to make the rhamnolipid – benzene aqueous feed solution. The permeate concentration was 21.6 mg/l. The feed concentration then increased to 1445 mg/l. However the permeate concentration decreased to 10 mg/l. The added rhamnolipid concentrations were more than twenty eight times the CMC which means that most of the added rhamnolipid monomers have been transformed to micelles and only a few monomers were able to pass through the membrane filter pores to the permeate stream. As mentioned above in determining the efficiency of biosurfactant JBR425 for economical aspects, the concentrations of rhamnolipid in the permeate of rhamnolipid-benzene aqueous solutions has to be evaluated.

Figure 4.18 demonstrates the rejection efficiency of the membrane for the above experiments. Increasing the rhamnolipid concentration from 1080 to 1445 mg/l resulted in an increase in the rejection percentage from 98.0 to 99.3%. This was in agreement with the previous results of Figure 4.17 since the highest rejection means the lowest rhamnolipid concentration in the permeate and the retention of all the micelles by the membrane filter. Figure 4.19 illustrates the results of the surface tension measurement of rhamnolipid permeates which was compatible with the results mentioned above. Chapter two showed that the high surface tension is an indication of low rhamnolipid concentration. Therefore the permeate of 99.3% rejection had a surface tension of 49 mN/m while the permeate of 98% rejection had a surface tension of 33 mN/m.

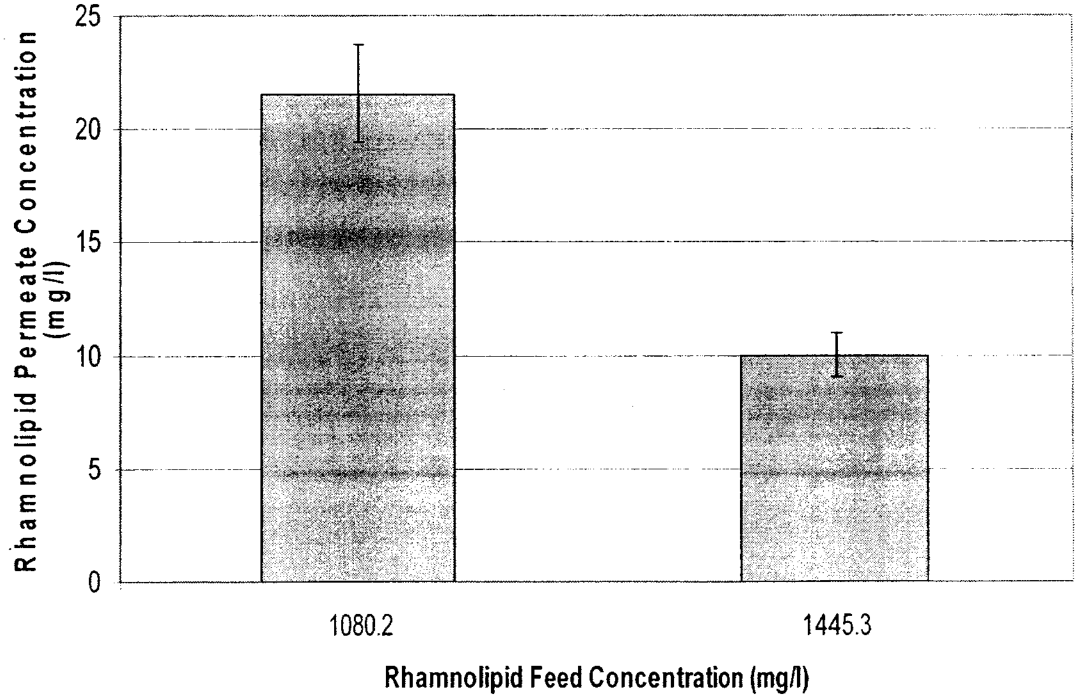


Figure 4.17 Permeate rhamnolipid versus feed rhamnolipid concentration.

Figure 4.10 illustrates that increasing the copper concentration increased the rhamnolipid removal efficiency for the same molar ratio (MR = 5.41) because the required quantity of rhamnolipid at 3.1 mg/l of Cu is near to cmc and with increasing the copper concentrations the rhamnolipid concentration will increased too which means more micelles will form and eventually higher rejection.

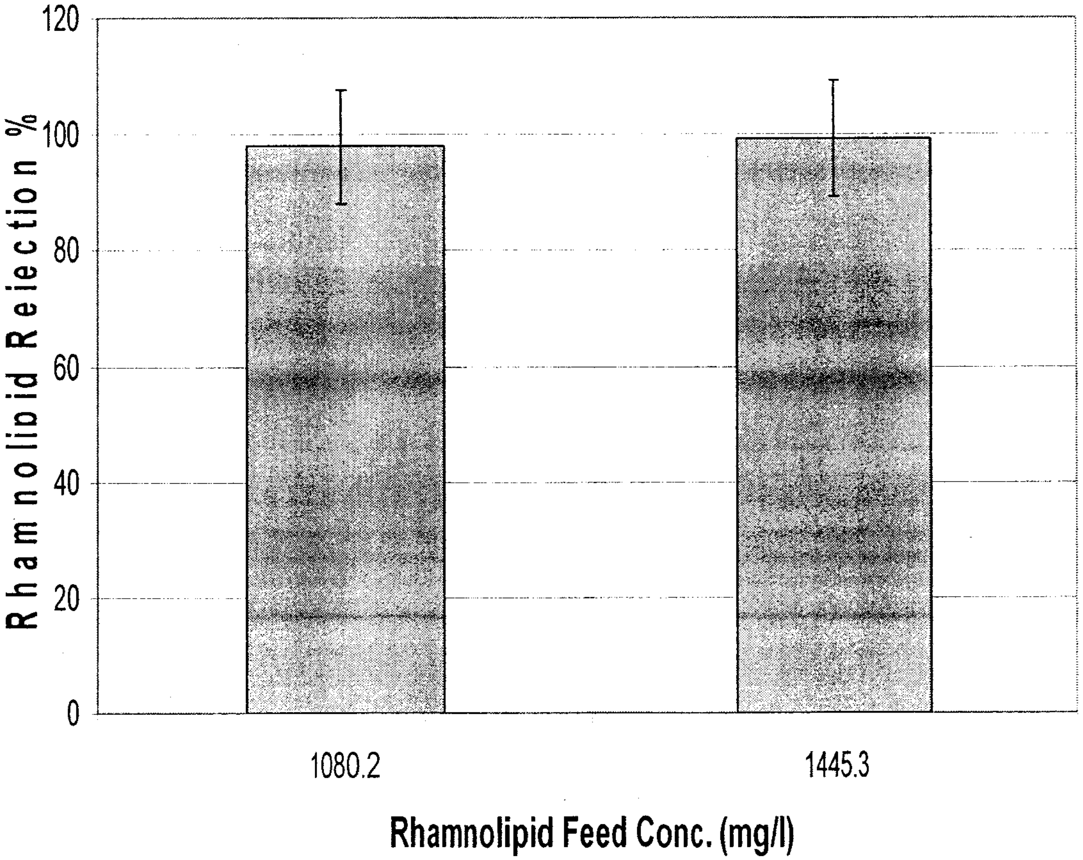


Figure 4.18 Rejection percentage of two rhamnolipid feed solutions.

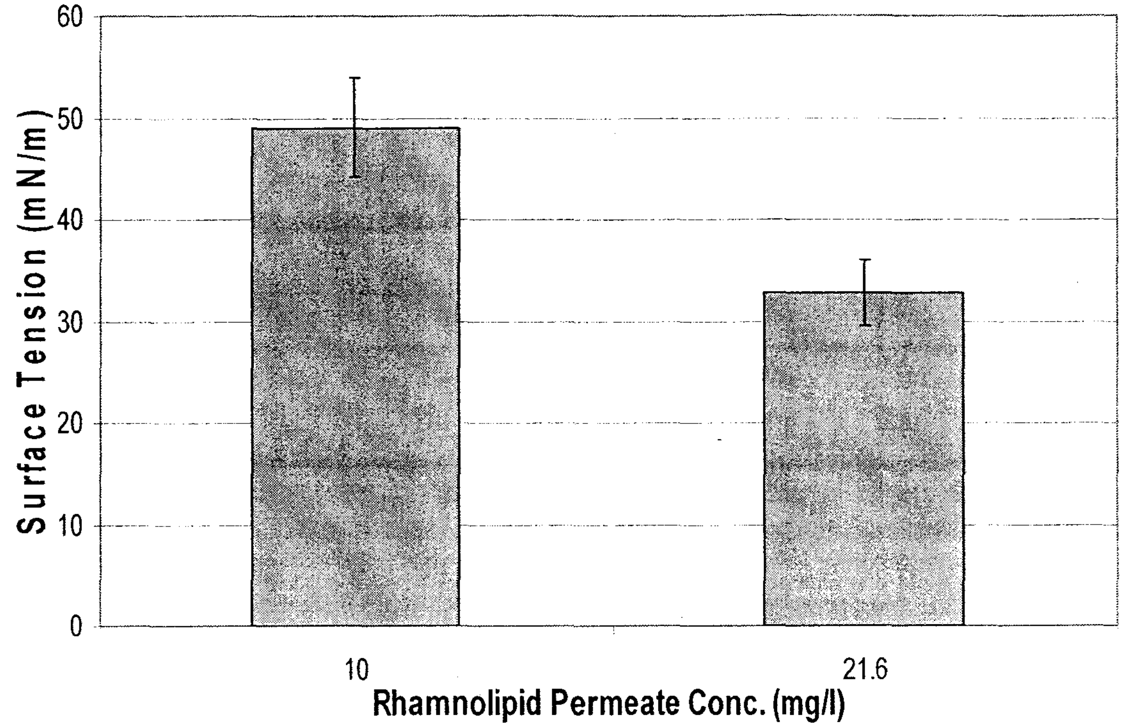


Figure 4.19 Surface tension of rhamnolipid-benzene solutions permeates.

4.5 EXPERIMENTS OF GROUP THREE: THE EVALUATION OF RHAMNOLIPID CAPABILITY TO SEPARATE COPPER IONS AND BENZENE MOLCULES SIMULTANEOUSLY

The evaluation of rhamnolipid capability for the removal of copper ions and benzene molecules simultaneously, required preparing two subgroups of experiments with two objectives, primary and secondary. The primary objective was to observe the effect of the presence of the added contaminant on the 100% rejection molar ratio of the other one. That was repeated at two different concentrations of the main contaminant. The secondary objective was to determine that the molar ratio of the added contaminant was affected as well.

4.5.1 EXPERIMENTS OF FIRST SUBGROUP: THE EFFECT OF BENZENE PRESENCE ON RHMNOLIPID CAPABILITY TO REMOVE COPPER

This objective, which is the primary one of the first subgroup, was performed by adding 90 mg of benzene to two rhamnolipid-copper aqueous solutions of 100% rejection molar ratio which is equal to 6.25 to investigate the effect of benzene presence on the 100% rejection MR. The copper concentrations of the first and second solutions were 6.2 and 8.3 mg/l respectively. The effect of benzene presence on the 100% rejection MR for copper has been examined by analyzing the copper ions content of the permeate samples since the presence of copper ions in them means that MR of 6.25 is no more being the 100% rejection MR which indicates the negative effect of benzene presence. The atomic absorption spectroscopy did not detect any presence of copper ions in the permeate samples which meant that benzene presence had no negative effect on rhamnolipid capability to remove copper and the 100% rejection MR, 6.25 did not change as illustrated in Figure 4.20.

For the same experiment the benzene presence in the permeate samples were analyzed additionally as the secondary objective to check the effect of copper presence on the removal of benzene molecules at that amount of rhamnolipid which was enough to achieve 100% of copper rejection and eventually if there will be any positive or negative change on the benzene 100% rejection MR. This was repeated for the two concentrations of copper, 6.2 and 8.3 mg/l. Depending on the percentage of benzene presence in permeate samples, the simultaneous removal efficiency was determined. The lower the percentage of benzene presence, the higher the simultaneous removal efficiency is. HPLC results showed that benzene was not detected. Figure 4.21 illustrated the new 100% rejection molar ratios that have been achieved with less amount of rhamnolipid. The copper improved the benzene 100% rejection MR which was 1.33 and decreased it to 0.77 with 8.3 mg/l of copper then to 0.56 with 6.2 mg/l of copper. The above experiments (first subgroup of group 3) did confirm the ability of rhamnolipid biosurfactant to remove both, the copper ions and benzene molecules simultaneously from their aqueous solutions. In addition, an improvement of the 100% rejection MR of benzene has been obtained.

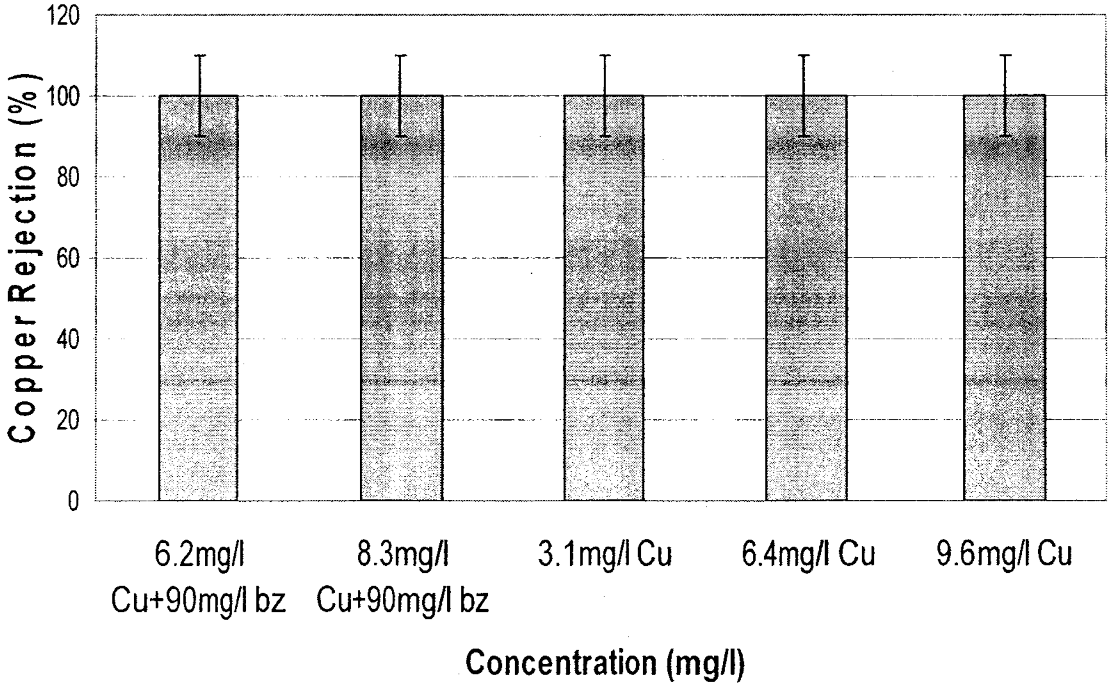


Figure 4.20 Effect of 90mg/l benzene on copper MR of 100% rejection (MR = 6.25).

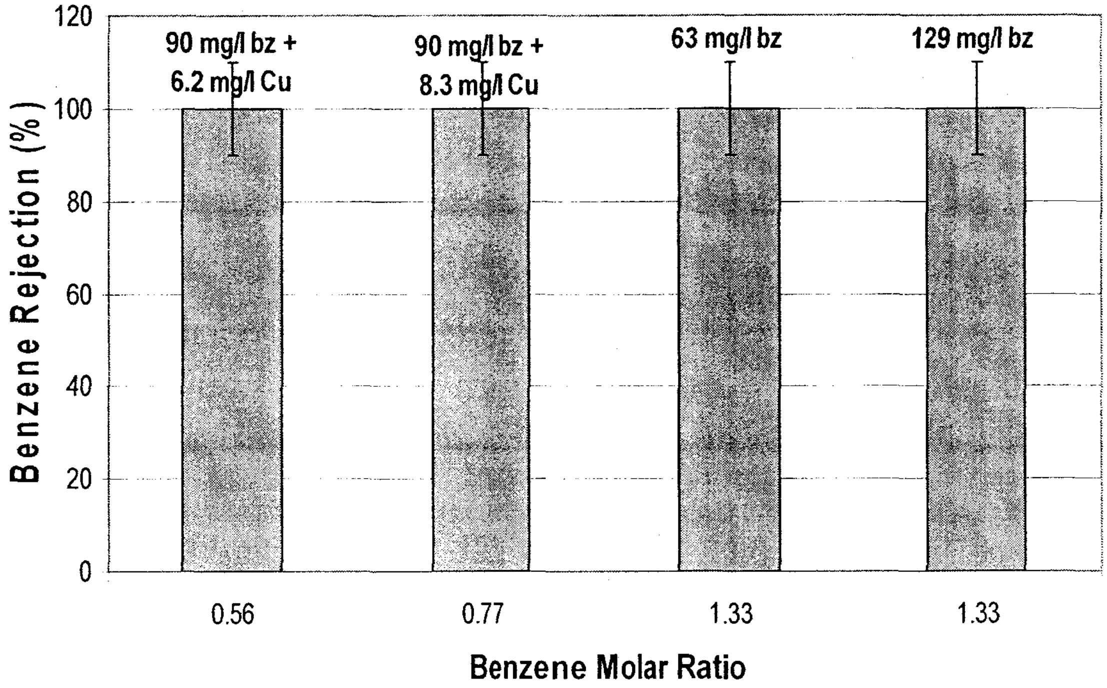


Figure 4.21 Effect of 6.2 and 8.3 mg/l copper on rhamnolipid-benzene MR.

4.5.2 EXPERIMENTS OF SECOND SUBGROUP: THE EFFECT OF COPPER PRESENCE ON RHMNOLIPID CAPABILITY TO REMOVE BENZENE

The primary objective of the second subgroup was illustrated in Figure 4.22 and the secondary in Figure 4.23. The primary is to investigate the effect of copper presence on benzene new molar ratio (MR) for 100% rejection, 0.77, which were obtained from the first subgroup experiments. The secondary objective was to determine how the molar ratio of added contaminant, and the copper, was affected with each new molar ratio. The effect of copper presence on the new 100% rejection molar ratio of benzene was investigated to evaluate the capability of rhamnolipid biosurfactant to remove the benzene molecules and copper ions simultaneously. To do so, a certain weight of copper (8.3 mg) was added to two benzene aqueous solutions of 100% rejection molar ratio which became equal to 0.77.

The benzene concentrations for the first and second solutions were 43.7 and 63 mg/l respectively. The effect of copper presence on the 100% rejection MR for benzene was examined by analyzing the benzene content of the permeate samples. HPLC results showed that benzene was not detected which meant that 8.3 mg/l of added copper did not affect the capability of rhamnolipid to remove the benzene and the new 0.77 molar ratio has been confirmed to be the 100% rejection MR as shown in Figure 4.22. To determine the second objective, the permeate samples were analyzed to determine copper presence and to check the effect of benzene on the removal of copper ions. Depending on the percentage of copper presence in permeate samples or copper rejection by rhamnolipid, the simultaneous removal efficiency was determined. The atomic absorption spectroscopy showed the presence of copper in permeate samples and that the copper rejection decreased slightly to 97% for both experiments of 63 and 43.7 mg/l of benzene as shown in Figure 4.23. However these rejections of 97% for 8.3 mg/l of copper have been obtained with molar ratios of 4.72 and 2.33 respectively comparing to 6.25 for 100% rejection for copper concentrations less than 8.3 mg/l. Figure 4.24 shows that benzene addition improved the MR of copper rejections of less than 100% and with the lower concentration of benzene the rejection was the same.

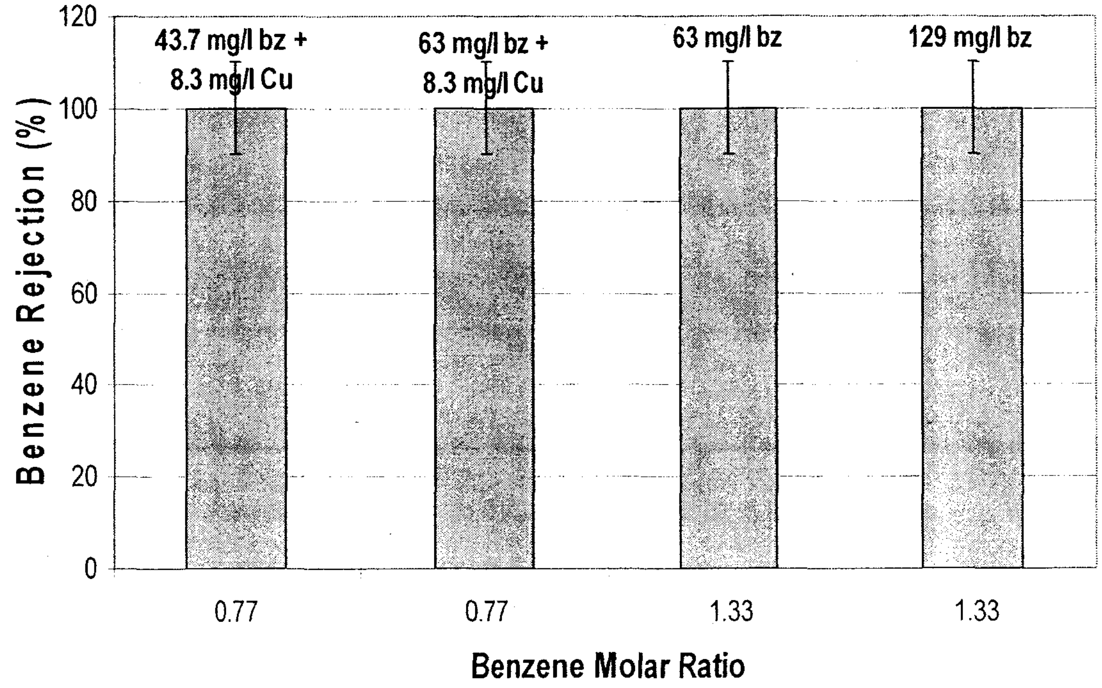


Figure 4.22 Effect of 8.3 mg/l copper on the new benzene MR (0.77) of 100% rejection.

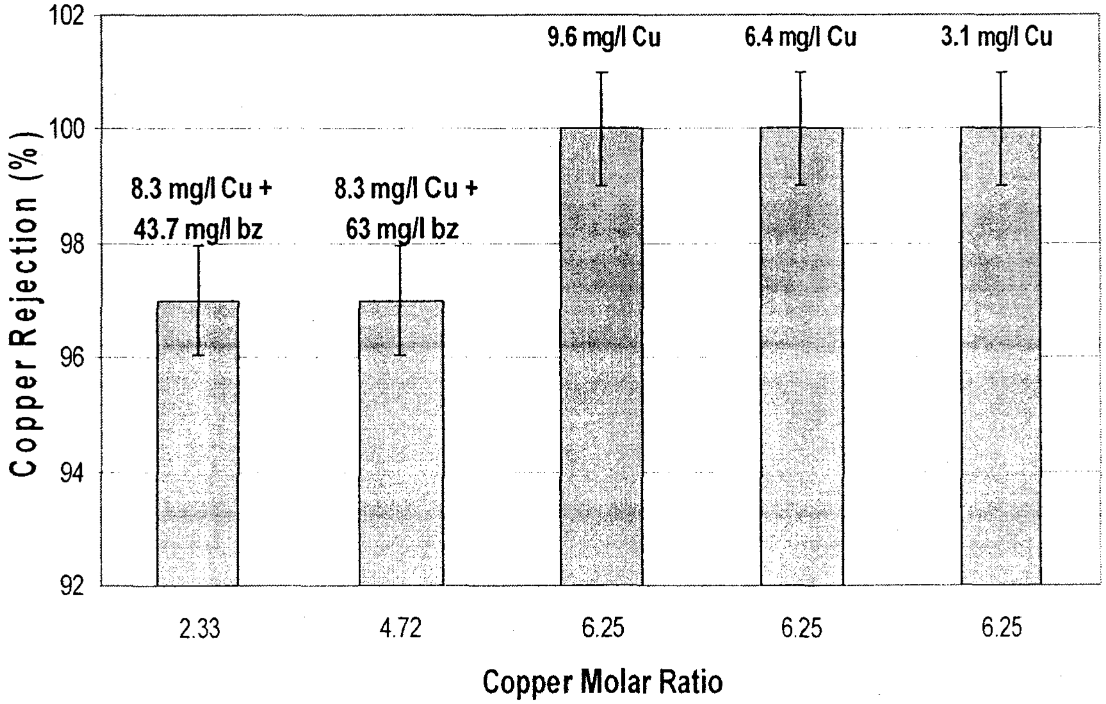


Figure 4.23 Benzene effect on copper MR compared to 100% rejection MR.

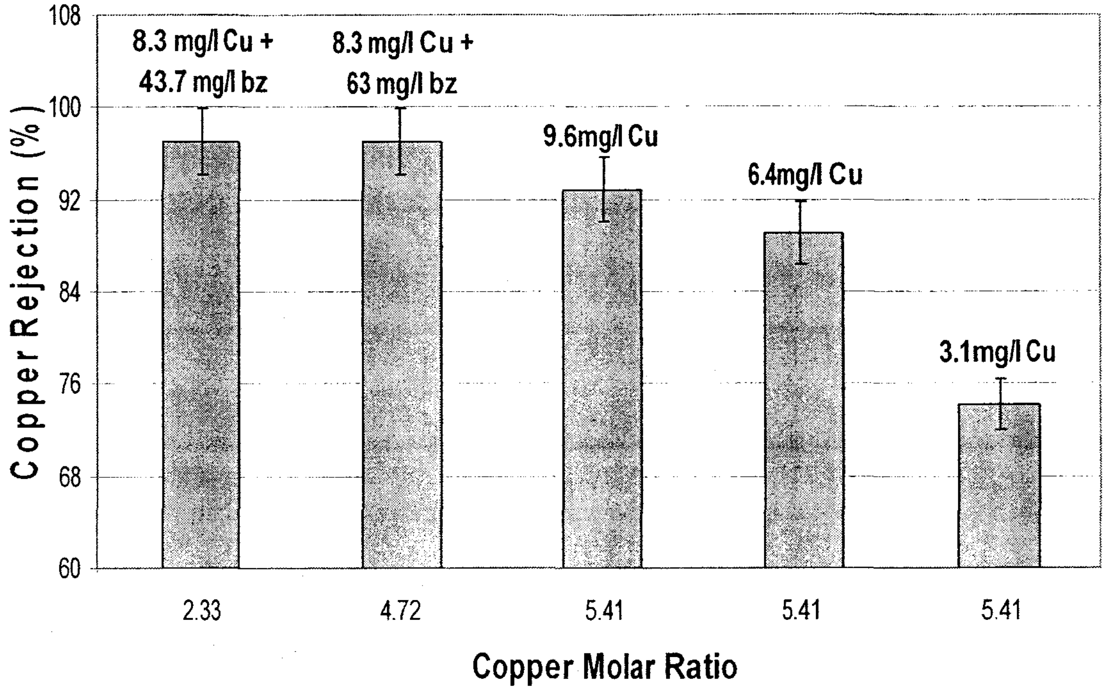


Figure 4.24 Effect of 43.7 and 63 mg/l benzene on copper MR compared to MR of less than 100% rejection.

4.6 RESULTS SUMMARY

The following tables summarize the important results of this study. Tables 4.1 and 4.2 show that MR (molar ratio) of less than and equal to 100% rejections for three different concentrations of copper (3.1, 6.4, and 9.6 mg/l) using rhamnolipid biosurfactant JBR 425 are 5.41 and 6.25 respectively. Other studies [34] showed that a molar ratio of 5 is required to remove more than 99% of 12.7 mg/l copper when the chemical surfactant sodium dodecyl sulphate (SDS) was used [34]. For 50 mg/l of copper the required molar ratio to remove 99.2% was 18.5 by SDS chemical surfactant [27].

Table 4.1 Effect of copper feed concentration on copper rejection using a MR of 5.41.

Cu feed conc.(mg/l)	Cu Rejection%
3.1	74.2
6.4	89.1
9.6	92.8

Table 4.2 Effect of copper feed concentration on copper rejection using a MR of 6.25.

Cu feed conc.(mg/l)	Cu Rejection %
3.1	100
6.4	100
9.6	100

Tables 4.3 and 4.5 show that MR's (molar ratios) for less than 100% rejection of two different concentrations of benzene, 190 and 264 mg/l, and molar ratios for 100% rejection of 63 and 129 mg/l of benzene using rhamnolipid biosurfactant JBR 425 are 0.77 and 1.33 respectively. A study showed that a molar ratio of 0.5 was required to remove 81.4% of 15.6 mg/l benzene using the chemical surfactant sodium dodecyl sulphate (SDS) [28].

Table 4.3 Benzene feed concentration effect on benzene rejection using a MR of 0.77.

Benzene feed conc.(mg/l)	Rejection %
190	95.7
264	90.2

Table 4.4 showed that benzene presence had no effect on the 100% rejection molar ratio (6.25) of copper but in the same time a significant improvement, because of the copper presence, in 100% rejection molar ratio of benzene was observed, from 1.33 to 0.77 in the presence of 8.3 mg/l of copper then to 0.56 in the presence of 6.2 mg/l of copper. Table 4.5 shows that copper presence had no effect on the new benzene 100% rejection molar ratio (0.77). However, an improvement of copper molar ratios of less than 100% rejection was obtained. A molar ratio of only 2.33 was needed to achieve 97% removal of 8.3 mg/l copper while a molar ratio of 5.41 was needed to achieve 89.1% removal of 6.4 mg/l.

Table 4.4 Effect of benzene on 100% rejection molar ratio of copper.

Cu MR	Cu Rejection%	Cu (mg/l)	benzene (mg/l)	benzene Rejection %	benzene MR
6.25	100	9.6	0	0	0
6.25	100	6.4	0	0	0
6.25	100	3.1	0	0	0
6.25	100	8.3	90	100	0.77
6.25	100	6.2	90	100	0.56

Table 4.5 Effect of copper on 100% rejection molar ratio of benzene.

benzene MR	benzene Rejection %	benzene conc. (mg/l)	Cu conc. (mg/l)	Cu Rejection %	Cu MR
1.33	100	129	0	0	0
1.33	100	63	0	0	0
0.77	100	63	8.3	97	4.72
0.77	100	43.7	8.3	97	2.33

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 SUMMARY AND CONCLUDING REMARKS

The main objective of this research was to determine the efficiency of anionic rhamnolipid biosurfactant (JBR 425) in removing both copper ions and benzene molecules simultaneously from water and wastewater streams. Cross-flow micellar-enhanced ultrafiltration (MEUF) system has been used to achieve this objective.

The removal depends on the presence of rhamnolipid biosurfactant JBR 425 which has the ability to form micelles when it is added with concentration higher than its critical micelle concentration (CMC). The formed rhamnolipid micelles have hydrophilic surfaces where the copper ions have been bound and the hydrophobic core where benzene molecules have been solubilized and these micelles are big enough to be retained by the hollow fibre membrane filter and rejected by a separate stream, the retentate, leaving the clean water to pass through membrane pores with acceptable concentrations of rhamnolipid monomers and contaminants. Part of the objective of this study was to observe the effect of operation parameters on the process efficiency such as fouling, TMP, temperature, concentrations of contaminants and the biosurfactant, and the peristaltic pump speed. The other part of this study which is the most important to achieve the objective was conducting experiments to determine the rhamnolipid - contaminant molar ratio for copper and for benzene separately and then to investigate the effect of contaminant presence on the other one molar ratio and vice versa.

Through the conducted experiments, the following observations and conclusions were made based on the obtained results.

- The operating parameters had different effects on the micellar-enhanced ultrafiltration process. For clean water, transmembrane pressure had a higher effect than temperature within the range studied. The pH value of the solution was kept in the range of 6.81 to 7.11 since the rhamnolipid efficiency starts to decline below this range.

- Since the fouling effect increases with speed, and to have a high flux is an important objective of the ultrafiltration process, therefore it was always better to keep the system at low speed, 4 rpm (maximum pump rpm is 100). The high and low speed values were determined by the solution nature and operation parameters.

- The effect of increasing rhamnolipid concentration on the surface tension of contaminated aqueous solutions beyond CMC was minimal. However this increase creates more micelles to remove the contaminants and eventually increases the rhamnolipid efficiency.

- The contaminant type had a significant effect on permeate surface tension depending on the obtained results. However, that effect was very little on rejections. For concentrations higher than CMC, permeate surface tension of two different copper-rhamnolipid solutions with NaOH for pH adjustment was 62.5 mN/m for both which is much higher than that of benzene-rhamnolipid solutions which were 32.8 and 49 mN/m. For the same previous solutions, the rhamnolipid rejections of rhamnolipid-copper solutions were ≥ 99.8% with rhamnolipid feed concentration much less than that of the benzene. However the rhamnolipid rejection of rhamnolipid-benzene solution was ≥ 98%.

- The molar ratio (MR) which is the required quantity of rhamnolipid to remove either copper or benzene in the separate case was not the same when the removal was done simultaneously. This indicated the influences of the two contaminants on each other. This influence was positive since the required MR to remove copper and benzene simultaneously was either equal to or less than its required value to remove them separately.

- Fouling was the limiting factor of the process. Within ten minutes of filtration, the flux declined by 42.1%.

5.2 RECOMMENDATIONS FOR FUTURE WORK

This study tries to present an effort to deal with a serious problem and to participate in finding a solution but it by no means completely solves this challenging problem and for that reason future research is required. Depending on the theoretical and practical knowledge acquired in the current study the subsequent recommendations for future work can be made:

- In the present study the evaluation of micellar-enhanced ultrafiltration process was limited to a membrane of 5000 NMWC. Therefore a membrane filter with larger pores which means a higher NMWC such as 10,000 or 30,000 is required to increase the flux.

- Since the fouling, which is the main factor affecting the process flux, is caused by interaction of contaminants with the material of membrane, then using membranes with different materials will help to investigate the best membrane material matching the system requirements and eventually the process efficiency.

- The efficiency of rhamnolipid JBR 425 in removal of benzene and copper, separately or simultaneously, is very high. However an attempt to investigate the efficiency of another biosurfactant at lower cost is recommended to enlarge the area of MEUF applications depends on finding inexpensive sources of biosurfactant to compete the chemical ones in the market.

- Preparing wastewater samples with more than two contaminants and testing the rhamnolipid efficiency to remove them all will help more to understand the full capacity of the rhamnolipid removal efficiency.

- Evaluating the treatability of actual wastewater samples to observe the other factors like suspended solids on rhamnolipid efficiency.

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