APPLICATION OF HIGH SHEAR ULTRAFILTRATION ALONG WITH OTHER TERTIARY ROOTS IN INDUSTRIAL WASTEWATER TREATMENT

Thesis submitted by

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(Index No.: 176/13/E)

Doctor of Philosophy (Engineering)

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February 2017

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Thesis submitted for the degree of

Doctor of Philosophy (Engineering)

Submitted to

Jadavpur University

By

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Dedicated

To

My Beloved

Parents

JADAVPUR UNIVERSITY

KOLKATA – 700032, INDIA

INDEX NO. 176/13/E

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ACKNOWLEDGEMENT

At the very beginning, I would like to show my sincere and utmost gratitude to Prof. Chiranjib Bhattacharjee, Professor, Chemical Engineering Department, Dean, Faculty of Engineering and Technology, Jadavpur University, Kolkata, India, for giving me this opportunity to pursue my PhD under his expert supervision. Thanks to him, for having faith on me when I myself was not confident in my research tenure.

I want to show my sincere gratitude to Dr. Dwaipayan Sen, Assistant Professor, Department of Chemical Engineering, Heritage Institute of Technology, Kolkata, India, for his kind support and valuable guidance during my research. Thanks to Dr. Sen for always motivating me to carry on my research from my master's days. Without his push today, I might not be pursuing my career in this academic field.

I am very thankful to each lab mate and senior scholars of Membrane Research Laboratory of Chemical Engineering Department, Jadavpur University for maintaining a nice work environment. Very special thanks to Shubhrajitda, Santanuda, Ankurda, Bipasha for being awesome colleague. I would also want to thank Avik, Souptik and Sanjukta for being wonderful supportive juniors. A special thanks to Ankita for her extensive support during final days of the thesis preparations.

I want to show my sincere gratitude to professor, staffs and colleagues in the Department of Chemical Engineering, Jadavpur University, for their kind support and concern throughout my academic tenure from my bachelor days.

Thanks to Prof. Gisle Øye, Ugelstad Laboratory, Chemical Engineering Department, NTNU, Norway, for giving me the opportunity to work under his supervision as well.

I am indebted to my colleagues of Ugelstad Laboratory for their enormous support during my exchange stay at NTNU. I want to acknowledge Bertek, May, Bicheng, Camilla, Sebastien, Marcin for their help and insights during my experimentation. Support of the master student Arnt is highly appreciated as well. Thanks to Alex and Birgitte, my first officemates in NTNU for welcoming me every morning with their warm greetings. Thanks a ton to Ahmed for tolerating me with my little toddler during his work hours.

A big thank to my families, Putatunda's as well as Bandyopadhyay's. Thanks to Maa and Baba for having faith on me to pursue my academic work. It was not possible without constant push from Maa to being a PhD researcher. Thanks to my second parent, my parent in law, Dr. Maa and Dr. Baba for their immense encouragement and comfort after my marriage. Without their cooperation, I would not have been able to prepare my thesis in stipulated time being a married woman.

Thanks to Soha, our rebel princess for providing me my needed work hours to complete my submission.

Now it is time to thank my friend, come officemate, and come better half Sulalit for providing all those professional as well as emotional support throughout the final days of my thesis. Thank to him for taking care of our little Soha at the verge of his PhD dissertation just to give me out some time to carry out my work.

I want to acknowledge UGC, India and SIU, Norway sponsored An Indo-Norwegian Collaborative Project INCP (Project Number: INCP-2014/10060 (Vide sanction letter no. F. No. 58-3/2014(IC) dated December 2014)) for giving me the opportunity to work in NTNU, Norway.

This dissertation would not have been possible without the guidance and the help of several individuals during the preparation and completion of this study.

Finally thank you God for everything you have given to me.

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List of Publications

International Publications:

1. ***Sirsha Putatunda***, Dwaipayan Sen, Chiranjib Bhattacharjee, Emulsified oily-waste water: pretreatment with inorganic salts and treatment using two indigenous membrane modules, RSC Advances, 5, 2015, 52676– 52686.
2. ***Sirsha Putatunda***, Dwaipayan Sen, Ankur Sarkar, Ranjana Chowdhury, Debasish Sarkar, Chiranjib Bhattacharjee, Two indigenous high sheared membrane modules' performance expatiation for the ultrafiltration of polyethylene glycol, RSC Advances, 4, 2014, 6435– 6446.
3. Arnab Baksi, ***Sirsha Putatunda***, Dwaipayan Sen, Ankur Sarkar, Chiranjib Bhattacharjee, Protocol Development for the Carbohydrate Quantification in Black Liquor with Brix Refractometer, Journal of The Institution of Engineers (India): Series E, 93 (2), 2013, 69-74.

Communicated:

1. ***Sirsha Putatunda***, Souptik Bhattacharya, Dwaipayan Sen, Chiranjib Bhattacharjee, A review on the treatment of oil-water emulsion in case of oil contaminated water. (*Communicated in Water Research*)

Conference Papers:

1. ***Sirsha Putatunda***, Dwaipayan Sen, Chiranjib Bhattacharjee, Oily wastewater purification using electrocoagulation and electroflotation process: a review, 30th National Convention of Chemical Engineers' on the Theme 'Recent trends in research, development and innovations in Chemical Industries', 2014, NIT Agartala, Tripura.
2. Souptik Bhattacharya, ***Sirsha Putatunda***, Dwaipayan Sen, Chiranjib Bhattacharjee, Microbial bioremediation of oil spill present in Industrial effluent: a review, 30th National Convention of Chemical Engineers' on the Theme 'Recent trends in research, development and innovations in Chemical Industries', 2014, NIT Agartala, Tripura.
3. ***Sirsha Putatunda***, Dwaipayan Sen, Chiranjib Bhattacharjee, Emulsified oily wastewater: an approach to the treatment using two indigenous membrane modules, CHEMCON 2013, ICT Mumbai.

4. ***Sirsha Putatunda***, Dwaipayan Sen, Chiranjib Bhattacharjee, From Grey to Green: How to improve the sustainability of wastewater and drinking water, EU-India STI Cooperation Days 2012, Hyderabad.
5. ***Sirsha Putatunda***, Dwaipayan Sen, Ankur Sarkar, Debasish Sarkar, Chiranjib Bhattacharjee, Performance of high shear membrane module on rheopectic PEG separation: A comparative study with Radial Flow Membrane Module and Turbine Flow Membrane Module, CHEMCON 2012, Jalandhar.
6. ***Sirsha Putatunda***, Ankur Sarkar, Santanu Sarkar, Dwaipayan Sen, Debasish Sarkar, Chiranjib Bhattacharjee, Effect of high shear membrane module on PEG separation: A comparative elucidation with Radial Flow Membrane Module (RFMM) and Turbine Flow Membrane Module (TFMM), CHEMCON 2011, Bengaluru.
7. Santanu Sarkar, ***Sirsha Putatunda***, Ankur Sarkar, Arnab Baksi, Dwaipayan Sen, Chiranjib Bhattacharjee Measurement of Carbohydrate in Black Liquor using Brix Refractometer, CHEMCON 2011, Bengaluru.

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ABSTRACT

Present world is defined with geminate catastrophe of water dearth and environmental debasement. One of the key components of wastewater is oil. Severe issue of oil contaminated wastewater is the emulsion formation of oil and water. The wastewater drained to cities' sewerage system, ultimately conveys the water to some river or sea. Thus the drainage of such oily wastewater without proper processing, will finally lead to an accretion in pollution load of water resources. Presence of oil in water hampers the aquatic environment as it restricts the avenue of sunlight through water surface, which finally constrains the aquatic life. Moreover, sustainable water reclamation attributes to the reuse and conservation of usable water for future need. Industries prime contributors in the oil contaminated wastewater generation are petroleum industries and automobile industries. During the extraction of crude petroleum from the reservoirs, large amount of effluent produced water comes out as a by-product of the process, 3:1 in ratio with extracted petroleum. To recycle this produced water in crude wells for enhanced oil recovery might be an option of the produced water management. Effect of surfactant, Sodium dodecyl benzene sulfonate (SDBS) on dynamic surface tension of produced water has been studied at different pH with varied concentration of SDBS concentration below and beyond critical micelles concentration (CMC). The air liquid interface seems to be get affected to a large extent with SDBS concentration lower than the CMC.

Automobile industries also cultivate oily wastewater comprising of free oil, dispersed oil and emulsified oil. In the present work the wastewater coming out of automobile shops has tried to ameliorate through demulsification with the aid of electrolytes, high shear ultrafiltration and bioremediation. The assessment was carried out with oil-in-water (o/w) emulsion after being treated with different electrolytes and the results from the treated feed to the membrane were compared with the untreated feed to the membrane. Two high sheared modules, namely, a turbine flow membrane module (TFMM) and a radial flow membrane module (RFMM), were compared to understand the superlative performance in removing oil from its o/w emulsion (either treated or untreated) using a 25 kDa polysulfone (PSf) membrane at different temperatures and pressures. It was observed that the permeate flux is 30–38% higher in all the cases with TFMM, depending on operating temperature and pressure. Furthermore, among the electrolytes used, 15% sodium sulfate (Na_2SO_4) solution shows a maximum of 26% oil removal from emulsion, while TFMM shows a 45% higher permeate flux compared to RFMM with this pretreated feed compared to the module. In this present study an attempt was made towards the bioremediation of spent oil from waste stream. Oil degrading bacteria isolated from contaminated waterways using *enrichment culture* technique. Among several isolated strains, two strains named as "A_3" and "A_4" were found effective in degrading hydrocarbons. Further, in between these two strains, A_3 showed 41 % removal of spent oil, at 35°C and pH 8, which was almost 5% more compared to strain called A_4. The growth study for both the strains was done at 120 rpm for 30 days in Bushnell-Haas (BH) media. Strain called A_3 was further studied towards the remediation of o/w emulsion for 7 days preserving other previous conditions, which showed around 21% removal of oil from emulsion. The result was found comparable to the free oil at the same parametric conditions for strain called A_3.

1 Chapter 1: Introduction

Aims of the Chapter

This chapter illustrates an overview on research activities that were carried out during the preparation of this thesis.

Urbanisation in today's world excels the growth of human population per capita of a city that subsequently creates a high demand for an increasing every day's needs among the people. As an extension of a comfortable urban life, people are prone to buy vehicles; and the fact can be well understood by the growth in number of registration of cars in India either in the form of transporter or personal vehicles. According to Society of Indian Automobile Manufacturers (SIAM) and Confederation of Indian Industry (CII), the number of registrations has been increased by around 22-25% in every segment of the vehicles' form. To fuel up these vehicles as well as to meet up the other basic needs, modern people are prone to consume more and more fuels. This whopping growth in fuel consumptions is continuously increasing the need of crude oil extraction from oil reservoirs. At the time of oil extraction, produced water (PW) come as a by-product. Produce water is nothing but emulsion of reservoir crude oil and the reservoir water. This old reservoir waters are generally saline in nature due to presence of different salts. In general, to produce one barrel of oil, seven to ten barrels of produced water (Hagstørm et al. 2016) forms. The National Energy Technology Laboratory (NETL) (2014) reports that approximately 9000 billion gallons of produced waters are generated annually in the United States including onshore and offshore production.

The growth in the usage of cars creates a substantial increase in the water pollution load in the form of oily-waste that results from an automobile industry. It was found from the current statistics by several authorized bodies that on an average 20 to 30 cars' washing generate almost 151 to 230 L of oily wastewater in each and every car washing facility. Therefore, without proper measures if these oil contaminated waters will be ultimately conveyed the water to some river or sea, will populate the hydrocarbons in the flowing or stagnant aquatic environment and perturbs the aquatic life by attenuating the entrance of sunlight through the surface of the water. Therefore, in this present context, management of such oily waters have been opted as the point of concern.

According to Cheryan et al. (1998), conventional approaches such as dissolved air flotation, chemical coagulation-flocculation, centrifugation to treat such emulsified oily wastewater might not ensure proper separation of oil from water. Many researchers have studied different biological routes, membrane bioreactors, carbon adsorption, advanced oxidation process etc for the treatment of oily wastewater. During the design of experiments of the present study, the objective was to promote an economically viable treatment process for the low income group end users, especially in a country like India. Moreover, for a membrane separation process, even in an industrial scale, it is hard to separate higher hydrocarbons using membrane, as without any prior primary treatment membranes are prone to be fouled by sticky oil attributing to a low process life for the membrane (Srijaroonrat et al 1999).

Especially, one of the intricate issues with the treatment procedures for oily wastewater is the formation of emulsion between oil and water.

In this thesis, first study deals with produced water management, where the surface active component Sodium dodecyl benzene sulfonate (SDBS) has been added to three different produced water to study the wettability alteration through surface tension measurement. This surfactant injection process is a very popular enhanced oil recovery (EOR) process from crude well. So by this the produced water can be recycled for more oil recovery after the primary oil recovery from the crude reservoir.

In the second study, management of emulsified oily wastewater produced from car wash facility has been studied. Here as a primary study the research work has been carried out with an understanding of the low cost demulsifier acting based on ionic effect; that can release the oil from water. Different concentrations of various low cost electrolytes have been used as demulsifier to understand the salt breaking mechanism prior to sending for the membrane separation process. After demulsication, the waste stream has been sent to a high shear membrane separation module to ensure less concentration polarization and fouling of the membrane.

In the third study microbial route has been adopted for biodegradation of the spent oil and spent oil contaminated emulsified wastewater, coming from automobile industrial waste stream.

Finally, at the end an indigenous membrane assisted Electroflotation-Electrocoagulation module has been designed for the emulsified wastewater stream purification.

2 Chapter 2:

Literature Review

Aims of the Chapter

Present chapter is a survey of the previous research work on the enhanced oil recovery and oil contaminated wastewater management. The survey highlights the insight of both the application as well as the treatment procedures of emulsion and emulsified wastewater stream. Finally, the chapter elucidates an industrial overview of current scenario towards the wastewater remediation describing the present approaches of the effluent treatment plants.

2.1 Produced water and produced water management

Petroleum is the major source of energy for many countries today, so its production is one of the most important industrial activities in the twenty-first century (Oliveira et al., 2005). Crude petroleum is produced with large volume of wastewater, more than 80% of liquid waste and this amount can be as higher as 95% for ageing oil and gas fields (Azetsu-Scott et al. 2007 and Kaur et al. 2009). Natural water, also known as formation water, is always present together with petroleum in crude reservoirs. To maintain the required hydraulic pressure of the crude well additional water is usually injected from outside during the extraction of oil and gas. Along with the natural water and injected water, there can be water breakthrough from outside the reservoir area, and as oil and gas production continues, the time comes when production of water initiates beside the hydrocarbons. This mixture of water is the produced water (PW) or oilfield brine, the largest volume of by product produced at the time of crude oil and gas recovery operations (Reynolds, 2003 and Chan et al., 2002). So finally PW is a mixture of injected water, formation water, hydrocarbons and sometimes comprises of treating chemicals too (Strømgren et al., 1995).

Depending on the sources, PW can be classified as oil field produced water, natural gas produced water and coal bed methane produced water. The volume of produced water from gas field is less than in oilfields. 250 million barrels of PW is produced daily from oil and gas fields worldwide. More than 60% of this PW is generating daily from oilfield (Fakhru'l-Razi et al., 2009).

2.1.1 Composition of Produced water:

Though PW has a complex composition, its constituents can be broadly classified into organic and inorganic compounds (Hayes and Arthur, 2004), comprising of dissolved and dispersed oils, grease, heavy metals, radionuclides, treatment chemicals, formation solids, salts, dissolved gases, scale products, precipitated solids, clays, slits, waxes, microorganisms and dissolved oxygen (Fakhru'l-Razi et al., 2009, Hayes and Arthur, 2004 Srivedhin et al., 2004). Dissolved and dispersed oil content of produced water is dangerous to the environment [Hayes and Arthur, 2004 and Hudgins, 1994]. Dissolved oils in PW are comprises of benzene, toluene, ethylbenzene and xylene (BTEX), phenols, aliphatic hydrocarbons, carboxylic acid and other low molecular weight aromatic compounds, where less-soluble poly aromatic hydrocarbons (PAHs) and heavy alkyl phenols are the constituents of the dispersed oil (Igunnu and Chen, 2014).

PW comprises of high concentration of dissolved inorganic compounds or minerals, which classified as cations and anions along with naturally occurring radioactive materials and heavy metals. Cations and anions play the key role in the chemistry of PW. Na^+ and Cl^{2-} are responsible for the salinity of PW, and its concentration can varied from a few ppm to ~300 000 ppm (Igunnu and Chen, 2014) Cl^{2-}, SO_4^{2-},CO_3^{2-}, HCO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Fe^{2+} and Sr^{2+} affect conductivity of the PW stream.

Treatment chemicals can be pure compounds or compounds containing active ingredients dissolved in a solvent or a co-solvent, and used to inhibit corrosion, hydrate formation, scale deposition, foam production, wax deposition, bacterial growth, gas dehydration and emulsion breaking in order to improve the oil and water separation (Hansen and Davies, 1994). Dissolved gases in PW are mainly carbon dioxide, oxygen and hydrogen sulphide.

2.1.2 Effect of PW on environment:

Oil droplets and dispersed oil do not precipitate at the bottom of the waterbodies but rise to the surface of water, which disturbs the sunlight entrance and hence inhibit the growth of aquatic life. Presence of volatile and toxic compounds (nonpolar organic compounds) increase the biochemical oxygen demand (BOD) of the affected water (Stephenson, 1992, Elias-Samlalsingh and Agard, 2003). For fresh water animals hydrogen sulfide and hydrocarbons present in PW are very toxic (Neff, 2002). Metals and hydrocarbons contents of PW are very toxic to the ecosystem and organs and fertility of fish exposed to alkyl phenols of PW got adversely affected(Grant and Briggs, 2002). Toxicity of PW can be defined as acute or chronic toxicity, where the acute toxicity can be easily measured by the LC50 test, chronic toxicity are difficult to quantify (Hansen and Devies, 1994). Treatment chemicals can accumulate and precipitate in marine sediments (Grigson et al., 2000).

2.1.3 PW management:

Objectives of PW managements are; removal of dispersed oil and grease, removal of suspended particles and sand, removal of soluble organics, removal of dissolved gases, removal of naturally occurring radioactive materials (NORM), desalination, disinfection and softening of the water to lower the excess water hardness(Igunnu and Chen, 2014). To meet up these, many single and combined physical, biological and chemical treatment processes for the management of PWs.

However, general legislation for discharging PW into sea is 40 ppm of oil in water, but due increased environmental concern many countries follow much strict regulatory standards. To achieve the EU Water Framework Directive (WFD) adopted ‘zero discharge’, the Norwegian Oil Industries Associations developed the Environmental impact factor (EIF), which considers all the contaminants in produced water (Nature technology group, 2005) from 2005. The Oslo Paris Convention (OSPAR) decided to reduce the maximum discharge limit to 30 ppm oil in water and zero discharge pollutants into the sea (Nature technology group, 2005).

2.1.3.1. Physical treatment processes:

Several physical treatment processes includes adsorption, filtration, gas flotation, evaporation, hydrocyclone separation, electrodialisis and dissolved air precipitation (DAP). Variety of adsorbents, such as activated carbon, organoclays, activated alumina and zeolites has been used to remove manganese, iron, total organic carbon (TOC), BTEX, oil and high amount of heavy metals from PWs (Han et al., 2010 and Spellman, 2003). For oil and grease removal media filtration has been used and upto 90% removal has been reported from this process (Han et al., 2010). Hydrocyclones is preferentially used in combination with other treatment processes as pre-treatment technique to remove slits and small dirts (Han et al., 2010). Gas flotation is also used for removal of suspended solids. Freeze thaw evaporation can remove more than 90% of heavy metals, dissolved solids, volatile and semi-volatile organics, suspended solids and total recoverable petroleum hydrocarbons from PW (Boysen, 2007). Electrodialysis can be used to reduce the dissolved salts load in PW (Dallbauman and Sirivedhin, 2005). Plenty of dissolved aliphatic and aromatic hydrocabons can be removed via DAP.

2.1.3.2. Chemical treatment processes:

Chemical precipitation and chemical oxidation, electrochemical processes, photocatalysis, fenton process demulsification and ozone treatments are widely used various technologies in PW management. Chemical oxygen demamd (COD) as well as BOD can be regulated using electrochemical processes (Ma and Wang, 2006). Combination of flocculation and fenton oxidation process can reduce COD value as well as oil content of PW to a great extent. Ozonolysis is a well accepted process in dissolved organic compounds removal from PW (Morrow et al., 1999). Surfactants are used to demulsify the emulsion present in PW (Deng et al., 2005).

2.1.3.3. Membrane process:

Membrane based treatment processes are seems to be very promising in present decades to overcome use of toxic chemicals, large footprints for process installation. There are four pressure driven membrane processes in basis of the pore size of the membrane, microfiltration (MO), ultrafiltration (UF), reverse osmosis (RO) and nanofiltration (NF). MF separates suspended particles, UF separates macromolecules, RO separates dissolved and ionic components and NF is selective for multivalent ions (Judd, 2003 Madaeni, 1999, Xu and Drewes, 2006,). Where MF and UF can be used as a standalone technology for industrial wastewater treatment, RO and NF are usually used for water desalination.

2.1.3.4. Biological treatment process:

Biological aerated filter (BAF) is a biological technologies comprising of a permeable media that uses aerobic conditios to facilitate biochemical oxidation and removal of organic compounds from polluted water(EPA, 1980). BAF can remove oil, ammonia, suspended solids, nitrogen, COD, BOD, heavy metals, iron, soluble organics, trace organics and hydrogen sulphide from PW (Su et al., 2007). This process can remove up to 70% nitrogen, 80% oil, 60% COD, 95% BOD and 85% suspended (Su et al., 2007). Water recovery from this process is almost 100% as the waste produced in this process in solid form (Ball, 1994).

2.2 Wettability alteration of PW and EOR from oil well through altered PW injection

EOR is nothing but the tertiary oil recovery processes; used to maximise the oil production from the crude reservoir after initial oil recovery by primary means. After primary production; certain amount of oil, often called "residual oil," remains entrapped in the reservoir. Different EOR processes applied to a mature reservoir or field when the primary processes are frazzeled to recover these "residual oil" of the reservoir. EOR maximises the oil recovery upto 40 percent while primary oil drilling processes can produce only 10 to 15 percent of the total oil content of the reservoir (Farouq Ali and Thomas, 1996). The total world oil production from EOR is about 3.5 per cent of the daily oil production. Three basic principles of EOR are viscosity contraction of the oil, extraction by means of solvent and wettability alteration to achieve desired mobility ratio of displacing fluid and displacement fluid and low interfacial tension value.

Mobility ratio (M), is the ratio of mobility of the displacing fluid divided to the mobility of the displaced fluid. If M>1, the displacing fluid, water in a water flood, moves more easily than the displaced fluid, oil. Thus, the mobility ratio influences the efficiency of oil displacement within the reservoir pores. For a very high M value, the displacing fluid will pass the accumulated trapped oil in the reservoir. To maximise the displacement efficiency, M~1 is most favorable (Thomas, 2008).

Depending on reservoir characteristics and the reservoir fluid characteristics, these mechanisms are opted for the oil recovery and finally lead to the following type of EOR;

I) Thermal methods (viscosity reduction of oil by means of heat injection)

II) Miscible flooding method (solvent or injection)

III) Chemical methods (chemical injection to alter the wettability of the oil, injected fluid and surface of reservoir)

2.2.1 Thermal EOR process:

Thermal methods mostly applicable for recovery of heavy, viscous crudes; heavy oils and tar sands. It provides heat to the reservoir to decrease the viscosity of the oil as some of the oil vaporizes with increase in oil temperature (Owens and Suter 1965 and Denbina et al 1991). Cyclic steam stimulation, steam flooding and steam assisted gravity drainage (SAGD) involved steam or hot water injection technique. Whereas hot air or oxygen is injected in the crude wells for in-situ combustion. Oil is ignites in in-situ combustion and the set up high heat internally in a narrow area. Sometimes water or gas used as additives along with the air in in-situ combustion or fire flooding. Toxic gas production and critical corrosion is the main drawback of in-situ combustion (Chu 1977, 1982). Though this process is not as much popular as steam injection (Farouq and Meldau, 1979, Stokes and Doscher, 1974), it has been used in India for heavy oil sandstone wells.

2.2.2 Miscible flooding method:

Miscible slug process, enriched gas drive, vaporizing gas drive and high-pressure gas injection involves the miscible flooding method for light oil recovery from sandstone and carbonate reservoir. The injected displacing fluid is miscible with the reservoir oil in miscible flooding and called as single contact miscible (SCM) or multiple contact miscible (MCM) depending upon the first contact or various contact miscibility (Stalkup, 1992). Miscible slug process is an SCM type process propane or pentane, is injected in a slug form, where in enriched gas drive and vaporizing gas drive are MCM processes with natural gas, N_2 injection. In high pressure gas injection process either CO_2 or N_2 is injected in the reservoir (Holm, 1959, Sanchez et al, 2005). Poor displacement efficiency as well as viscous instabilities are the cons of miscible slug process. MCM process applicability is limited to reservoirs that can withstand high pressures. Economic viability and lack of infrastructure for CO_2 injection are the limiting the applicability of high pressure CO_2 injection process though it ensures disposal of green house gas.

2.2.3 Chemical flooding method:

Chemical flooding or chemical EOR aims to maximize the oil recovery by either one or a combination of the following means: (i) mobility control, and (2) hike in capillary number by reducing surface tension (Thomas and Farouq Ali 1999). In polymer flooding water soluble polymers are used to reduce the mobility of injected water (Chang, 1978). Loss of polymer through the porous media restricts its commercialization. An aqueous solution of hydroxide, carbonate or orthosilicate of sodium is injected in alkali flooding to reduce the surface tension (Johnson, 1976). Reactions of alkaline chemical and reservoir fluids restrains the alkali flooding (Froning and Leach, 1967). The main components of micellar flooding method microemulsion or micellar slug and a polymer slug are driven using brine to ensure the ultra low interfacial tension (Gogarty and Tosch, 1968). Alkaline-Surfactant-Polymer (ASP) flooding is the newest chemical EOR process (Wyatt et al., 2002).

2.2.3.1. Surfactant flooding:

It is also popular as miceller-polymer flooding or microemulsion flooding or detergent flooding. Though the idea of surfactant flooding arrived around 1920's, its proper research and pilot scale trials has started only at 1970's. For this application following factors are very important to be considered, oil composition, formation water salinity and divalent contents, pressure, temperature and clay content. Surface-active components, surfactants are highly competent in reducing surface tension of oil and water interface and improves the wettability of porous rocks allowing water to flow through them faster hence ensure more oil displacement. Hence it ensure higher displacement of oil from the reservoir rock. Generally optimal activity of surfactant lies in a confined range of salinity and it has a tendency to get adsorbed or involved in reaction with reservoir rock. Low retention of surfactant is always preferable to avoid the scope of adsorption of surfactant in reservoir rock surface. An aqueous surfactant slug or accompanied with a polymer slug are driven through brine. As polymer introduces a convenient viscous condition with well mobility control for the surfactant slug, surfactant along with polymer flooding is technique that is much more favourable (Green and Willhite, 1998, Rosen et al., 2005).

Recent developments in Surfactant Enhanced Oil Recovery have greatly reduced the surfactant concentration required; which, increasing economic viability of the process. Surfactant flooding also producing more advanced and safer EOR products at a lower cost than ever before. Modern progress of the process ensuring augmented environment and human health. Some of the latest EOR surfactants are derived from plant resources such as sunflower oil, soy and corn oil. The process is very good alternative for the reservoirs where polymer and alkali applications are not feasible.

Selection of surfactant for EOR always comprises a lot of factors, which includes compatibility with electrolytes and polymer, thermal and aqueous stability, low retention, good solubility range in oil as well as water and moderate cost. Anionic surfactants are more favourable for use in EOR as these show low interfacial tension, good ability to create self-assembled structures, well stability, low adsorption on reservoir rock and can be economical viability (Green and Willhite, 1998).

2.2.3.2. Surfactant:

The flooded chemical system in surfactant flooding consists of polymeric molecules which are surface active agents, surfactants, that lower the interfacial tension between the flooded fluid solution and the residual oil of the reservoir. At low concentrations surfactants get adsorbed on a surface or fluid/fluid interface. Structurally surfactants look like tadpoles comprising of a nonpolar hydrocarbon 'tail' and an ionic polar 'head'. The structure is shown in figure 2.1.

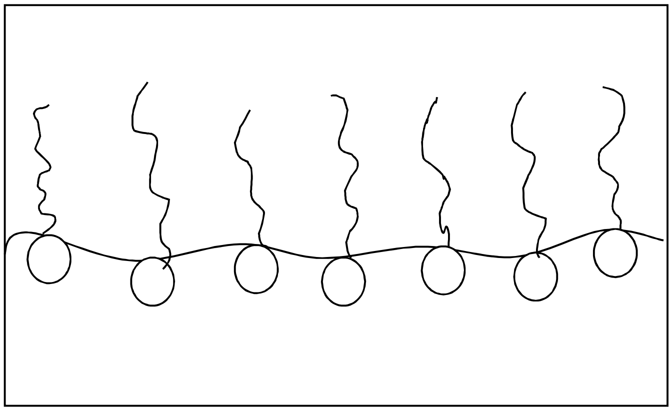


Figure 2.1 Structure of Surfactant

Presence of both hydrophilic and hydrophobic parts make surfactants amphiphilic in nature. Amphiphiles get adsorbed to interfaces and decreases the interfacial energy. In surfactant flooding EOR the hydrophilic head interacts with water molecules and the hydrophobic tail interacts with the residual oil and finally lead to formation of water-in-oil or oil-in-water emulsions(Pashley and Karaman, 2004).

The primary surfactant forms the microemulsion in surfactant flooding EOR. Co-surfactant, if there is any, pushes the activities of the primary surfactant, through the change of surface energy or the viscosity of the fluids. Due to chromatographic separation of surfactant, co-surfactant and any other components, inside the reservoir, multicomponent surfactant system build up could be an issue throughout the flooding process. The disadvantage of separation is that the control of the system degrades within the reservoir and henceforth it must be avoided. Co-surfactants restrict the gel formation and reduce the equilibration time, it is hard to get rid of them from the flooded surfactant systems.

Classifications of surfactants are carried out from the ionic nature of the head group, as anionic, cationic, non-ionic. Most commonly used surfactants for EOR, are anionic sulfonated hydrocarbons due to their relative better stability, ability to create self-assembled structures, relatively low adsorption on reservoir rock and cost effective production (Green & Willhite, 1998). Anionic surfactants, having negatively charged head groups, dissociate in water to form an amphiphilic anion and a cation and the cation is typically be an alkaline metal such as sodium (Na+) or potassium (K+). Cationic surfactants consists of positively charged head group and while dissociate in water, produce an amphiphilic cation and anion, mainly a halide (Br-, Cl- etc.). Cationic surfactants synthesis is an expensive process compared to anionic surfactants, as they undergo a high pressure hydrogenation reaction. As a result use of cationic surfactants are much more restricted than anionic and nonionic surfactants (Standnes & Austad, 2003).

Generally, co-surfactants, which are used to promote surfactant efficiency in EOR process, are non-ionic surfactants. Non-ionic surfactants are consists of no charged head groups and their hydrophilic group is of a non-dissociating in nature, not ionizing in aqueous solutions (Gupta and Mohanty, 2007). Examples of nonionic surfactants are alcohols, phenols, ethers, esters or amides.

2.2.3.3. Critical micelles concentration (CMC):

Apolar long-chain hydrocarbon “tail” and polar “head” groups of surfactant proceeds towards self-association or micellization in polar solvents. Surfactant molecules arrange themselves into organized molecular assemblies called micelles. In water, the hydrophobic part forms the core of the micelle and the polar head groups went to the micelle–water interface. Depending on the chemical structure of the surfactant monomer molecule, cationic, anionic, ampholitic or non-ionic micelles form. Though macroscopically micelles are often homogeneous, they are heterogeneous on a microscopic scale. This leads to behave the aqueous surfactant solutions as microheterogeneous media (Domínguez et al., 1997). The concentration above which surfactant forms micelles is called the critical micelle concentration (CMC). CMC get affected by temperature, pressure, hydrocarbon chain-length of the apolar groups, and for ionic surfactants on the nature and concentration of counter-ions in solution. Added electrolytes or the salinity of the solution lowers the CMC, and the effect increases with decreasing charge density of the counter-ion.

2.3 Remediation of emulsified oily wastewater

One of the mostly acclaimed issues presently around the world is the growth of per capita population that manifests the industrial growth and henceforth, the concentrated economy among the people through urbanisation (Datta, P., 2006). India might be one of the most badly affected countries from their perspective because of the lack of conscience among the people and due to population outburst. It had been seen that such growth rate reaches almost five times more than the growth rate in the developed zones (Madlener and Sunak, 2011) and such inflation attributes to an increased energy demand, which in turn invokes the energy supplying services. Moreover, seeing this demand's interrelations between energy consumers and supply chains, it can be confirmed that growth in urbanisation attributes to a growth in industrial sector. This eventually increases the growth in demand for development in transportation sector both for cargoes and manpower transport. In 2005, compared to other developed Asian countries, the paratransit service was maximum in India (Laquian, 2005) manifests an increaseing pollutants' load on the surface as well as ground water because of the run-off from the various oily wastes. Hence, in present scenario, oily wastewater, which might be the run-off from either restaurants or domestic zones or industrial zones or automobile shops, attracts more attention from the scientists to articulate proper wastewater management scheme for the urban zones. The present review is thus concentrating on such oily water, their issues with the treatment once they are getting mixed to form a homogeneous oil-water mixture and what are the strategies that can be adopted in such oily wastewater management scheme at different parts of the world.

2.4 Sources: Oily wastewater and its emulsified form

One of the key concerns in a populated urban system with less civic awareness, is an uncontrolled discharge of wastewater to the urban drainage system from different small scaled industries like restaurants, gasoline filling stations, road-side automobile repairing shops, metal-cutting shops etc. that contain oil along with other organic and inorganic pollutants. Once the oils are mixed with water, it forms primarily three kinds of oily wastewater - free-floating oil, unstable oil/water (o/w) emulsion and stable o/w emulsion. Ghosh and Rousseau (Ghosh and Rousseau, 2011) found that the stability of the o/w emulsion increased because of the presence of triacylglycerides, polymers etc. present in the continuous phase. Surface active fat particles are anchoring themselves on the interfaces of the dispersed phase and restrict the droplets to coalescence through reducing the interfacial tension. Thus it reduces the scope for sedimentation of the droplets through coalescence together during the treatment of wastewater. Moreover, the particles are continuously combined themselves to form a crystal network that encases the dispersed phases present in the emulsion and henceforth, restricts there free movement within the continuous phase (Ghosh and Rousseau, 2011). This forms a stable emulsion. The stabilisation of o/w emulsion substantiates primarily in the urban wastewater stream, because of the presence of various surfactants like fat, alcoholic substance, detergents etc. coming from different sources. Hence, destabilisation of such emulsions and thereafter the removal of oil phases have been considered the most critical part in the urban wastewater management, especially when large area and amount of the water body needs to be managed. This variability of the components along with the oily waste material within the wastewater involves huge expenses to settle down a treatment plant. Especially, the issue becomes magnified, when the oily waste emitter are from small scale business and are not capable of large investment to develop such sophisticated water treatment procedures.

Several techniques have been proposed to destabilise such o/w emulsions in order to separate the oily layer from the water phase and henceforth, reducing the possibility of “oil pollution” prior to its discharge. Subsequent sections will discuss in detail the alternative origin of emulsified oily water other than the urban system, especially from the perspective of the oil field PW and emulsion from pharmaceutical industries.

2.5 Applications of oil-water emulsion technology

In presence of the surfactant, the surfactant got adsorbed at the surface of the emulsion droplets to restrict them in coalescence by reducing the surface tension and gets settled down by gravity. These surfactants are called emulsifier. During the addition of emulsifier towards the stabilisation of emulsion, the characteristic adsorption time at the oil-water interface must be less than the period for collision between two droplets (Danov et al., 2001). In other word one can say the rate of adsorption at the interface should be large enough to maintain the stability of emulsion. Hence, the formation of double layer will be mobilised with the adsorption of the emulsifier and thus the repulsive force between the droplets is increased attributing to larger time scale for collision. Now, the stabilised form of the emulsion can be categorised into two forms – one, where the stability is because of kinetic stability of the emulsion and the other one, is where the stability is because of the thermodynamic stability (Kegel et al., 1999; Kraft et al., 2010; Sacanna et al., 2007). However, one of the key concerns in discussing the stabilisation of emulsion is the lifetime of stable emulsion that guides the usages of emulsion for different industrial applications. It was seen by Pal et al. (Pal et al., 1986) that when the oil concentration in an oil-in-water emulsion if goes beyond 50%, it shows non-Newtonian behaviour and this can be varied till 80-84%. Beyond this limit the emulsion will be unstable and a clear phase separation will be visible. According to them, the emulsion viscosity gets increased, when the dispersed phase volume becomes increased and therefore, the flow pattern of the fluid also gets affected. The flow pattern or in brief the rheology of emulsion is one of the critical factors that will decide on its usages. For example, in case of oil exploration, if the viscosity of the O/W emulsion gets increased because of increased oil concentration, the transportation of heavy oil will be cost intensive with high pressure drop.

2.5.1 Emulsion an application in oil exploration industry during drilling process:

One of the critically assessed process in oil exploration industry is the designing of drilling process in order to reduce the cost of the oil exploration as drilling comprises of 80% of the total well cost (Shah and Ogugbue, 2010). During drilling, a fluid is injected in the oil field to extract the deep oil and transport it to the surface from the crust. Hence, one of the primary concerns in drilling is selecting the injection fluid for drilling operation. A well-known drilling fluid is the oil-based-mud (OBM) system, which is basically an water in oil emulsion system, that helps the injection process through the shales by lubrication, cooling and maintaining the pressure during drilling process to have the well control (Ali et al., 2004; Ravitz et al., 2006). With this emulsion system, the continuous oil phase provides lubrication during the creation of the oil well. However, one of the typical problems with the OBM system is felt during the completion of the well, when the oil wetted filter cake and other materials deposited can not be cleaned up with the cleaning completion fluid system. This will reduce the well performance by restricting the hydrocarbons to be permeated from the pores. On the contrary water-based-mud (WBM) system has a potential disadvantage of sticking the muds, cements etc. along the sidewall of the drilling pipe (Ravitz et al., 2006) and also, the clay materials are more prone to dissolve in water that ultimately leads to collapse of the well. Therefore, to alleviate such issues with the OBM, scientists are looking for a system, where the oil wetted materials, mainly clay, can be dispersed from the aggregate and henceforth, dissolved in water. In mid 90's, pH was seen as the controlling agent, where the reversal of the emulsion from water-in-oil to oil-in-water could be possible. This will eventually disrupt the aggregate of oil wetted materials and dissolve the clay part, which is nothing but calcium carbonate. Hence, the resistance to oil flow from pores can be controlled with better well performance. However, there are some demerits with this invert emulsion process identified by Quintero et al. (Quintero et al., 2007). The primary one is the cyclic process in order to change the wettability of filter cake from oil to water followed by dissolution of the solids using acids or other solution. Secondly, inverted emulsion, also called OBM has a high affinity to dissolve gas under pressure, which could be released with low pressure resulting possible well damage. Quintero et al. here formulated a Winson IV single phase microemulsion (SPME) with surfactants, co-surfactants, brine and oil as a soaking solution in an acidic media to perform three conditions – one, to solubilise oil in OBM, second one is to reversal of the wettability and the last one is to dissolution of the cake solids in acid. Rather, the first objective here complements the second and the second complements the third. Once, the oil gets dissolved in SPME, the surface tension between the solids and the oil decreases. This releases oil from the solids, which has now more affinity for water and gets dissolved in the acid present in water. The SPME technology, which was referred as S/OBM technology has an advantage of withstanding the stability of the emulsion even at high temperature and high pressure. However, the key issues with the technology is the change in the nature of the emulsion because of its contact with varied electrolytes that might alter the dissolution of oil and hence, the subsequent dissolution of cake solids. Therefore, the major concern here is the sensitivity of the emulsion not only to the temperature and pressure, but also the other impurities that might change the performance of SPME. On increasing the active surface area and lowering the interfacial tension a more stable emulsion could result, which might be resistant even with the presence of impurities. Nanoparticle mediated or nano-fluids are the most coveted injection fluid in present days because of the increased interfacial area they have, which results in lowering the interfacial tension (Agarwal et al., 2013; Ragab, 2014). Moreover, nanoparticles increase the energy required for the adsorption at the interface during emulsification, which at the same time increases the resistances against the effects because of impurities. Another reason that might encourage the formulation of such nanomaterial emulsifier is to replace the organic emulsifier, which breaks during high pressure and high temperature drilling operation. These motivates the drillers to use such nano based inverted emulsion mud technology with an enhanced oil recovery around (Ali et al., 2004; Saini and Norman, 2012). One of the basic negative issues with any oil based mud is its cost compared to water based mud even though oil based has some prompt advantages over water based. Therefore, the scientists are still looking for good drilling fluid option, where they can maintain the stability of the emulsion at adverse condition, cleaning up the filter cake, increasing the permeability of hydrocarbons in the well, and balancing the formation pressure with the hydrostatic pressure to avoid well instability.

However, one of the mostly discussed issues with the drilling operation is the waste generation, during cutting of the well and the used fluid. As said, WBM is the mostly used drilling fluid system during oil exploration and accounts for 80% of the global market. It does not pose too much environmental pollution and because of such eco-friendliness of WBM it is allowed to discharge off-shore. On the contrary OBM has lot of issues as it has the continuous oil phase that is impacting environment like when oil is being spilled over the water body. It results a light impervious layer at the top of the aquatic region and through increase in biological-chemical oxygen demand it causes low dissolved oxygen to the aquatic living beings.

2.5.2 Nanoemulsion – A step towards the future of pharmaceutical industry:

Nanoemulsion preparation is one of the remarkable footsteps in the field of biomedical sciences that advances the world medicine a step ahead to the formulation of nanodrug system. In nanoemulsions the mean droplet sizes ranging from 50 to 1000 nm. One of the well-established techniques in the preparation of drug nanoparticles is by emulsion solvent evaporation method, where the solvent dissolves the emulsion stabiliser and the drug particle along with the sodium dodecyl sulphate (SDS) as an emulsifier. The mixture is continuously agitated until the organic solvent is completely vaporised (Hoa et al., 2009). However, unlike microemulsion, nanoemulsion requires energy involvement during its preparation and based on the facts the nanoemulsion preparation can be of two types – one is called high energy and the other one is called low energy (Ahmad et al., 2014). One of the typical properties in nanoemulsion based drug is the release of the drug. Ahmad et al. (Ahmad et al., 2014) used non-ionic surfactant called 2-hexyldecyl-β(/α)-d-glucoside (2-HDG) and 2-hexyldecyl-β(/α)-d-maltoside (2-HDM) that stabilise the nanoemulsion prepared by phase inversion composition method along with a property of faster release after intake of the medicine. According to Dixit et al. (Dixit et al., 2008), the nanoemulsion injection will be more feasible in order to dissolve the water insoluble drugs, such as carvedilol, a cardiovascular drug. Moreover, nanoemulsion based drug delivery is of the mostly coveted technologies adopted by several researchers nowadays to formulate effective drug delivery system for cancer treatment. Primo et al. (Primo et al., 2008) had investigated the possible use of nanoemulsion loaded or encapped zinc pthalocyanine (ZnPc) for the treatment of skin cancer and also magnetic maguemita (Fe_2O_3) citrate nanoparticles so as to form the magnetic nanoemulsion. Their conclusion was based on the penetration of the drug through the skin layers both for ZnPc-nanoemulsion and ZnPc-magnetic nanoemulsion drugs in order to understand the efficacy of the formulations in healing the skin cancer. Almost five-fold increase was observed for the accumulation of magnetic nanoemulsion encapped drug compared to normal nanoemulsion for the innermost epidermis/dermis layer. Similar study with magnetic nanoemulsion technology had been made again by Primo et al. (Primo et al., 2008) in the treatment of neoplastic cell. Fang et al. (Fang et al., 2009) had studied an acoustically active nanoemulsion based drug delivery system towards the fighting against cytotoxicity of cancer. They had encapsulated camptothecin, an anticancer agent against a broad spectrum of cancer, with the coreshell of nanoemulsion made up of perfluorocarbon and coconut oil. Nanoemulsion protects the lactose ring of camptothecin from being hydrolysed in blood plasma to inactive carboxylate, while lower range of ultrasound will enhance the release of drug from the system to a targeted delivery of the drug. In 2009, Ge et al. (Ge et al., 2009) proposed a nanoencapsulated vaccine called “MAGE1-HSP70 and SEA complex protein” with a purpose of enhancing immunity against tumor cells, where nanoemulsion acts as a potential carrier. In recent past, Tian et al. (Tian et al., 2013) proposed the application of nanoemulsion technology for the regeneration of bone tissue followed by the encapsulation of hydroxyapatite and laminin in an emulsion electrospun nanofibres. However, lack of proper understanding of interfacial chemistry and the requirement of energy intensive expensive emulsion preparation process limit the widespread applicability of nanoemulsion technology in drug delivery design (Lovelyn and Attama, 2011).The following subsection elaborates the various methods manifesting the preparation of nanoemulsion in drug delivery system.

2.5.2.1 Preparation of nanoemulsion – an aid to the nanotechnology:

The significant utility in the preparation of emulsions can be identified with the nanoparticle encapsulation technology that had been a pave way for the nanodrug delivery system. One of the significant nanoparticles in this respect is the polymeric nanoparticles, which is prepared from biocompatible and biodegradable polymers of size in the range between 10-1000 nm (Nagavarma et al., 2012). However, the course of action or the utilities obtained from nanoparticles is the technology adopted for the preparation of nanoparticles. Among several techniques discussed so far by various researchers, emulsion/solvent diffusion (ESD) along with the encapsulation of the nanoparticles for lipophillic drug was found to be the most effective one (Quintanar-Guerrero et al., 1998). However, one of the primary disadvantages with this operation is the chances of leakage of the water soluble drugs into the aqueous phase reducing the encapsulation efficiency. On the contrary, the reduction of water phase in this procedure without altering much of the thermometric condition eliminates the possibility of conformation changes of the biopolymers. Salting-out is supposed to be an alternative to thermometric procedure for water evaporation that will also enhance the strength of the encapsulants (Couvreur et al., 1995). In 2013, Palamoor and Jablonski (Palamoor and Jablonski, 2013), formulated the process towards the formulation of highly water insoluble effective ocular drug celecoxib loaded poly (ortho ester) nanoparticle through ESD leading to a formation of oil-water-water emulsion. In their study they had achieved almost 98% encapsulation, which is stable and had a property of control release of the drug from biodegradable core nutshell of the encapsulation. Furthermore, high surface to volume ratio of nanoparticles distributes the molecules or atoms on the surface that increases reactivity of the target specific nanoparticles. In addition the shape of the material dictates the ever changing properties of the nanomaterials due to the dispersion of electrons at different directions within the materials. In case of 0D shape, the confinement of the electrons within the shape is distributed in equal extents towards the all directions and the material is called isotropic. On the contrary in case with the 1D, 2D and 3D nanostructures, the properties of the material can be controlled with variation in the shape (Figure 2.2). These types of materials are called anisotropic (Sajanlal et al., 2011). Hence, such property can be explored in order to detect the biomolecules and especially, for the transportation of the nanomaterials in a disturbed route (An et al., 2012; Nam et al., 2012). In recent past, Nam et al. (Nam et al., 2012) had formulated an anisotropic nanoemulsion based drug tocopheryl acetate, which is a prodrug compound of α-tocopherol a form of vitamin E. The anisotropic form exhibits better absorption of tocopheryl acetate on the skin through a facilitated transportation of hydrophobic molecules through a lipid-rich domain present in the skin. The concept of anisotropic nanoparticles, where two or more distinct properties could be observed on the same surface, leads to a formulation of Janus particle, named after Janus (Lattuada and Hatton, 2011).

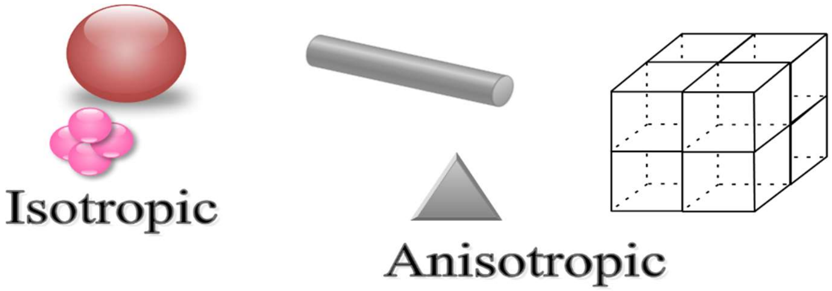


Figure 2.2 Various kinds of nanomaterials.

In present days, Janus particles attracted much attention because of their diversified surface properties. However, the performance of these particles depends on several factors as surfactants used, initiators of emulsion process, seeding process etc. (Kaewsaneha et al., 2013). Among several techniques, pickering emulsion is one of the effective and simple techniques in which the Janus particles are formed through selective adsorption of the particles at the interface of oil-water emulsion. Subsequently, the oil phase is solidified to restrain the particles in place, while the exposed surface is modified chemically. Finally, the solid phase gets dissolved and the particles are separated through filtration. Indalkar et al. (Indalkar et al., 2013) had described the fabrication of silica based Janus particles in wax-water emulsion system through pickering emulsion technique. Kaewsaneha et al. (2013) (Kaewsaneha et al., 2013) proposed a method for the preparation of anisotropic submicron magnetic Janus nanoparticle, where the magnetic nanoparticles are formed after mixing $FeCl_3/FeCl_2.4H_2O$ with 25% ammonium hydroxide in a molar ratio of 2:1 and again the resultant was mixed with oleic acid. The formed nanoparticles and polystyrene are dissolved in styrene monomer, which is again mixed with the 1% (w/v) SDS solution to stabilise the emulsion. The emulsion was ultrasonicated at 60 amp for 1 min and then the styrene monomer was evaporated to have the magnetic nanoparticles. According to their study large water content compared to the oil phase stabilises the particle formation after restricting the coalescence of the particles. The solvent (styrene monomer) evaporation reduces the solubility of both polystyrene and magnetic nanoparticles within the droplet. However, because of the low solubility of Fe^{+3}/Fe^{+2} in styrene monomer compared to polystyrene, the nanoparticles are precipitated out within the droplets, while the organic phase gets accumulated on the other side of the nanodroplet attributing to a property of Janus particle (Figure 2.3).

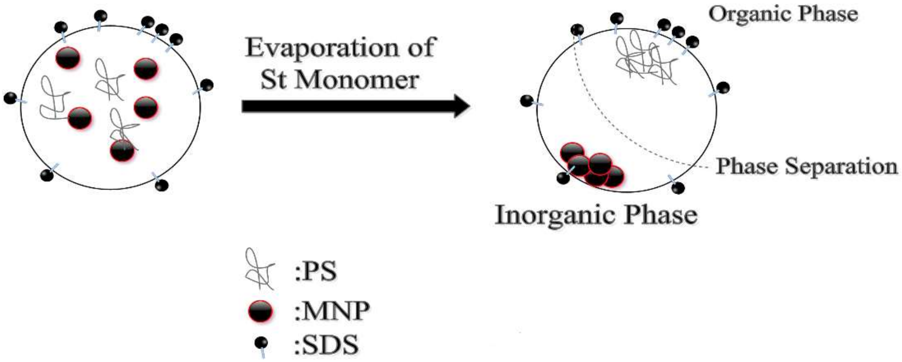


Figure 2.3 Formation of Janus like magnetic nanoparticles during solvent evaporation process.

One of the critically acclaimed applications of such nanoparticles is in the biomedical applications. Moreover, in present days, the combinatorial approach with both therapies (eg. biomarkers) and diagnosis (eg. drugs) called "theragnostics", becomes a powerful tool in medical science. Thus, with the aforesaid impregnated nano-magnetic Janus particle, one of the key benefits obtained is the reduction in the drug wastage within the blood stream through this fabricated more target specific nano-drug (Indira and Lakshmi, 2010). The utility of the preparation procedures using emulsion technique will enable one to have full control over the size of the nanoparticle, which is crucial in case of drug formulation. It was seen, when the size is less than 5 nm, it will be excreted by urination and more than 100 nm will be uptaken by macrophages (Schladt et al., 2011). At the same time, surface modification of the nanoparticles using miniemulsion/solvent evaporation method like in case of Janus particle, will be an important parameter promoting protein binding during flow in the blood stream (Schladt et al., 2011). Thus the fabrication of two faced Janus particles add a phenomenal success in cancer therapy, bioimaging etc.

However, sometimes the oily wastewater comes out from different industrial sectors, oil exploration unit forms emulsion because of the presence of emulsifier, fats, oil and grease (FOG). This promotes the fouling of the pipelines through deposition and also it increases turbidity of the river water disrupting the aquatic flora and fauna. Therefore, before the emulsified oily water is disbursed into the aquatic region, pretreatment is required that separates the mixture of oil-water. Following sections are dealing with such pretreatment procedures for emulsified oily-waste water.

2.6 Oily-waste water emulsion treatment

Oily-waste water is one of the primary waste streams that was identified by US Environmental Protection Agencies and a thorough work had been carried out since 90's to reclaim the water that is mixed with the oil homogeneously (Baker et al., 1990). One of the reasons behind the formation of emulsified oily water is the presence of the dirt in the water that acts as an emulsifier. Baker et al. (Baker et al., 1990) proposed a method, where the emulsified oily-waste water was pressurised just above the vapour pressure of at around 2500 psig and 350°C separating the emulsified oil into three different layers – oil at the top, water beneath the oil and the solid dirt at the bottom as a sediment. However, one of the concerns with the process is the cost involvement because of generation of high pressure and temperature. Therefore, technology search begins for alternative strategic plan towards the treatment of emulsified oily wastewater. Conventional oily wastewater treatment methods such as gravity separation and skimming, air flotation, coagulation, demulsification, flocculation were found less along with its high operating cost, corrosion and recontamination problems that subsequently lead to an inefficient removal of oil droplets of micron and sub-micron sizes from its emulsified form (Pagidi et al., 2014). Hence, looking for an effective low cost technology for the treatment of emulsified oily wastewater is one of the primary demands for total water reclamation from its homogeneous mixture with oil.

2.6.1 Acidulation of emulsified oily-water:

Acidification of emulsified oily water is one of the low cost treatment technologies, where acid is usually dosed at a low pH in order to separate acid-oil from acid water phase (Mag et al., 1983). According to them (Mag et al., 1983), the process includes three distinct consecutive operations – (a) continuous acidulation (b) gravity separation of acid oil from acid water followed by acid oil decantation and (c) separation by coalescence of "emulsified" acid oil from acid water. Coalescence shows a substantial reduction of fat/lipids in acid water phase (Mag et al., 1983). Previously, Woerfel (1981) (Woerfel, 1981) had investigated the process of acidulation over emulsified soapstock, a byproduct results from the alkali refining of soyabean oil and contains less amount of total fatty acid. Primarily acidulation technique was studied with the vegetable oily-waste water (Mcdermott, 1976) coming out as an effluent from oil production unit. Aforesaid, acidulation was employed to separate oily phase from water, which is again decanted from a gravity separator. However, the "acid-water" collected as a middle product from the decanter requires neutralisation. According to McDermott, U.S. regulations defined two different modalities for the treatment of wastewater – one the treatment at the discharge end and the other one is the treatment at a prefixed wastewater conveyance zone, which was called "joint-treatment". The later one is the mostly used modality in any of the urban areas, although one of the important aspects of this modality is the degree of variations in the wastewater components. Hence, the design of a proper technology in order to treat the wastewater is a big challenge because of such variations in the wastewater. This finally leads to an inception of effluent treatment plant (ETP) for in-plant treatment of the industrial discharge. According to environmental protection agency, wastewater with pH less than 5.0 is restricted to direct disposal in the sewerage system (Mcdermott, 1976) because of the possibility of disruption of aquatic flora and fauna once it is discharged into any aquatic body. However, after acidulation, the acid water from decanter, is rich in fatty acid having a pH of 2-2.5 and therefore, it requires neutralisation before discharge. Kaliniichuk et al. (Kaliniichuk et al., 1972) had adjoined the acidulation process with the coagulation process (Ferric sulphate and ferric chloride coagulant solution that ultimately yields ferric hydroxide with the oil-water emulsion) in separating petroleum from the adsorbent used to break the emulsified petroleum-water. In the process, they had applied the acidulation technique to dissolve the ferric hydroxide in order to release the adsorbed petroleum over it. Hence, it is quite obvious that acidulation is either a secondary technique that was used following the primary coagulation step (Kaliniichuk et al., 1972) or the primary one followed by coalescence (Mcdermott, 1976). Recently, Daaou and Bendedouch (Daaou and Bendedouch, 2012) had studied the effect of pH on the destabilisation of crude oil-water emulsion. According to them, the most stable form of the oil-in-water emulsion was confirmed at neutral pH, while at moderate acidic pH (their study shows pH was 5), the maximal instability occurred. Moreover, with high basic condition of pH (>10-11) the instability increases as observed by them. Poteau and Argillier (Poteau and Argillier, 2005) had made a similar study on the effect of pH to demulsify the oil-in-water emulsion in the presence of asphaltenes, an amphoteric compound found in petroleum, due to a reduction in interfacial tension. Reduction in interfacial tension increases the possibility of dispersed phase coalescence, which finally separates oil from water from its homogeneous mixture.

2.6.2 Membrane and electrochemical technology for the treatment of oily wastewater:

Several hybrid technologies have been designed in order to separate oil from its emulsion phase with water in order to make the process more effective and economic. Salahi et al. (Salahi et al., 2011) applied combined ultrafiltration (UF)/reverse osmosis (RO) technology in treating emulsified oily wastewater, where they had removed almost 95-100% of the oil-grease content. They had fed Tehran refinery unit wastewater to the membrane units comprising of UF (20 kDa polyacrylonitrile membrane) and RO (polyamide membrane) in tandem. It was seen that most of the organic molecules, bacteria, suspended solids, COD etc. were being reduced by the UF membrane, while the salts were rejected by RO attributing to the lost corrosiveness of the RO permeate. Table 2.1 shows the characteristics of the treated and untreated wastewater, which had been investigated by them. However, energy intensive processes like RO might increase the treatment cost and hereafter, the final cost of the process will also be increased.

Table 2.1 Characteristics of the wastewater and the treated wastewater (UF and RO) (TMP = 3 bar, Cross Flow Velocity = 1 m/s and T = 40°C)

(*Reprinted after permission from Desalination and Water Treatment, 28(1-3), 2011, 75-82*).

Parameter	Unit	Feed	Treatment	
			RO	UF
TSS	mg/l		60 Trace	Trace
TDS	mg/l	2028	1424	96
Content of oil and grease	mg/l	78	0.2	0
COD	mg/l	124	41	2
TOC	mg/l	81	17.6	2
Turbidity	NTU	53	0.4	0

Compared to RO and nanofiltration(NF), forward osmosis (FO) membrane process; which utilizes an osmotic pressure gradient to extract water across a semi-permeable membrane from a feed of lower osmotic pressure to a draw solution of higher osmotic pressure consumes much less energy during the operation. In 2017, Ong et al. (Ong et al., 2017) has developed a double skonned forward osmosis membrane comprising of a fully porous sublayer, sandwiched between a highly dense polyamide layer for salt rejection and a fairly loose dense bottom zwitterionic layer for emulsifed oil particle removal. Though using this double skinned membrane they obtained a good quality permeate water with oil rejection >99.9% with a reasonably fair water flux for 10,000ppm oil in water feed solution, the original water flux dropped to 50%. Bakeri and Fallahnezad reported (Bakeri and Fallahnezad, 2016) 100% oil rejection by a nanostructure polyethersulfone (PES) hollow fiber membrane through a cross-flow ultrafiltration (UF) system.

In recent past, El-Naas et al. (2014) (El-Naas et al., 2014) applied “three step” technology for the treatment of petroleum oily water, where the setup was fabricated after equipping electroflotation cell (EC), spouted bed bioreactor (SBBR) filled with immobilised bacteria within polyvinyl alcohol beads (Figure 2.4) and activated charcoal bed (AD) in series (schematic diagram is shown in Figure 2.5).

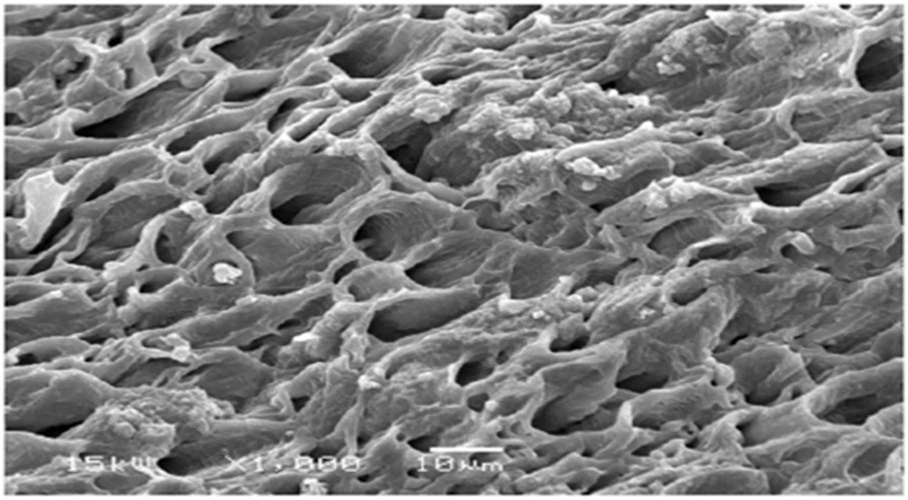


Figure 2.4 SEM image for immobilised bacteria in PVA (Reprinted after permission from Journal of Environmental Chemical Engineering, 2, 2014, 56-62).

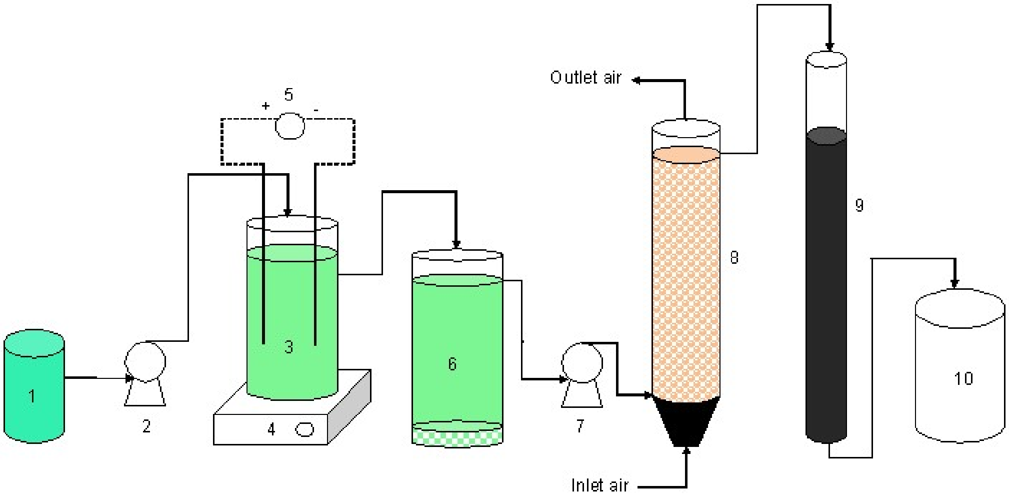


Figure 2.5 A schematic representation of the integrated system for the treatment of oily water (1) Feed tank, (2) Feed pump, (3) Electrocoagulation reactor, (4) Magnetic stirrer, (5) DC power supply, (6) Settling tank, (7) Pump, (8) Biological reactor, (9) Adsorption column, (10) Product tank (_Reprinted after permission from Journal of Environmental Chemical Engineering, 2, 2014, 56-62_).

Table 2.2 Characteristics of the wastewater and the treated wastewater (EC-SBBR-AD) (*Reprinted after permission from Journal of Environmental Chemical Engineering, 2(1), 2014, 56-62*).

Parameter	EC		SBBR		AD	
	In	Out	In	Out	In	Out
pH	7.2	9.1	7.8	8.2	8.2	8.2
Conductivity (mS)	5.4	6.2	6.2	6.73	6.73	8.24
TSS (g/l)	0.072	0.244	0.11	0.17	0.05	0.01
TDS (g/l)	3.38	3.6	3.6	4.03	4.03	4.95
COD (mg/l)	4190	2267	2267	1116	1116	110
Phenol (mg/l)	12.2	8.1	8.1	4.8	4.8	0
m, p-Cresol (mg/l)	75	64	64	33	33	0

It was well understood from table 2.2 that according to their process, almost 98% reduction in COD and 100% reduction in phenol, were observed according to their study. Rincón and Motta (Rincón and La Motta, 2014) had shown some combined effort with electro-coagulation/flotation (ECF) to remove oil, grease and heavy metals from bilge water discharge the primary contributors to the marine pollution and thereby, disruption of the whole biodiversity belonging to the marine environment.

In order to study the outcome of the combined EC/EF process, they had prepared synthetic bilge wastewater with a composition given in table 2.3. In the process, the anode releases metal ions (Fe^{3+} from carbon steel anode or Al^{3+} from aluminium anode), which is accepting the OH^- ion release by the cathode.

Table 2.3 Characteristics of the wastewater and the treated wastewater (EC-SBBR-AD) (*Reprinted after permission from Journal of Environmental Management, 144, 2014, 42-50*).

Constituent	Concentration (mg/l)
Total oil	5000
Emulsified hexane extractable materials	1278
Tween 40®	2500
Sodium chloride	600
Acrylic paint	200
Copper chloride	5
Zinc chloride	2.5
Nickel chloride	1.5

Alkali metal forms its hydroxide and is being precipitated along with the dirt and other impurities present in the emulsion to remove these pollutants from water. While, at the same time, bubbling because of the gaseous hydrogen released at cathode and oxygen released at anode will demulsify followed by the flotation of oil at the top of the water surface. The reactions for the same are given as below:

Anode reaction:

$$2H_2O\ (l) \rightarrow 4H^+(aq) + 2O_2(g) + 4e^- \qquad 2.1$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad 2.2$$

Cathode reaction:

$$2H_2O\ (l) + 2e^- \rightarrow H_2(g) + 2OH^- \qquad 2.3$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad 2.4$$

Coagulation recation:

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3\downarrow \qquad 2.5$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3\downarrow \qquad 2.6$$

One of the prime reasons behind employing the ECF, is its low cost and quick removal of the pollutants. However, the prime feature in case with ECF is the selection of electrodes, which is crucial in order to enhance the removal efficiency and at the same time, the chosen electrode should not impart additional cost to the system. Rincón and Motta (Rincón and La Motta, 2014) had employed different electrode systems to decide on their suitability in order to make the process efficient. According to them, metal removal was achieved with almost 99%, while the oil and grease content removal was almost 96% with iron electrode. However, one of the typical concerns in electrochemical process is the impurities present in the water that may affect the oxygen and hydrogen transfer rate (Kotti et al., 2009; Kroon et al., 2006). According to them (Kotti et al., 2009; Kroon et al., 2006), the presence of oil within the wastewater requires maximum current density in order to have proper oxygenation and hydrogen simultaneously. However, with the concentration of surfactant the requirement of current density for oxygenation was decreased. One of the major problems associated with electrochemical process is the incrustation of cathodes (figure 2.6) that ultimately reduces the process performance over the days (Lima and Vilar, 2014).

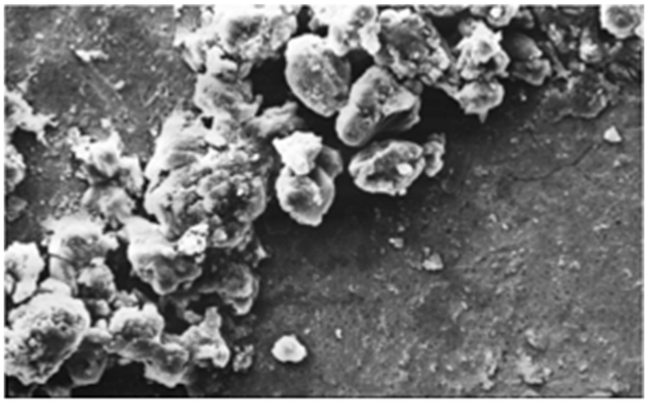


Figure 2.6 SEM of a sample cathode (1x2 cm) showing incrustation formed primarily from calcium and magnesium carbonates (1000x)

(*Reprinted after permission from Ultrasonics sonochemistry, 21, 2014, 963-969*).

Ultrasonic enhanced process reduces the incrustation attributing to an increased life of the cathodes (Lima and Vilar, 2014). The problems related to the incrustation occur because of the presence of impurities (like carbonates) present in the wastewater that deposits over the surface of the cathode reducing the polarity of it and ultimately reduces the redox reaction. Primarily, if the the bicarbonate will be present as in case of hard water, the carbonates are formed through electrochemical reaction. This carbonate is deposited on the surface of the cathode leading to an incrustation.

$$2H_2O\ (l) + 2e^- \rightarrow H_2(g) + 2OH^- \qquad 2.7$$

$$O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^- \qquad 2.8$$

$$2HCO_3^- + 2e^- \rightarrow H_2 + 2CO_3^{2-} \qquad 2.9$$

Application of ultrasound creates microholes over the surface of the cathode that releases the adhered impurities from its surface. According to Lima and Vilar (Lima and Vilar, 2014), the incrustation time (that is the time requires to have the cathode incrusted) was increased by almost 25% with ultrasound enhanced electrolysis process. This manifests the fact on reduced incrustation with the ultrasound enhanced process. However, even these conventional procedures may not be such efficient in order to remove the organic matters present in the wastewater and therefore, the process will not be enriched with a permissible value for COD or BOD. Hence, a new technology has been proposed, where hydroxyl free radical that acts as a potential agent for the oxidation of the components present in the waste stream (Ángeles et al., 2014) manifesting effective oxidation of organic matter. In recent days, the most traditional process in the treatment of wastewater is the advanced oxidation process (AOP). In this regard, degradation of the organic pollutants using Fenton's reagent is one of the prime considerations nowadays, where hydroxyl radicals are generated through Fenton reaction at iron anode (Priambodo et al., 2011) as shown below. One of the critically acclaimed advantages with Fenton's oxidation process i.e. the conversion of Fe(II) to Fe(III) is few minutes in presence of excess amount of hydrogen peroxide (Munter, 2001). Moreover, application of UV exposure to Fenton process enhances the degradation process. Figure 2.7 shows a comparative view on the oxidative efficiency for ethylenediaminetetra acetic acid (EDTA) using AOP technique. Liu et al. (Liu et al., 2014) had seen that about 25% COD of ETA had been oxidised in first 22 mins because of the OH free radical generation and the fact was confirmed with the free radical scavenger tertiary butanol. However, according to them, free radical is the sole responsible species that enhances the oxidation process and because of that, addition of tertiary butanol reduces the oxidation process.

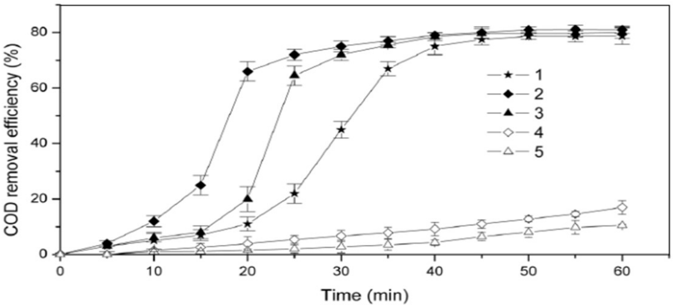


Figure 2.7 Comparison of oxidation efficiency of EDTA by different processes (1) Fenton, (2) UV/Fenton, (3) Fenton + $K_2C_2O_4$, (4) UV/Fenton + tert-butanol (5) Fenton + $K_2C_2O_4$ + tert-butanol. Experimental conditions: EDTA: 50 mM, H_2O_2: 1.5 M, Fe^{2+}: 15 mM, $K_2C_2O_4$: 11 mM, tert-butanol: 10 mM

(*Reprinted after permission from Scientific Reports, 4, 2014, 1-4*).

Presently, AOP process using Fenton reagent following the pretreatment of the emulsified oily wastewater is one of the topic of interests among the people, where primarily the emulsion is treated with electrolytes to destabilise the emulsion followed by AOP (Tolosa et al., 2006; Zhuannian et al., 2011). Abundant amount of Fe^{3+} ion coagulates as $Fe(OH)_3$ following the AOP and the hybrid process removes almost 100% of COD (Zhuannian et al., 2011).

Fenton: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet$ 2.10

Photo-Fenton: $Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+$ 2.11

$Fe(OH)^{2+} \leftrightarrows Fe^{3+} + OH^-$ 2.12

$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^\bullet$ 2.13

However, one of the difficulties in separating the oil from emulsion either using membrane separation or the UV/Fenton process can't serve the true purpose because of the presence of other impurities in case with the emulsion. Especially, presence of such impurities such as detergent, surfactant adsorb on the surface of the membrane that eventually fouls the membrane and reduces the performance of the process in separating oil from its mixture with water (Faibish and Cohen, 2001). On the contrary, with the UV/Fenton process, the rate of bubbling concludes the separation of oil and henceforth, its oxidation that reduces the COD of the process. However, it was seen that in case of car-wash water or diesel-water emulsion such advanced oxidation process reduces only 60-61% of the COD load, while addition of TiO_2 enhances the oxygenation. This increases the separation of oil from water and hereafter around 80% COD load reduction could be observed (Tony et al., 2009). One of the major problems poses with the Fenton process is the disposal of iron or TiO_2 that imparts an adverse effect to the environment (Tony et al., 2009). In view of that membrane separation could be a better alternative that might be designed with low fouling membrane to enhance the process efficiency in separation oil from oil-water emulsion. Especially, the wastewater stream is populated with several particulate matters that are observed in spent oil-water emulsion such as the combustion particles (of size ranges from 10-50 nm), surfactants etc. These foul the convention membrane and resist the water reclamation process. In view of that, nano-fibrous membranes, a recent applications developed in sixties (Barhate and Ramakrishna, 2007) are the most coveted membrane units in dealing with the such particulates removal from the wastewater. In 2016 Medeiros et al. (Medeiros et al., 2016) prepared hybrid for membranes of polyamide6 (PA6) with montmorillonite and porogenic agent calcium chloride for separation of water-in-oil emulsion in a dead end filtration system. They fed emulsion having droplet diameters varying from 3 to 8 μm, with oil concentration of 50,100 and 200 ppm in water and reduced a significant amount of oil in the permeate upto 20 ppm concentration.

2.6.3 Nano based treatment of oily wastewater:

Nanofibrous membrane (Figure 2.8 (Barhate and Ramakrishna, 2007)) that provide a high surface to volume ratio, high permeability, low basis weight (g/m^2) and small fibre diameter (Balamurugan et al., 2011). Until now, mostly the polymeric nanofibrous membrane is limited to air filtration and yet to commercialise in the water treatment field. In case of air filtration process the air permeability increases with the decrease in web basis weight of the membrane and with the increase in fibre diameter (Hassan et al., 2013). The primary feature in the filtration process with nanofibrous membrane is the aerodynamic slip that occurs at the surface of the fibre, which eventually controls the pressure drop across the membrane (Faibish and Cohen, 2001). However, such slip can't be concluded in case of separation of the macromolecules from the solution as the liquid has more viscous effect compared to the air and this leads to an increase in the pressure drop across the membrane. Nanofibrous membrane after surface modification, such as grafting the hydrophilic group over the membrane to alleviate fouling of the membrane, was found to be a good alternative in manipulating the water treatment (Anwar et al., 2013).

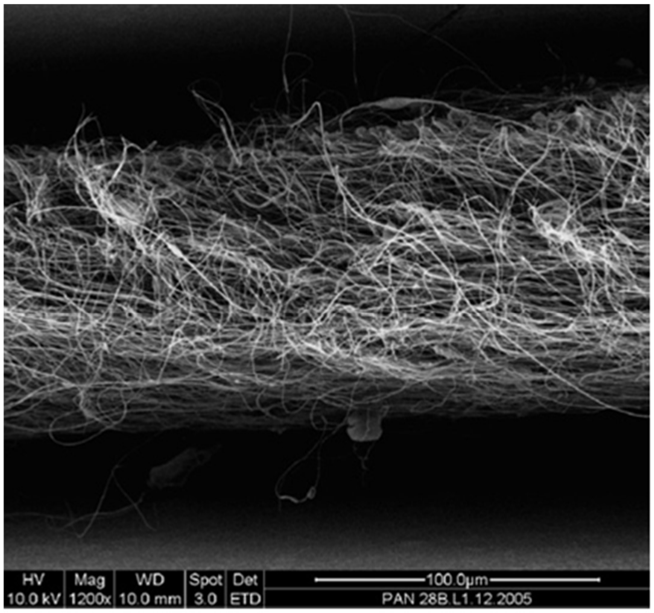


Figure 2.8 SEM images for nanofibrous filtering media

(*Reprinted after permission from Journal of Membrane Science, 296, 2007, 1-8*).

One of the critically acclaimed benefits with the nanofibrous membrane is its low fouling characteristics and possibilities of surface modification by varying the size of the nanofibres attributing to a varying surface to volume ratio. Moreover, controlling the surface to volume ratio of the fibre, the affinity and the selectivity of the membrane can be modulated after shifting the band gap for semi-conductor based nanofibres attributing to a change in the surface energy (Herbert et al., 2013; Viter et al., 2013). Increased band gap reduces the surface free energy that increases the selectivity of the fibre for oil and the technique is successfully implemented in the separation of oil/water (Ong et al., 2014). Yoon et al. (Yoon et al., 2006) had developed a three coated ultrafiltration membrane, where the scaffold for the membrane of average fibre diameter 750 nm was fabricated with two layered polyacrylonitrile (PAN) polymer and this shows 73% surface porosity. Over the membrane there is a layer of hydrophilic chitosan that remains undissolved in water at neutral pH and hence, shows resistance to water. Nonwoven polyester substrate was used as the support layer to form aforesaid three tier composite UF membrane. However, the fabrication of nanofibrous membrane and thereof, the performance of the process depends on the method of fabrication. Among several techniques, electrospinning operation towards the fabrication of nanofibrous material is the mostly adopted technologies, where a high voltage electric field is applied to create an electrically charged jet of a polymer solution from a syringe. When the voltage difference will overcome the surface tension of the polymers' solution, a Taylor cone will spin down the solution as a fibre in the range of 10-100 nm to the collector (Anwar et al., 2013). Figure 2.9 (Bhardwaj and Kundu, 2010) shows the schematic for the electrospinning operation. The most important advantage with the electrospun technique is its control over the nanofibres' size, which is again deciding the performance of the membrane.

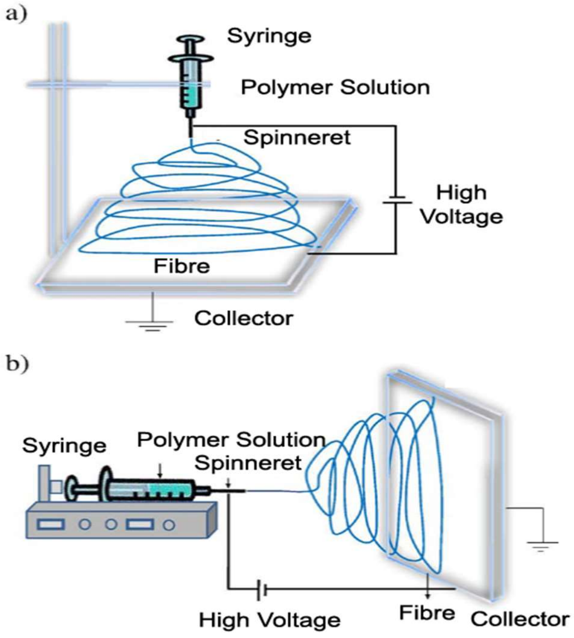


Figure 2.9 Schematic diagram of electrospinning set-up (a) vertical set-up (b) horizontal set-up

(*Reprinted after permission from Biotechnology Advances, 28, 2010, 325-347*).

Viswanadam and Chase (Viswanadam and Chase, 2013) had applied tubular nanofibre membranes made up of syndiotactic polypropylene (SPP) on a steel compression spring to separate oil-water with 98% efficiency. They had adopted the electrospinning process to produce the nanofibrous membrane, when this process introduces roughness at a micron level and this induces the oleophillic property of the membrane. In recent days specifically for separating the oil-water emulsion, a thin film composite (TFC) membrane was employed, where the top layer consists of a skin layer followed by a middle layer is of nanofibrous structure on a polymeric support. Khamforoush et al. (Khamforoush et al., 2015) fabricated polusulfone (PSf) coated conventional ultrafiltration membrane with cellulose acetate (CA) dosed polyacrylonitrile (PAN) nanofibrous membrane on polyester support. According to them, the nanofibrous TFC membrane shows almost 100 times more flux to conventional PSf asymmetric membrane because of low web basis weight in case of nanofibrous membrane. Hydrophilic CA reduces the fouling of the membrane, while nanofibrous membrane increases the flux. Furthermore, the surface modification for the nanofibrous membrane will be done to fabricate superhydrophilic membrane that could effectively separate water rich oil-in-water phase with low fouling characteristics. Recently, Kota et al. (Kota et al., 2012) had developed a superhydrophilic membrane, where they had used a mixture of fluorodecyl polyhedral oligomeric silsesquioxane (f-POSS) and cross-linked poly(ethylene glycol) diacrylate (x-PEGDA) to fabricate a modified hygroresponsive membrane. However, the limitation of the membrane is its low strength against the applied pressure that reduces the longevity of the membrane and restricts its applicability to a wider membrane application. Raza et al. (Raza et al., 2014) had fabricated the superhydrophilic membrane of high surface energy, which is having more mechanical strength withstanding upto 14 MPa. They had cross-linked the polyethylene glycol diacrylate (PEGDA) over 8-12% w/w polyacrylonitrile (PAN)/polyethylene glycol (PEG) nanofibrous scaffold to prepare nanofibrous membrane (fibre diameter ranges from 157-228nm) of 1.5-2.6 micron pore size. However, the cross-linking was done using UV intensity of 254nm for around 30 s. During the experiment they had used different combinations of oil water mixture and treated with different set of membranes, where the PAN concentration varies during fabrication. Figure 2.10(a) shows a substantial removal of oil from water using different sets of membrane and can be seen that with the increase in the concentration of PAN attributing to higher basis weight (because of higher fibre diameter) reduces removal of oil either from oil-water mixture or oil-water emulsion. Even the same trend could be observed with the fouling of the membrane also. It is seen (Figure 2.10(b)) the membrane prepared with low range of nanofibre diameter shows more reusability attributing to low fouling of the membrane.

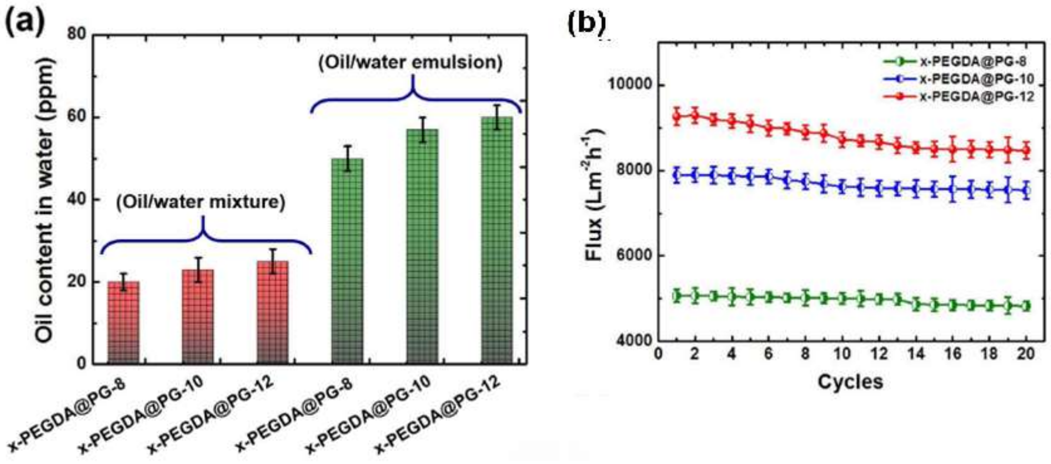


Figure 2.10 Oil water separation results of various x-PEGDA@PG NF membranes. (a) Oil content in the filtrate after permeating oil/water mixture and oil in water emulsion through various x-PEGDA@PG-8, x-PEGDA@PG-10, and x-PEGDA@PG- 12 NF membranes. (b) Real time monitoring of the flux with increasing cycle number using relevant x-PEGDA@PG-8, x-PEGDA@PG-10, and x-PEGDA@PG-12 NF membranes (Reprinted after permission from Journal of Materials Chemistry A, 2, 2014, 10137-10145).

One of the other techniques in the nanotechnology based membrane treatment is the nanoparticle impregnated membrane that eventually shows good result in compare to the conventional membrane in some cases. In 2007, Colle et al. (Del Colle et al., 2007) shows the performance of the membrane in separating oil (sunflower) from its w/o emulsion after impregnating zirconium as a zirconium citrate precursor along with the formed nanoparticles of oxides of zirconium in the ceramic microporous tubes using calcination. They found that the calcination process during impregnation has an appreciable effect on the demusification process because of the variation in the surface property of the membrane due to change in the crystallinity of the impregnated nanoparticles. 600-900°C temperature of calcination shows substantial increase in the separation of oil from its w/o emulsified form. Zhou et al. (Zhou et al., 2010) had applied a modified alumina microfiltration membrane, where the impregnated nanoparticles are zirconium oxides. The presence of its oxides over zirconium exposes more hydroxyl group (-OH) on the surface making the surface hydrophilic that repels oil and keep away from the surface. Thus it reduces the possibility of membrane fouling and thus maintains a high moderate flux value over time. In 2011, Yi et al. (Yi et al., 2011) have enhanced the performance of PVDF membrane after modifying the membrane surface using nano TiO_2/Al_2O_3 nanomaterials. Substantial increase in the membrane performance and almost 7% more flux recovery could be observed with this modified PVDF membrane. Impregnation of nanoparticles within the membrane increases its rigidity and resists its permanent fouling. In case of a polymeric membrane, oil droplets sticks with the pores' inner surface during permeation because of pores' tortuosity. Hence, pressure increases over the membrane due to the permanent clogging of the pores that ultimately increases the strain with the membrane with the applied stress (Yi et al., 2011). However, unlike polymeric membrane, impregnation of nanoparticles within the membrane increases its strength and restricts the insertion of the oil droplets within the pores. Figure 2.11 shows a complete recovery of water flux after cleaning of the surface modified membrane manifesting its low fouling characteristics.

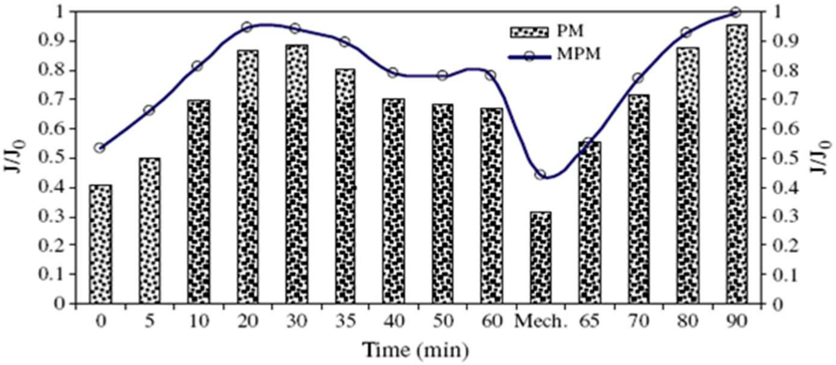


Figure 2.11 Pure water Flux Recovery after different cleaning method (0: pure water RF of fouled membranes; 0–30 min: pu*re water cleaning; 30–60 min: pure water reversed cleaning; Mechanical: sponge balls* cleaning; Mechanical–90 min: NaClO solution cleaning)

(*Reprinted after permission from Desalination, 281, 2011, 179-184*).

2.7 Bioremediation of oily wastewater

Bioremediation mainly refers to a complete mineralization of organic contaminants into carbon dioxide, water, inorganic compounds, and cell protein. It is the transformation of complex organic contaminants to other simpler organic compounds by biological agents like microorganisms, bio surfactants, and enzymes. Natural process, employing microorganisms, is considered to be very effective, economic and environmentally acceptable technology towards the degradation of hazardous oily effluent. Bacteria are the most active agents in petroleum degradation, and they work as primary degraders of spilled oil in the environment (Brooijmans et al., 2009; Rahman et al., 2003). Several bacteria, such as hydrocarbonoclastic bacteria, and fungi are the primary genres of such microbes taking part in the bioremediation of oilywastewater (Yakimov et al., 2007). Floodgate (Floodgate, 1984) said about such 25 genera of hydrocarbon degrading bacteria and fungi individually, which were isolated from marine environment, while Bartha and Bossert (Bartha and Bossert, 1984) told about 22 genera of such bacteria and 31 genera of fungi. Several yeast species, like *Candida lipolytica*, *Rhodotorula mucilaginosa*, *Geotrichum sp.* and *Trichosporon mucoides* are isolated from oil polluted water. Singh had reported several fungal species like *Aspergillus*, *Cephalosporium*, and *Pencilliumare* that have a substantial capability of degrading hydrocarbons spilled over the aquatic environment (Singh, 2006). In earlier days, the extent to which bacteria, yeast, and filamentous fungi participate in the biodegradation of petroleum hydrocarbons was with a limited scope of the study, but was there to be of great concerns on its effect on the ecosystem and how their performance is controlled by local environmental conditions. However, these days several researches have been carried out on their mechanism to degrade oil, especially in case of oil-spill in the marine environment. In 1975, Walker *et al*. (Walker et al., 1975) isolated an algae, *Prototheca zopfi* that was capable of degrading n-alkanes and isoalkanes along with the aromatic hydrocarbons present in the crude oil. Cerniglia *et al*. (Cerniglia et al., 1980) had examined nine cyanobacteria, five green algae, one red alga, one brown alga, and two diatoms strains in oxidation of naphthalene, an aromatic hydrocarbons when drained in the aquatic environment will exhibit toxic, carcinogenic and mutagenic properties. One of the key benefits with the bioremediation of oil pollution is the mitigation of global warming issue after absorbing carbon dioxide from environment during algal culture (Sivakumar et al., 2012). However, one of the critical issues with the usage of algal biomass in bioremediation of hydrocarbon pollutants is the supply of nitrogenous and phosphorous nutrients that may disrupt the ecosystem balance. In recent past, a novel green algae strain *Pseudochoricystis ellipsoidea* MBIC 11204 was proposed which can consume oil even at nitrogen deficient condition (Ito et al., 2013).

Oil contaminants in a large region of aquatic environment are primarily treated by hydrocarbonoclastic bacteria (HCB) (Yakimov et al., 2007) that can cleave the hydrocarbons of oil leading to a production of several metabolites through cellular metabolism and maintain the aquatic ecosystem. The population of these bacteria increases significantly, where the concentration of oil is substantial. However, high concentration of hydrocarbon manifests an inhibitory effect to these microorganisms. One of the extensively studied bacteria in this case is *Alcanivorax borkumensis*, a gram negative, aerobic, rod-shaped bacteria, that breaks down straight and branched chained alkanes into metabolites. Moreover, one of the key advantages that prevail with this particular bacteria is the production of biosurfactant during its metabolism after inheriting oil as their food from marine environment. Now the formation of these biosurfactants reduces the surface tension of water and forms o/w emulsion dissolving oil in water (Qiao and Shao, 2010; Sabirova et al., 2006). Presence of nitrogen and phosphorus increases its growth rate, called biostimulation. However, the addition of these nutrients in order to stimulate its growth in aquatic pool to remove oil from the “oil-spilled” region is also the reason to grow algae in water. Subsequently, significant increase in the algal growth disrupts the biological ecosystem through an increased competition for food resources, oxygen between the living organisms in aquatic life (Schneiker et al., 2006). Yakimov et al. (Yakimov et al., 1998) proposed a strain SK2 of this bacterium isolated from Isle of Borkum using n-alkane as sole carbon rich source. Figure 2.12 shows the transmission electron micrograph of the strain SK2 growing at the water-n-hexadecane interface (Martins dos Santos et al., 2010). It produces glucose lipids, a good biosurfactant (Faria et al., 2014), where 3-hydroxydecanoic acids are linked with the C-1 of glucose through glycosidic bond and four units of this acids are interlinked through ester bonds (Qiao and Shao, 2010). Another new strain called *Alcanivorax dieselolei* B-5 proposed by Qiao and Shao that produces biosurfactant, which reduces the surface energy of water by almost 50% that forms stable emulsion and thus it enhances the possibility of bioremediation by consuming oil through microorganisms (Qiao and Shao, 2010).

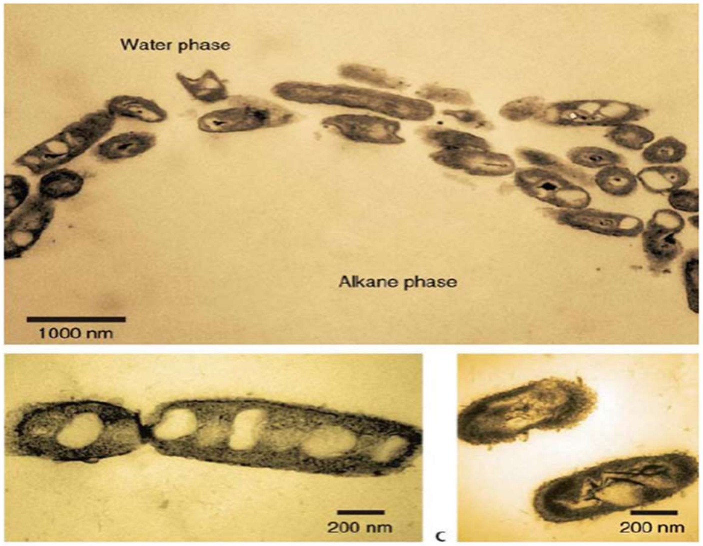


Figure 2.12 Transmission electro micrograph for SK2 strain of *Alcanivorax borkumensis* at the water-n-hexadecane interface

(*Reprinted after permission from V. Martins dos Santos, J. Sabirova, K. N. Timmis, M. M. Yakimov, P. N. Golyshin, Alcanivorax borkumensis in Handbook of Hydrocarbon and Lipid Microbiology, Eds. K. N. Timmis, Springer Berlin Heidelberg, 2010, pp. 1265-1288*).

One of the basic features of biosurfactants attribute to an increased surface area of hydrophobic water insoluble components, which enhances the uptake of hydrocarbons by the microorganisms (Nikolopoulou and Kalogerakis, 2010). However, not much insight on these biosurfactants has been enlightened so far.

One of the concerns with the mostly used *Alcanivorax sp.* is the thermal condition of the marine environment in which the microorganism works. It has been seen that with the cold marine atmosphere *Oleispira sp.* is more effective compared to *Alcanivorax sp.* in degrading alkanes (McGenity et al., 2012). Moreover, apart from hydrocarbons, additional toxic compounds, such as pyridine present in crude oil are degraded by *Micrococcus* and *Rhodococcus sp*., while poly aromatic hydrocarbons (PAH) are removed through *Sphingomonas sp.* (Daugulis and McCracken, 2003). However, sole microorganism can’t eliminate such aromatic hydrocarbons from the aquatic environment effectively due to its low availability and because of the interdependencies between the microorganisms for metabolism. Hence, bacterial consortium plays a good role in alleviating the oil contaminants in marine environment. Addition of bio-surfactants producing organism in the bacterial consortium increases the uptake of PAH (Figure 2.13 (McGenity et al., 2012)) after increasing the surface area for bioavailability. According to McKew et al. (McKew et al., 2007), *Alcanivorax sp.* popoulation is stimulated and enhanced by the nutrient addition along with the addition of biosurfactant JBR-215. It had been seen by them that from day 5 onwards the degradation of PAH occurs by *Cycloclasticus sp.* because of the production of glucose-lipid biosurfactant that enhances the bioavailability of PAH. Bento et al. (Menezes Bento et al., 2005) had isolated *Acinetobacter junii* strain from soil that shows the highest reduction of surface tension because of the biosurfactant it produced during oil degradation procedure. In recent days, due to growing economy, automobile industries are continuously growing day by day and it results in discharge of the spent engine oil continuously flown down to the river bed. Hence, one of the major concerns in bioremediation process is the degradation of the pollutants that are primarily because of the used engine oil percolated through the aquifers. In case of used oil the concentration of high molecular weight PAH, alkyl benzene, naphthalene and methyl naphthalene are high enough (Qbayori et al., 2014). Therefore, single strain would not remediate the pollutants present in aquifers. It is seen that anaerobic degradation of ethylbenzene and toluene was done by denitrifying strain EbN1 through a different substrate binding pathway (Champion et al., 1999).

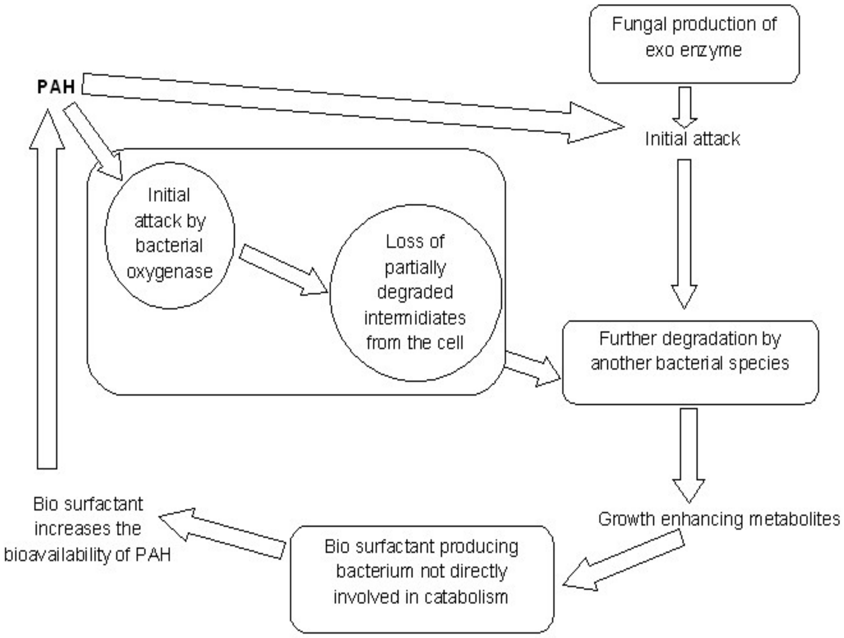


Figure 2.13 Microbial consortium for degradation of PAH.

Obayori et al. (Qbayori et al., 2014) isolated *Pseudomonas aeruginosa* strain LP5 from oil contaminated soil that grows on pyrene shows more than 90% of oil degradation along with the production of biosurfactants. The strain was found effective for both fresh and used oil. Table 2.4 shows the performance of removing crude oil as a pollutant using different strains, where the percentage is 90% removal of oil using *Sphingomonas sp.* strain (Ibrahim et al., 2013).

Table 2.4 Rate of degradation (%) of crude oil by bacterial isolates incubated at 30^{O}C for 20 days

(*Reprinted after permission from International Biodeterioration and Biodegradation, 81, 2013, 28-34*).

Bacterial isolates	Rate of degradation (%)
Achromobacter xylosoxidans	80
Bacillus licheniformis	20
Micrococcus kristinae	40
Bacillus firmus	30
Sphingomonas paucimobilis	90
Serratia marcescens	90
Bacillus lentus	20
Proteus vulgaris	85
Proteus mirabilis	90
Vibrio metschnikovii	70
Yersinia enterocolitica	20

One of the most conventional techniques in bioremediation of the oil spilled over the marine environment or in other water body is injecting the oil into the deep water horizon to form a “cloud” like environment. According to Atlas and Hazen (Atlas and Hazen, 2011), the deep water cloud has the highest oil degrading bacterial counts compared to the count outside the cloud. They had concluded that the strains are mostly γ proteobacteria with 3 families belong to *Oceanospirillales* class after analysing through 16S rRNA technique. The most promising factor with the γ proteobacteria is the consumption of high level of contaminants present in the deep sea (Popp et al., 2006). In recent past, Overholt et al. (Overholt et al., 2013) drafted genome sequences for 24 strains isolated from the seashore near Florida and Los Angeles, where the sequences are assembled in order to understand the metabolic potential in degrading hydrocarbon at the strain level. They had seen even at the same genus level, microorganisms’ potential in degradation of the hydrocarbons are different manifesting strain specific metabolic activity. However, during the remediation at *Deepwater Horizon* oil spill, genetically engineered microorganisms such as genetically modified harmless *E. coli* (“http://www.floridaoilspilllaw.com/genetically-engineered-strain-coli-bacteria-detect-oil/,” n.d.), was used. One of the primary reasons that urges for the genetically engineered microorganism is the performance of these organisms against the oil at 800-1400 m below the sea level where the oxygen atmosphere is depleted and the temperature is well below the surface temperature. Secondly, the dissolved gas at this depth causes a plume of hydrocarbons, which also has an effect in the microbes' performance towards the removal of crude (Redmond and Valentine, 2012). Hence, the common bacterial strain such as *Alcanivorax sp.* can't act effectively and requires engineered microbes. The primary advantages is the quick response of *Alcanivorax sp.* SK2 strain during the sudden oil contamination, when there is an imbalance between the hydrocarbons and the nutrients (Yakimov et al., 2007). In 2010, Oregon State University, had isolated *Pseudomonas aeruginosa* NY3 strain that can produce abundant quantity of biosurfactant, called "rhamnolipids", which degrades the oil and also some of the PAHs, the most toxic chemicals during oil spill ("http://www.sciencedaily.com/releases/2010/06/100611141527.htm," n.d.). The strain is quiet effective because the biosurfactant it produces is having high tolerance for temperature variation, pH and salinity attributing to a major issue in case of deep water oil spill. However, one of the major concerns here is the pathogenic action of these bacteria such as *Pseudomonas aeruginosa* has some serious issues with the human health, especially with the compromised immune system. Hence, genetical modification might add some additional hiccups to the vaccination formulation against these modified and sometimes mutated pathogens. This restricts the implementation of large scale unit in such a bioremediation with the modified microorganism. In 2016 Jamie et al. has proposed covalent immobilization of *Candida rugosa* lipase enzyme on modified multiwall carbon nanotubes for oily wastewater treatment processes. They have confirmef 30% enzyme loading with 98% biological retention activity of the enzyme.

2.7.1 Metabolic pathway for the microbes in bioremediation of oil and other toxic materials:

A key question in degrading the oil contaminant from water is the selection of proper strains that degrades the oil along with the toxic compounds present in either thewastewater or the marine environment. Moreover, the strains that are used in degrading crude oil or associated compounds are primarily pathogens that might spread infections. This subsequently activates the immunomodulatory proteins after being recognized by the receptors lying over the cell line (Dinamarca et al., 2013). Especially, once the living organisms are being infected, the infection will inflict the human body after taking the aquatic animals, such as fish, as their food. However, the benefit lies in the algal bioremediation of oily wastewater lies in absorbing carbon di-oxide (CO_2) form atmosphere leading to a reduction in the carbon footprint (Sivakumar et al., 2012), although the algal process is a slow process. Furthermore, genetically modified strains might impart less pathogenicity and hence, the widespread of the infection could be intervened. Hence, understanding the product profile after hydrocarbon degradation through metabolism becomes important in order to measure the follow-up toxicity that might excel. Figure 2.14 (Wentzel et al., 2007) shows the metabolic pathway for the degradation of the oil using anaerobic bacteria. From the figure it can be said that the n-alkane chain produces alcohols through cytochrome P450, particulate alkane hydroxylases (pAH) and subterminal alkane monooxygenase. The produced alcohol gives aldehydes and carboxylic acids through the action alcohol dehydrogenase and aldehyde dehydrogenase enzymes. Acids convert to Acyl-CoA after acyl-CoA synthetase, which is again further entering into the β-oxidation pathway. Sabirova et al. (Sabirova et al., 2006) had made a detailed analysis on SK2 strain of *Alcanivorax sp.*, where the proteins that are taking part in the degradation of oil primarily being expressed on the cell membrane in presence of alkanes and the subsequent metabolisim is taking place in cell cytoplasm. According to them, the recent analysis of ubiquitous *Alcanivorax borkumensis* SK2 strain possesses three enzyme systems that can convert alkanes to fatty acids. *alkB1* gene cluster, P450 cytochrome monooxygenase, flavin binding monooxygenase.

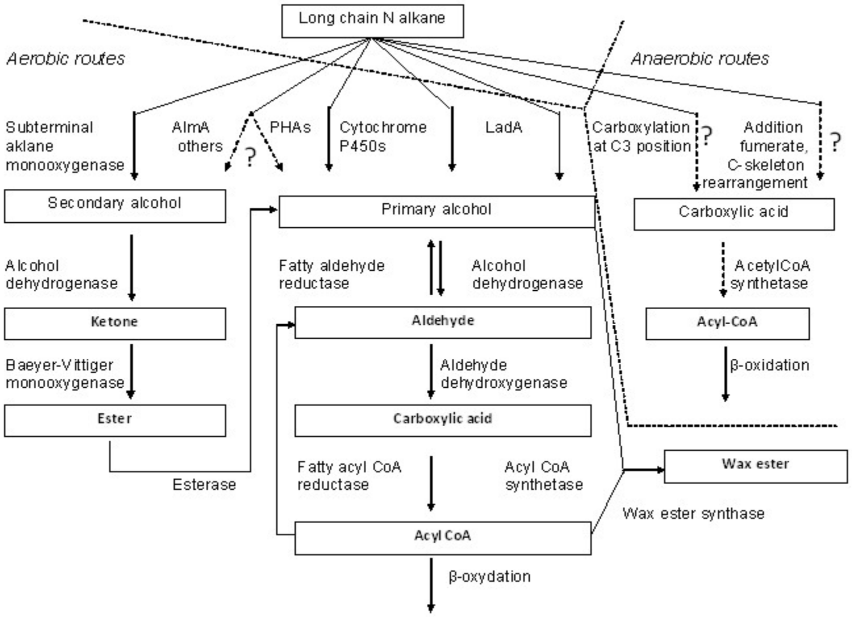


Figure 2.14 Pathways for aerobic and anaerobic bacterial degradation of long-chain n-alkanes and for synthesis of wax esters. Dotted arrows represent suggested metabolic routes

(*Reprinted after permission from Applied microbiology and biotechnology, 76, 2007, 1209-1221*).

Cytochrome P450 constitutes a super family of ubiquitous heme-thiolate monooxygenases, which play an important role in the microbial degradation of oil, chlorinated hydrocarbons, fuel additives, and many other organic compounds. Figure 2.15 (Schneiker et al., 2006) shows an overview of the metabolic oil degradation pathway for *Alcanivorax borkumensis* SK2. Higher eukaryotes generally contain several different P450 families that consist of large number of individual P450 forms, which may contribute as an ensemble of isoforms to the metabolic conversion of given substrate. However, in microorganisms such P450 multiplicity can only be found in few species (Zimmer et al., 1996). According to Sabirova et al. (Sabirova et al., 2006), *alkB1* gene comprises of AlkB1 alkane monooxygenase, AlkG rubredoxin, AlkH aldehyde dehydrogenase, and AlkJ alcohol dehydrogenase. While P450 monooxygenase is encoded by either cytochrome P450-1 or P450-2 and AlkJ2 alcohol dehydrogenase (Sabirova et al., 2006).

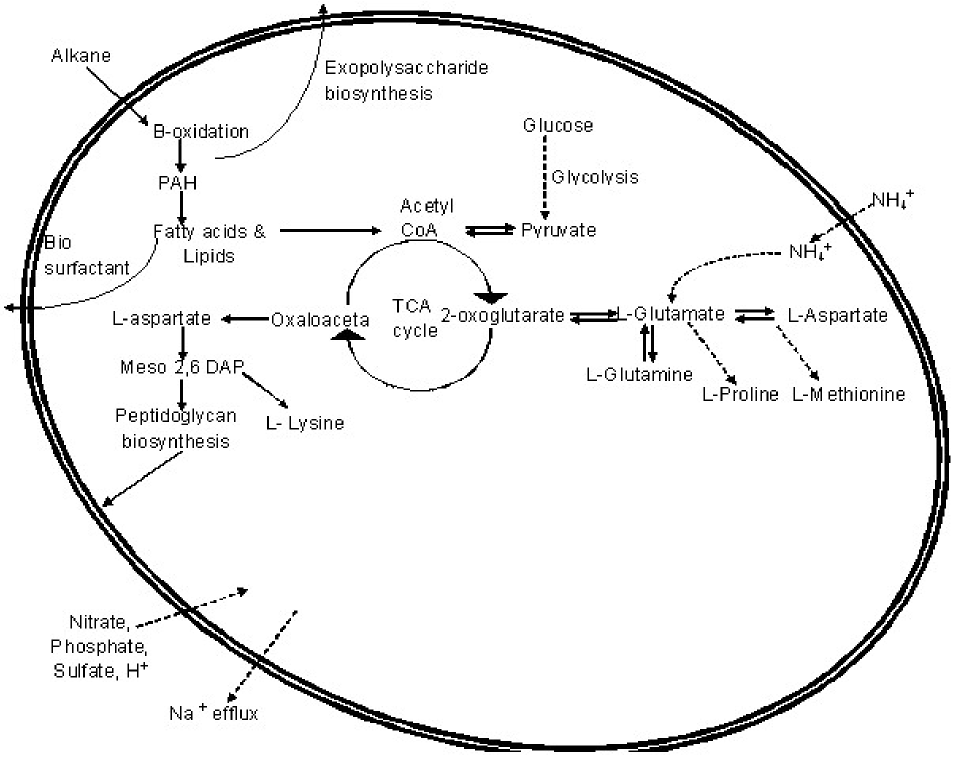


Figure 2.15 Schematic overview of metabolism and transport in *A. borkumensis* SK2. The background is a transmission electron micrograph (TEM) of an *A. borkumensis* cell grown on hexadecane. The insert in the right upper corner shows a TEM of *A. borkumensis* SK2 cells at the oil-water interface of hydrocarbon droplets in salt water. Predicted pathways for alkane degradation are depicted in marine blue. Predicted transporters are grouped by substrate specificity: inorganic cations (gray), inorganic anions (dark orange), amino acids/peptides/amines/purines/pyrimidines and other nitrogenous compounds (dark green), carboxylates (light green), drug efflux and

other (dark gray). Export or import of solutes is designated by the direction of the arrow through the transporter. The energy coupling mechanisms of the transporters are also shown: solutes transported by channel proteins are shown with a double-headed arrow; secondary transporters are shown with two arrowed lines indicating both the solute and the coupling ion; ATP-driven transporters are indicated by the ATP hydrolysis reaction; transporters with an unknown energy-coupling mechanism are shown with only a single arrow. The P-type ATPases are shown with a double-headed arrow to indicate they include both uptake and efflux systems. Where multiple homologous transporters with similar substrate predictions exist, the number of that type of protein is indicated in parentheses. Abbreviations of less common terms: EPS, extracellular polysaccharides; AA, amino acids: BCCT, betaine/carnitine/choline transporters; GSP, general secretion pathways; PRPP, 5'-phospho-alpha-D-ribose 1-diphosphate; Mhn, complex sodium/proton antiporter involved in sodium excretion (*Reprinted after permission from Nature Biotechnology, 24, 2006, 997-1004*).

Aerobic metabolism (Figure 2.14) of alkanes produces alcohols through enzymatic action of monooxygenase, when it is again degraded by alcohol and aldehyde dehydrogenase to form aldehydes and fatty acids respectively. Fatty acids produced here is again transformed into coenzyme A (CoA) induced fatty acid, which is again degraded by β-oxidation by enzymes like fatty acid CoA ligases, acyl CoA dehydrogenase, 3-hydroxyacyl-CoA dehydrogenase and enoyl-CoA hydratase. Several yeast species, like *Candida maltosa*, *Candida tropicalis*, and *Candida apicola,* grows after inheriting n-alkanes and other aliphatic hydrocarbons as a sole source of carbon, which produces energy after being mediated by multiple microsomal cytochrome P450.

Mardanov et al. (Mardanov et al., 2009) had isolated *T. sibiricus*, an anaerobic archaea, from deep sea oil reservoir that indicates its survival over time and its growth stimulated by cellulose, agarose, triacylglycerides and alkanes. According to them, the growth of the species is restricted with the cyclic hydrocarbons because of the absence of benzoyl-CoA reductase, 4-hydroxybenzoyl-CoA reductase, benzylsuccinate synthase, and 6-oxocyclohex-1-ene- 1-carbonyl-CoA hydrolase that are required for the anaerobic degradation of these hydrocarbons. However, the sustenance with the alkanes is prominent with the carboxylation of the third carbon atom in alkane. However, the enzymatic mechanism is still underlying and yet to develop for the anaerobic degradation of hydrocarbons. Figure 2.16 shows the metabolic pathway for *T. sibiricus* for its growth and products obtained. One of the acclaimed utilities of this sp. is its extracellular enzymes, such as lipase, that helps in the production of glycerol from triglycerides. After careful observation with this anaerobic organisms, it was seen by (Mardanov et al., 2009) that the growth of this species is restricted to long chained fatty acid. However, it grows on glycerol attributing to the absence of β-oxidation pathway here that helps to degrade fatty acid to alcohols. On the contrary it works perfectly with the olive oil suggesting the true presence of lipase that degrades triglycerides and produces glycerol extracellular attributes to easy extraction of glycerol.

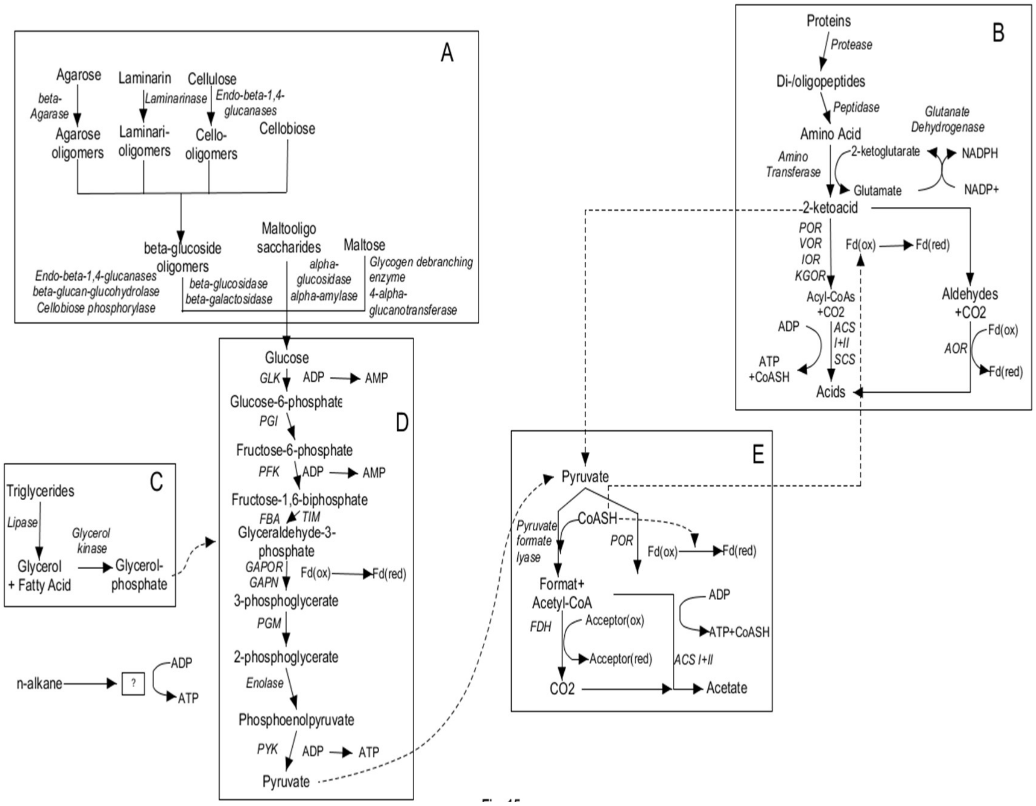


Figure 2.16 Overview of catabolic pathways encoded by the *T. sibiricus* genome. Panels: A, utilization of carbohydrates; B, utilization of proteins; C, utilization of lipids; D, glycolysis (modified Embden-Meyerhof pathway); E, pyruvate degradation; Abbreviations: ADP, Adenosine diphosphate; ATP, Adenosine triphosphosphate; POR, pyruvate:ferredoxin oxidoreductase; VOR, 2-ketoisovalerate:ferredoxin oxidoreductase; IOR, indolepyruvate: ferredoxin oxidoreductase; KGOR, 2-ketoglutarate:ferredoxin oxidoreductase; SCS, succinyl-CoA synthetase; ACS, acetyl-CoA synthetase; AOR, aldehyde:ferredoxin oxidoreductases; GLK, ADP-dependent glucokinase; PGI, phosphoglucose isomerase; GPI, glucose-6-phosphate isomerase; PFK, ADP-dependent phosphofructokinase; FBA, fructose-1,6-bisphosphate aldolase; TIM, triosephosphate isomerase; GAPOR, glyceraldehyde- 3-phosphate:ferredoxin oxidoreductase; GAPN, nonphosphorylating glyceraldehyde-3-phosphate dehydrogenase; PGM, phosphoglycerate mu- tase; PYK, pyruvate kinase; PGK, 3-phosphoglycerate kinase; FDH, formate dehydrogenase; Fd(ox), oxidized ferredoxin; Fd(red), reduced ferredoxin; NADPH, Nicotinamde adenine dinucleotide phosphate hydrogen; CoASH, coenzyme A.

In recent past Laachari et al. (Laachari et al., 2014) proposes a novel lipase enzyme from *B. pumilus* strain. The biggest advantages that are being confirmed with this lipase, is its thermostability and its survival even at high concentration of the detergent that are very common in oil-water emulsion from automobile industry. Moreover, the presence of Ca^{+2}, acts as a promoter to the lipolytic activity of the lipase that substantiates its industrial acceptability. Kamoun et al. (Kamoun et al., 2015) isolated lipase gene YLLIP2 and YLLIP8 from *Yarrowia lipolytica*, which is "generally recognized as safe (GRAS)".yeast used in several applications. Not much of the researches have been done so far on this lipase and have a very little information on the enzymatic action by lipase. However, both the clusters are acting in synergy to completely break down thee long chain triacyl glycerol (TAG) in to free fatty acid (Figure 2.17 (Athenstaedt and Daum, 2006)). The TAG molecule is being covered by the phospholipid layer, which can only be degraded by YLLIP2 followed by a less penetrant YLLIP8 attack on TGA releasing free fatty acid and glycerol.

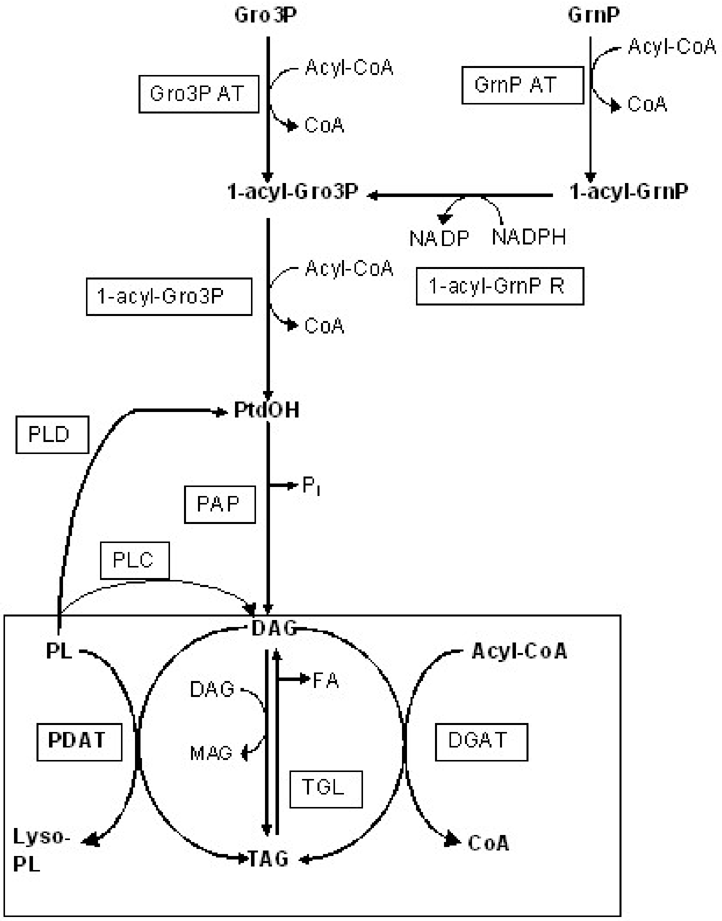


Figure 2.17 TAG metabolism via different pathways. In the upper part of the figure, enzymatic reactions leading to the synthesis of diacyl- glycerol (DAG) via the intermediate phosphatidic acid (PtdOH) are shown. The framed, lower part of the figure shows the different pos- sibilities for the final reactions yielding TAG. Enzymes:

1-acyl-GrnP R, 1-acyldihydroxyacetone phosphate reductase; 1-acyl-Gro3P AT, 1-acyl glycerol-3-phosphate acyltransferase; DGAT, diacylglycerol acyltransferase; GrnP AT, dihydroxyacetone phosphate acyltransferase; Gro3P AT, glycerol-3-phosphate acyltransferase; PAP, phosphatidate phosphatase; PDAT, phospholipid:diacylglycerol acyltransferase; PL C, phospholipase C; PL D, phospholipase D; TGL, triacylglycerol lipase. Substrates: 1-acyl-GrnP, 1-acyl dihydroxyacetone phosphate; 1-acyl-Gro3P, 1-acyl glycerol-3-phosphate; DAG: diacylglycerol; FA, fatty acid; GrnP, dihydroxyacetone phosphate; Gro3P, glycerol-3- phosphate; MAG, monoacylglycerol; PL, phospholipid; PtdOH, phosphatidic acid; TAG, triacylglycerol

(*Reprinted after permission from Cellular and molecular life sciences : CMLS, 63, 2006, 1355-1369*).

Recently, a lipase was isolated from a new strain called *Rhizomucor variabilis*, which can sustain at high alkaline pH and thermostable as well (Bancerz et al., 2015). After isolation of lipase, the stabilizer isolated from bacteria and fungi is called exopolysaccharides and are mixed with the lipase that enhances enzyme activity almost 21-31% increases. However, proper selection of biological strain to isolate industrially compatible lipase is a major challenge and several studies are still going on in order to have a better insight.

In 2016, Adibzadeh et al. (Adibzadeh et al., 2016) studied efficacy of electrostimulation on bacterial lipase activity as well as on the degradation of emulsified oil using a laboratory bioelectrochemical system of a stainless steel mesh as both anode and cathode. They reported that the maximum lipase activity of 38 Umol m/l reached at an applied current of 1 mA and a COD concentration of 1100 ppm. Beyond 1100ppm COD concentration the lipase activity gradually decreases. COD removal efficiency also went down with a reduced reaction time. Furthermore, the lipase activity increased when current was raised to 10 mA and the optimum pH reported for the lipase activity was 7. At the highest COD concentration, removal efficiency was about 90%.

2.8 Glycerol production during the treatment of oily wastewater and its application

One of the primary concerns of spent oil is the presence of heavy metals such as lead, halogenated compounds, poly aromatic hydrocarbons (PAH) that are considered as the hazardous materials. Therefore, treatment of such waste product will be one of the primary issues along with the inheritance of value added products from it (Lam et al., 2012; Russell and Chase, 2011; Sharaf et al., 2013) or recycling of it to the actual process (Hamawand et al., 2013; Ogbeide, 2010; Olugboji and Ogunwole, 2008). Triglycerides are cleaved to produce glycerol using lipase enzyme. In nature the glycerol is hygroscopic and absorbs water from the surroundings through an exothermic process. Because of this property it is used in adhesives to make the adhesive soft and restricts it from being dried out (Pagliaro and Rossi, 2008). Different biopharmaceutical industries are using glycerol as the fermentation aid to produce medicines. Cyclosporin A (CyA), a cyclic ring structured compound, primarily known as immunosuppressant, is produced through fermentation of wheat bran flour and coconut oil cake (1:1) at 70% initial moisture content using *T. inflatum* MTCC 557 strain. Supplementation with 1% glycerol along with the salts and ammonium sulfate produces almost 5454 ± 75 mg of CyA per kg of substrate (Survase et al., 2011). One of the primary advantages with glycerol is its abundance and economic availability. Paulo et al. (Paulo et al., 2009) had reviewed a process, where glycerol can be used as single carbon resources for uptake by the *Klebsiella*, *Clostridium*, *Citrobacter*, *Enterobacter* and *Lactobacillus* sp. The fermentative product from glycerol fermentation has been used widely in different sectors of industry. Citric acid is one of such compounds that are widely used in different food and beverage, medicinal industry etc. produced from submerged microbial fermentation on molasses using *Aspergillus niger*. However, economic as well as rich carbon sources are needed to produce citric acid more effectively in order to meet up the market demands. Imandi et al. (Imandi et al., 2007) used *Y. lipolytica* NCIM 3589 microorganism to produce citric acid, which has wide applications in food & beverages, cosmetics etc., from glycerol. Figure 2.18(a) (Amaral et al., 2009) shows the metabolic path for glycerol as a substrate used by *Y. lipolytica* producing acetate, butanol, ethanol, lactate etc., which are value added end products used in different sectors of industry. According to them the maximum concentration of 77.4 g/l citric acid was produced here, which is encouraging. Glycerol produced here is used as a cosubstrate for the biodegradation of polyaromatic hydrocarbons (PAH) present in large quantity in oil (Vasconcelos et al., 2013). According to (Vasconcelos et al., 2013), at a moderate concentration of glycerol the biodegradation of PAH was found almost 70% after 60 days. Production of biosurfactants are also enhanced by the uses of raw glycerol that will ultimately enhances the solubilisation of PAH and henceforth, more removal of these compounds from the contaminated environment. Saimmai et al. (Saimmai et al., 2012) had tested two bacteria called *Bacillus subtilis* TD4 and *Pseudomonas aeruginosa* SU7 that use glycerol as a single source of carbon to produce biosurfactants. Figure2.18(b) (Amaral et al., 2009) shows the pathway for the biosurfactant, where glycerol is used for the production of biosurfactant carbohydrate moiety as source of energy for microorganism growth.

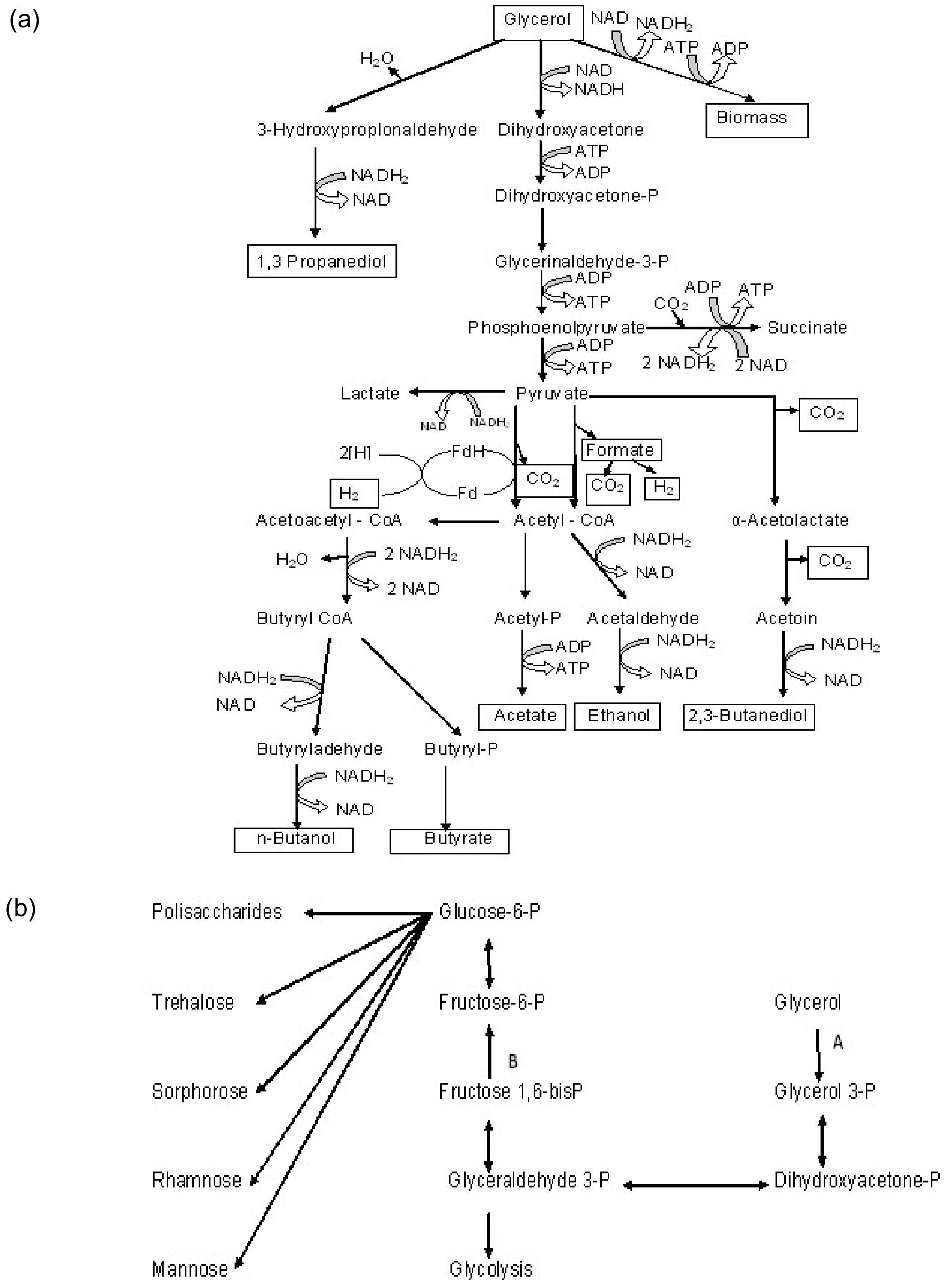


Figure 2.18 (a) Biochemical pathways of glycerol fermentation (*Reprinted after permission from Food and Biproducts Processing, 87, 2009, 179-186*). (b) Intermediary metabolism relating to biosurfactant precursor synthesis from glycerol substrates. Key enzymes are (A) glycerol kinase and (B) fructose-1,6-bisphosphatase

(*Reprinted after permission from Food and Biproducts Processing, 87, 2009, 179-186*).

2.9 Treatment of oil-water emulsion - Industrial overview

Nowadays, because of the increased sections of oil based industries that are continuously discarding substantial amount of oily wastewater, different technologies have been looked for in order to reduce the content of oil from water. In recent past, 2009, ABB had employed technology for the treatment of oily water that eliminates hydrocarbons from thewastewater almost seven times and suspended solid around 55 times more than the conventional treatment methods existing the present oil and gas industry ("http://www04.abb.com/global/seitp/seitp202.nsf/0/c6fc63be60956d52c12576a1004f716e/$file/oily+water+treatment+strategies.pdf," n.d.). In their process they had installed flocculation and floatation in tandem apart from the filtration unit, which projects low cost and footprint for the effluent treatment plant. In 2005, Ford Motor Company had installed a membrane bioreactor (MBR) followed by reverse osmosis system to treat 400,000 gallon per day of wastewater contaminated with organics, metals, surfactants, oil and grease, where 70% of the water is purified for reuse ("http://dynatecsystems.com/documents/Automotive%20Assembly%20Plant.pdf date accessed: 19.05.2015," n.d.). Merus Oil & Gas Pte. Ltd, a German based company had applied a fabrication at the upstream before and after the oil well, called "Merus Ring", in order to reduce almost 20% reduction in the possibility of emulsion formation and hereby reduce the operation cost almost 30% ("http://www.merusoilandgas.com/oil-water-emulsion Date accessed: 19.05.2015," n.d.). Malhis Engineering, another German company had used two steps floatation cell where 99% of the hydrocarbons are being removed from water after disruption of the emulsion along with the removal of 99% of the heavy metals ("http://www.malhis-engineering.com/test_e/Oil-Water-Emulsion.pdf Date accessed: 19.05.2015," n.d.). One of the commonest methods in demulsification techniques is heating up the emulsion in order to break the emulsion. However, this technique is vulnerable to fire hazard, especially with the light fuel fraction whose flash point/fire point is low. Therefore, treatment plants are interested in using the demulsifying agents that disrupt the emulsion. Dew Speciality Chemicals [P] Ltd., India is one of the renowned sectors in producing the emulsion breaker that breaks the emulsion in case of oil spill, tank cleaning etc. and has a widespread customers like Tata, Essar Oil and Gas, Jindal Steel and Power etc. ("http://www.dewindia.com/lnk0501.asp Date accessed: 19.05.2015," n.d.). Recently, GE Water had developed a new polyelectrolyte emulsion breaker, which they had used at the dissolved air floatation unit (Goldblatt et al., 2014). With this new polyelectrolyte, they had reduced the turbidity almost 50% attributing the efficiency of this new demulsifier in reducing the emulsion phase. Apart from such big names in speciality chemicals market, Rimpro India, Roemex Ltd., UK are the other leading oilfield chemicals and demulsifier manufacturers ("http://www.rimpro-india.com/articles1/importance-of-oilfield-chemicals-emulsion-breakers,-water-and-oil-line-corrosion-inhibitors.html Date accessed: 19.05.2015," n.d., "http://www.roemex.com/production/demulsifiers.htm Date accessed: 19.05.2015," n.d.). Moreover, apart from using chemicals, industries are nowadays more concerned to separate oil in order to balance ecology. Sweden JOWA AB, Sweden, who is continuously operating over 60 years in the field of fabricating environmental protection unit, had developed an emulsion breaking unit for bilge water treatment that separates 80% of water from emulsion ("http://www.jowa.se/page/products/equipment-for-treatment-of-oily-water/ebu---emulsion-breaking-unit Date accessed: 20.05.2015," n.d.). New Logic Research Inc., USA had applied Vibrating Shear Enhanced Processing (VSEP) technique, where they had fed almost 6000 GPD of untreated oily wastewater to VSEP UF module, to reduce the treated permeate to 600 GPD as a pretreatment scheme that reduces the treatment cost almost 10 times ("http://www.vsep.com/pdf/OilyWastewater.pdf Date accessed: 24.05.2015," n.d.). Indian Oil Corporation Ltd. (IOCL) Gujarat has the largest central effluent treatment plant, where they had a stage-wise treatment procedures operating subsequently ("http://www.plateseparator.com/indian-oil-corp-ltd-baroda-plantdetail.htm Date accessed: 25.05.2015," n.d.). In the first stage they had tilted plate interceptor followed by homogenisation tank for free oil. The first stage also comprises of the dissolved air flotation unit for emulsified oil, sulphides and suspended solids. In the second stage the effluent coming out of first stage is biologically treated followed by activated sludge process with enhanced aeration. In the third stage, the effluent is passed through pressure sand filter and activated carbon filters in tandem to remove residual BOD/COD and suspended solids. Finally, the effluent is disinfected using chlorination process. One of the major challenges in ONGC is the pollutants in the form of produced water in the form of either with emulsified oil or free oil. In view of that ONGC installed produced water conditioner (PWC) and sewage treatment plant (STP) at offshore platform, where through treatment using flash vessel, corrugated plate interceptor and sump caisson, they are separating oil to be wasted in produced water (Singh and Lal, 2010). Although several such processes are being developed in order to separate oil from its emulsified form, but still the actual low cost treatment process with 100% removal efficiency is yet to develop.

3 Chapter 3:

Effect of surface active compound sodium dodecyl benzene sulfonate (SDBS) on surface tension of synthetic produced water

Aims of the Chapter

In this chapter the effect of surface active component SDBS on dynamic surface tension of three different type of produced water has been studied with different brine pH.

3.1 Introduction

Produced water (PW) is a byproduct that comes along with oil and gas during the exploration from reservoirs. PW generally consists of different organic, inorganic compounds, oil grease along with naturally occurring radioactive compounds. Untreated discharge of PW stream to sea or ocean could be highly alarming for marine environment. To meet the environmental regulations, PW management is very crucial and reinjection of the PW into the crude well could be an option for enhanced oil recovery (EOR) (Amyx et al, 1960). Reinjection of PW is actually not very common. More common to discharge the water to sea, after removing emulsified oil (by hydro cyclones and gas flotation) so that environmental regulations are fulfilled, i.e. less than 30 ppm oil-in-water.

EOR is nothing but an adoption of different approaches to maximize the crude oil extraction from an oil field. In EOR, water or steam is used to heat the crude oil in the formation to reduce its viscosity or it’s resistance to flow and leads to an extended productive life of the field. As a result, the oil recovery goes upto 20 to 40 percent of the original oil of the operational place. Surfactant flooding is one of the acknowledged processes amongst distinct means. Fascination of surface active agent, surfactants are due to their good wettability alteration behavior, low adsorptive nature, compatibility with crude reservoir fluids and economic viability. Low surface tension of surfactants lowers the capillary forces of trapped oil in reservoir’s porous media and thus it ensure the maximized oil recovery from the well. Surfactants produces thermodynamically stable oil in water (o/w) emulsions. Lower surface tension reduces capillary forces and ensures better flow of mobilized oil within the crude well, and hence, increase the oil recovery (Gale and Sandvik 1973). Polymer and alkali are also added with the surfactants to ensure better EOR. Anionic surfactants are mostly used for sandstone reservoirs as its adsorption tendency is much lower on these reservoir rocks. Amphiphilic surfactants can be dissolved in aqueous as well as non-aqueous phases depending on their structure. At very low concentrations, surfactants remain as monomers in the solution and with increase in concentration they start aggregation or micelle formation. The concentration above which surfactants start forming micelles is called critical micelle concentration (CMC). So as the surfactant concentration increases beyond CMC more and more micelles form. Generally, PW is brine and consists of many electrolyte ions; univalent, divalent, multivalent. Presence of these ions have a huge impact on CMC (Chattopadhyay et al. 1996, Tichelkamp et al. 2014). It decreases the CMC value to great extent as electrolytes reduce the repulsion between the charged headgroups and thus navigate the micelles formation at a lower concentration (Kralchevsky et al. 1999, Fuguet et al. 2005, Xu et al. 2009). Surfactant SDBS can easily used for EOR processes along with polymers as well as co-surfactant to maximize the chances of oil recovery, which increase the the concern of interest of the study of interfacial phenomena of SDBS.

When surfactants are used in EOR, some of the surfactants will become back-produced together with oil and water. These surfactants could be adsorbed on oil drops, reduce interfacial tension and promote breakup of the oil drops as well as they could also get adsorbed on the solids and stabilize them towards separation, i.e. water quality becomes poorer. Surfactants could be get adsorbed at the water-gas interfaces (bubbles) during gas flotation. In 2013 Eftekhardadkhah et. al. shown that adsorption of crude oil components on gas bubbles reduce the flotation efficiency. The idea of the present work was to look at the effect of the surfactant on the adsorption process and to find out if there is any struggle between surfactant and dissolved oil components to get adsorbed faster. It might be also possible to have some insight of the effect the surfactant adsorption on flotation efficiency of the bubbles.

In this work the effect of surfactant SDBS has been has been studied at air water interface with three PWs consisting of three different crude oils at different pH values. SDBS concentration has been also varied below and above CMC to observe the variation in dynamic surface tension. Dynamic surface tension is the change in surface tension value before equilibrium is reached.

3.2 Theory

Diffusion coefficient calculation:

The Ward and Tordai equation take in accounts of the diffusion of monomers from the bulk to the interface, as well as the back diffusion into the bulk due to the overcrowded interface. At the start of the process monomers from get adsorbed directly, the assumption is that every molecule arriving at the interface is likely to arrive at an vacant site. However, as the subsurface becomes fuller, there is an increased chances that a monomer will arrive at an already occupied site. Back diffusion from the surface to the bulk must be considered then. If the subsurface concentration is known, then the Fick's diffusion equations could be involved for diffusion of molecules from the surface to the bulk. The classic Ward and Tordai equation is given below in its usual quoted from:

$$\Gamma(t) = 2C_0\sqrt{\frac{Dt}{\pi}} - 2\sqrt{\frac{D}{\pi}}\int_0^{\sqrt{t}} C_s d(\sqrt{t-\tau}) \qquad 3.1$$

where, $\Gamma(t)$= dynamic surface adsorption

C_0= bulk surfactant concentration

D= diffusion coefficient of the monomer

C_s= surfactant concentration in the subsurface layer

t= time

τ=integration variable

At gas-liquid interface when the surfactant concentration is low and time interval is short (<100ms), diffusion of molecules is the slowest and the diffusion coefficient (D) influences the surfactant behavior. In 1981, Joos and Rillaerts developed an asymptotic solution of the Ward-Tordai relating surface tension and D for diffusion controlled region with short time approximation ($t \to 0$);

$$\gamma_t = \gamma_0 - 2RTC\left(\frac{D't}{\pi}\right)^{0.5} \qquad 3.2$$

Where, γ_t=surface tension at surface age t,

γ_0= surface tension of the pure solvent

R= universal gas constant

T=temperature

C=additive concentration

D'=diffusion coefficient for short time and small concentrations

For long time interval (>1s) when $t \to \infty$ and high concentration, this diffusion controlled regime shifts to adsorption controlled and the asymptotic solution of Ward-Tordai equation (Ward and Tordai 1946) becomes;

$$\Gamma(t) = \sqrt{\frac{D}{\pi}}\left[2C_0\sqrt{t} - \int_0^t \frac{\phi(\tau)}{\sqrt{(1-\tau)}}d\tau\right] \qquad 3.3$$

where,

$\phi(t)$=concentration of surfactant at subsurface layer

The ratio between the surface area of a bubble and the volume surrounding the bubble decreases as the curvature of the interface increases, at spherical interphases. This lead to a faster diffusion toward the interface. This also reduce the time for molecular diffusion. It has been exhibited that the bubble radius at which curvature effects become prominent must be calculated for individual surfactant systems (Alvarez et al., 2010a, 2010b; Jin et al., 2004; Nguyen et al., 2006).

Liu and Messow modified the Ward-Tordai equation by solving the diffusion equation for a spherical interphase through Laplace transform (Liu et al. 2004). It provides an apt interpretation of dynamic surface adsorption for; (i) short time adsorption with no back diffusion, (ii) adsorption with back diffusion and (iii) long time adsorption. With short time approximation at a spherical interface dynamic surface adsorption is shown as;

$$\mathrm{r}(t) = \frac{DC_0}{r_0} + 2C_0\sqrt{\frac{Dt}{\pi}} \qquad 3.\ 4$$

where, r_0=capillary radius

The dynamic surface adsorption can be expressed in terms of the dynamic surface tension by applying an appropriate adsorption isotherm (often the Langmuir isotherm) in Gibbs equation and combining the resulting equation with equation 3.4. Gibbs equation relates the amount of surfactant adsorbed at the interface at equilibrium r_{eq} to the surfactant concentration and surface tension at equilibrium (γ_{eq}), as shown in the following equation:

$$\mathrm{r}_{eq} = -\frac{C_0}{nRT}\frac{d\gamma_{eq}}{dC_0} \qquad 3.\ 5$$

And using n =1 here the equation for the short-time adsorption is then become (Liu et al., 2004);

$$\gamma(t) = \gamma_0 - \frac{RTD}{r_0}C_0\left(\sqrt{t} + \frac{r_0}{\sqrt{\pi D}}\right)^2 + \frac{RTr_0}{\pi}C_0 \qquad 3.6$$

where, $\gamma(t)$= dynamic surface tension

γ_0= the equilibrium surface tension of the pure solvent

In order to calculate the diffusion coefficient, Equation 3. 5 can be rearranged as follows;

$$F = \sqrt{\frac{r_0(\gamma_0-\gamma(t))}{RTC_0} + \frac{r_0^2}{\pi}} \qquad 3.7$$

Equation 3.7 depicts that for a diffusion controlled adsorption process, there should be a linear relationship between F and square root of time and has been used to calculate the diffusion coefficients for the present study (Eftekhardadkhah et al. 2013). Consequently, it was assumed that the effect of interfacial curvature was small enough to be neglected in our experiments like Nguyen et al. (2006).

3.3 Materials and methods

3.3.1 Surfactant Selection:

Sodium dodecyl benzene sulfonate (SDBS) (Sigma Aldrich) has been used for the study and the structure of it is shown in fig 3.1. The CMC of SDBS in the synthetic brine has been measured to be 475ppm. The CMC has been determined by plotting the graph of surface tension versus log of the surfactant concentration. Sudden change of the slope confirms the CMC.

For the study, five different concentrations have been used -100ppm, 200ppm, 475ppm, 700ppm and 800ppm.

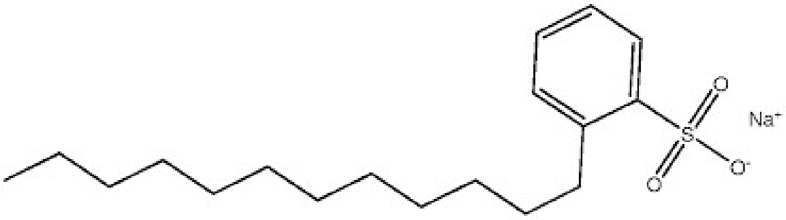


Figure 3.1 Chemical Structure of SDBS

3.3.2 Preparation of Brine:

Synthetic brine has been prepared by dissolving analytical grade of NaCl (99.5%, Merck, Germany), Na_2SO_4 (99%, Merck, Germany), $NaHCO_3$ (99.5%, Merck, Germany), $MgCl_2 \cdot 6H_2O$ (99%, Merck, Germany), and $CaCl_2 \cdot 2H_2O$ (99.5%, Merck, Germany) in water provided by a Millipore ultrapure water system. Brine composition is enlisted in Table 3.1 For carbonate precipitation prevention, the brine has been stored in a refrigerator and brought to the experimental temperature just before use.

Table 3.1 Composition of Synthetic Brine.

Ion	Concentration in ppm
Na^+	707.86
Ca^{2+}	66.06
Mg^{2+}	1818
Cl^-	1856.20
SO_4^{2-}	1
HCO_3^-	4.96

3.3.3 Synthetic Produced Water preparation:

The water soluble hydrocarbons of the crude oils (A, B and C) has been mixed into the aqueous phase by mixing 50% oil and 50% synthetic brine in a shaker (HS 501 digital IKA) at a mixing speed of 250 rpm for 24 hr at room temperature. After that the oil and water phases have been separated by centrifugation and finally the resulting aqueous phase was considered to be synthetic produced water samples. The samples were named PW-A, PW-B and PW-C, in accordance with the naming of the crude oils. In 2013 Eftekhardadkhah et al. have reported the physicochemical characteristics of the crude oils and those are provided in Table 3.2. Original pH of the synthetic brine is 6.2±0.15. and it have been varied to 2±0.15 and 11±0.15.

Table 3.2 Physicochemical characteristics of crude oils.

Crude Oils	*Density** *(g/cm³)*	*Viscosity** *(cP)*	*Saturates (wt %)*	*Aromatics (wt %)*	*Resins (wt %)*	*Asphaltenes (wt %)*	*TAN***	*TBN***	*C (wt %)*
A	0.81	2.71	79.66	18.29	1.9	0.12	0.20	0.59	83.26
B	0.92	78.44	44.35	38.76	16.39	0.49	2.28	4.37	84.24
C	0.94	487.00	25.61	49.55	10.91	13.93	0.57	1.34	80.94

*Density and viscosity measured at 20ºC

**TAN (total acid number) and TBN (total base number) are given in mg of KOH/g of oil

3.3.4. Dynamic Surface Tension Measurements:

Dynamic surface tensions have been measured by a maximum bubble pressure tensiometer (Krűss BP100, Hamburg, Germany). In bubble pressure tensiometer a hydrophobized glass capillary connected is to a pressure sensor and immersed into a 30 ml sample. From capillary air bubbles produced with surface ages varying from 10 ms to 100 s. Before each experimental reading the surface tension of ultrapure water has been confirmed to be 71.99 ± 0.11 mN/m. All measurements have been carried out at room temperature.

3.4 Result and discussion

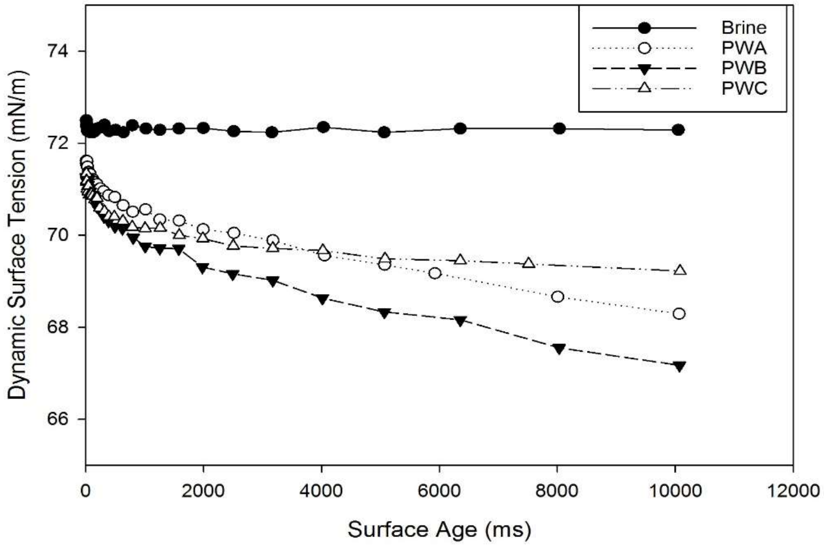
3.4.1 Dynamic surface tension:

Initial surface tension of the synthetic brine was 72.5±0.11 and of ultrapure water was 71.99±0.11. Dynamic surface tension values of the PWs and brine at different brine pHs are given in Figure 3.2a-c with respect to surface age. Surface age the time period from initiating of a surface or interface (here formation of the bubble at the capillary) to the time of the measurement of surface tension value. Higher surface tension of water with addition of salt happens due to surface excess of one or different type of ions (anion or cation) in general or sometimes both of the ions at air-water interface (Manciu and Ruckenstein 2012). In PWs, when both salts and organic molecules are present in the water phase, the salts properties affect the surface tension. Salting out behavior of salts in aqueous solution promote surface adsorption of organic molecules and lowers the surface tension value. Salting out initiates more organic molecules to more closely packed at the interface and hence the intermolecular interaction between surface and organic molecules become stronger in the presence of salt. The presence of salt in the water phase increases the surface tension of water, but organic adsorbates reduce the surface tension of water. This means that in a solution containing both inorganic and organic solutes the surface tension depends on the composition of the mixture.

Initially the surface tensions for all the three PWs are almost same like the surface tension value of pure water. In absence of absorbed compounds initially the air-liquid interface remains very clear when bubble formation just started. But just after that, the surface tension value evenly tends to a lower value approaching the equilibrium with time. It proceeds from short time interval to the long time adsorption. At long time interval the difference in the surface tension between the PWs are more prominent though PWA and PWC shows very similar. Among the studied three PWs PWC reaches the equilibrium first.

In case of pH lower value of surface tension approaching equilibrium increases a little with increase in brine pH from 2 to 6.2. It happens due to the ionization of components at the interface increase the interfacial activities. But when the brine pH is 11 the surface tension decreases. At this point fatty acids reacts with alkali at the interface while leading to much more interfacially pronounced ionized species and these higher species concentration reduces the surface tension value (Hutin et al. 2014). Also at high pH acidic compounds govern the surface tension, and in presence of Na^+ ions the dissociation of acids at the surface is promoted which lowers the surface tension.

3.2. (a)



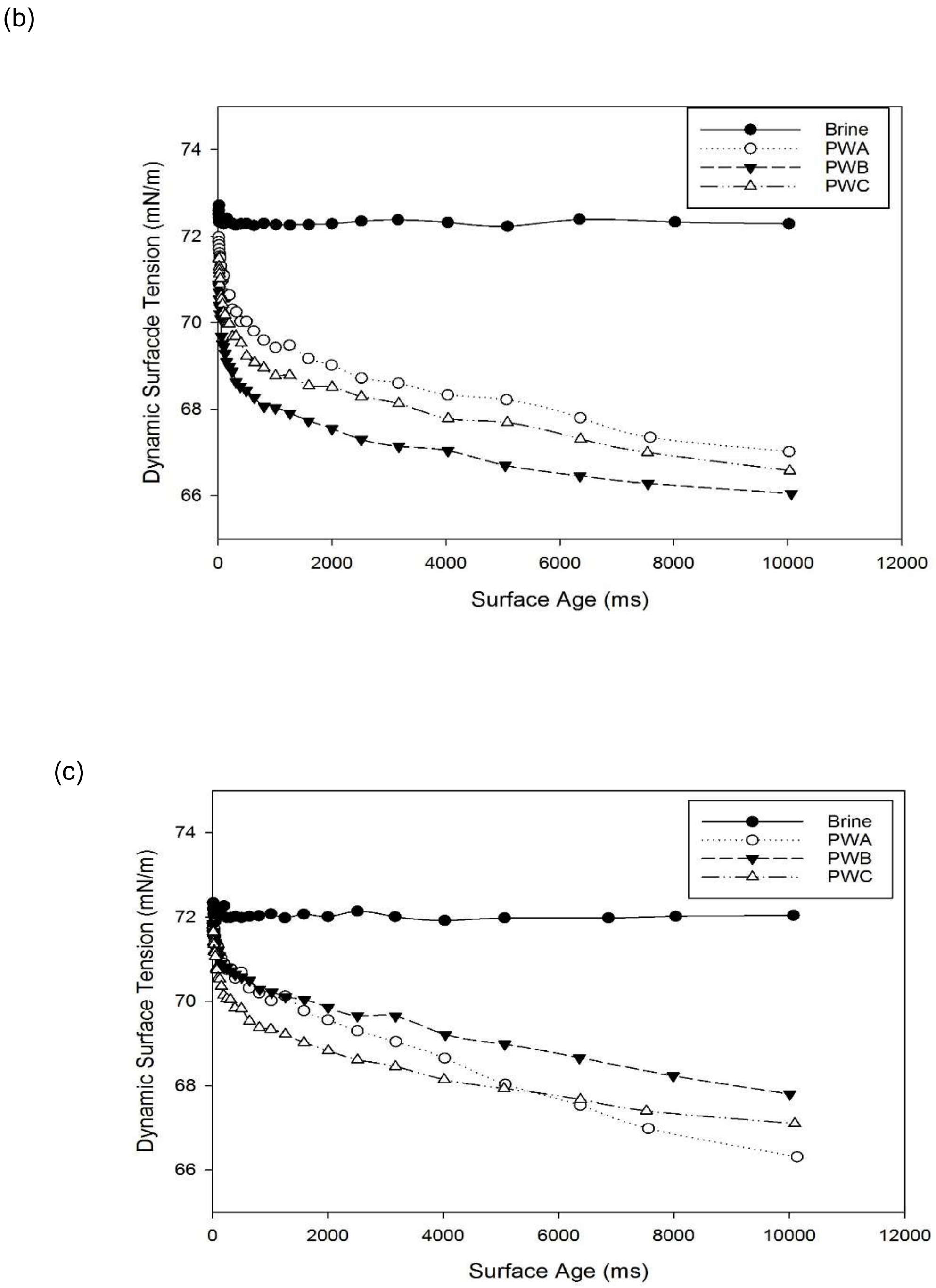
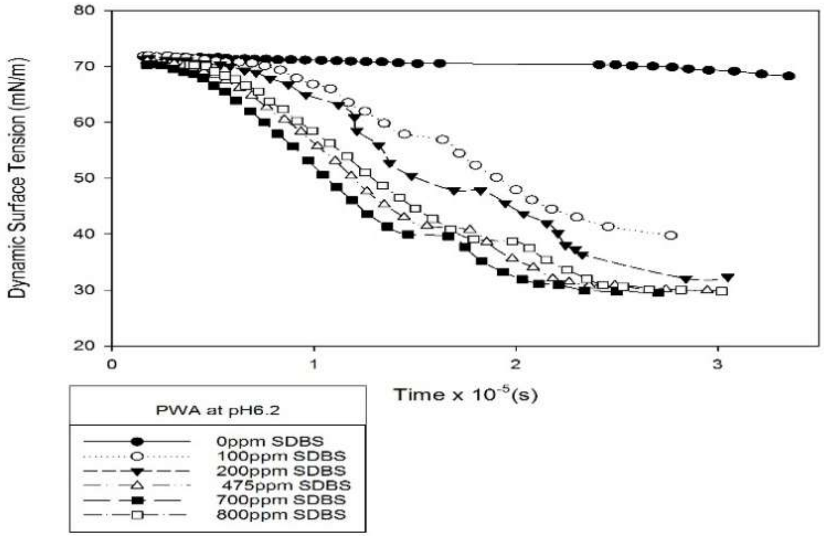


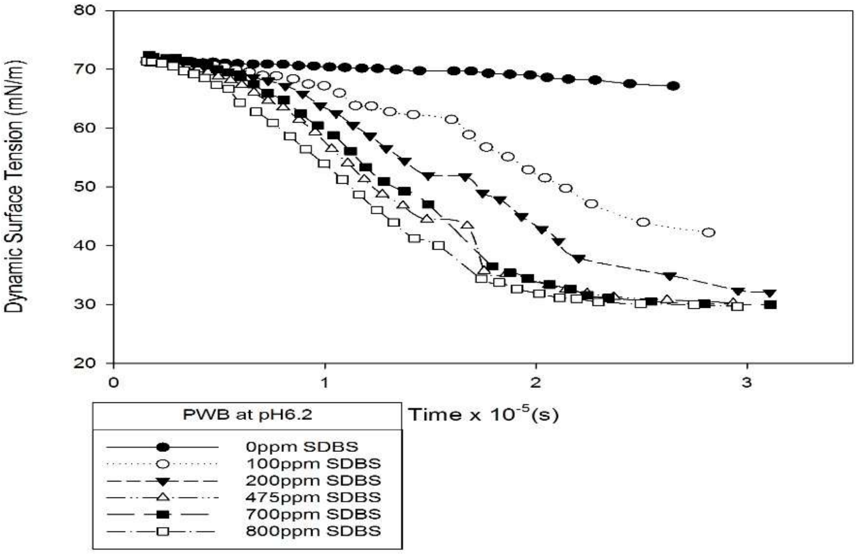
Figure 3.2 Dynamic surface tension of PWA, PWB and PWC and brine at different brine pH (a) pH 6.2, (b) pH 2 and (c) pH 11.

3.4.2 Effect of SDBS:

3.3. (a)



(b)



(c)

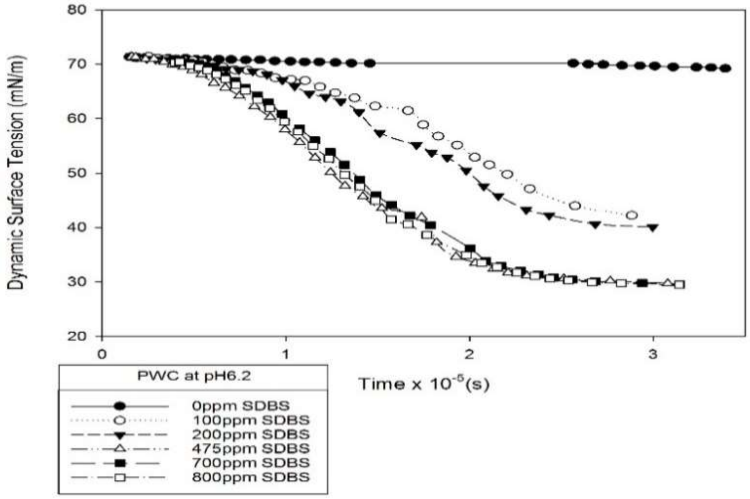
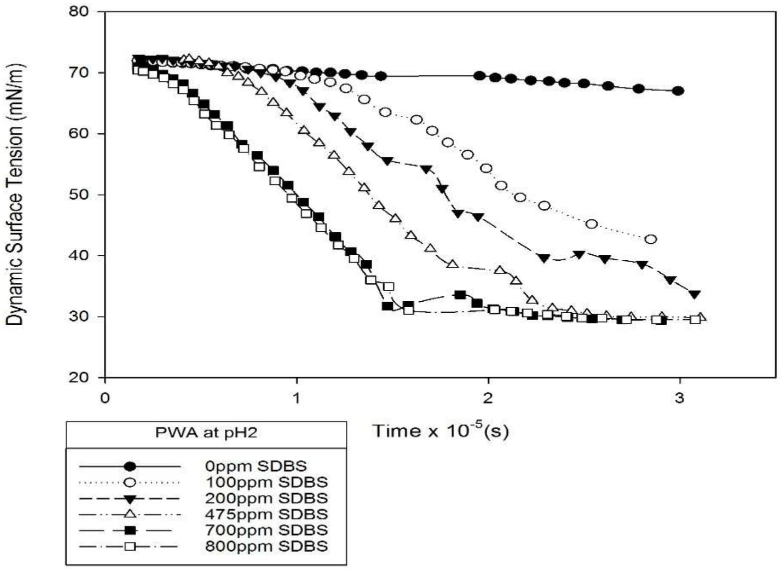


Figure 3.3 Dynamic surface tension of (a) PWA, (b) PWB and (c) PWC at different SDBS concentration at brine pH6.2.

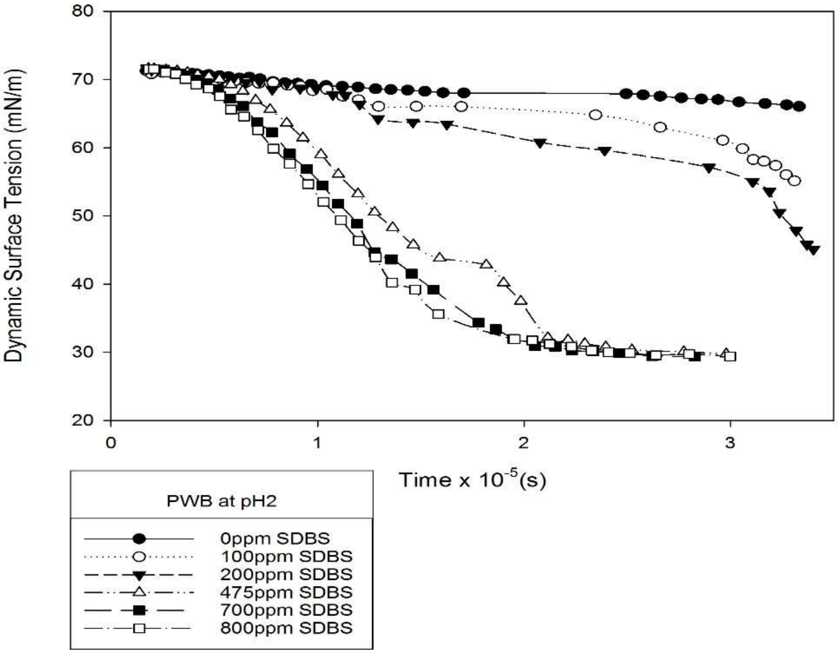
In Figure 3.3(a-c) dynamic surface tension of three PWs has been shown with different SDBS concentration. For each PW the trend of the dynamic surface tension seems to be similar and added surface active compound SDBS decreases the equilibrium value to great extent. The surface composition is same as the bulk composition at the instant when a new air-liquid (air-PW) interface is formed or the very first bubble initiates. These lead to close to the average surface tension value of the surface tension values of the pure components. Equilibrium is reached when the surface gets occupied entirely by surface active compound molecules. When the concentration of the surfactant further increased it finally reaches to CMC and micelles form. At equilibrium, the component with the lower surface tension preferentially adsorbed at the surface and create an excess of that component with the lower surface tension over there. Finally, at long time interval these reduce the surface tension value of the solution.

From Figure 3.3 it is evident that the drop in surface tension is huge with increased SDBS concentration upto the CMC. Beyond CMC, the equilibrium surface tension remains almost same with increased SDBS concentration. As SDBS concentration increases in bulk with time interval it increases at the air-PW interphase as well and leads to a lower surface tension value with higher concentration of surface active compound at interface. After CMC micelles formation starts and further increase in SDBS concentration does not promote increase in concentration of SDBS at interface; but it only agglomerates in more micelles and hence does not affect the surface tension value.

3.4 (a)


Dynamic Surface Tension (mN/m)
80
70
60
50
40
30
20
0
1
2
3
Time x 10^{-5}(s)
PWA at pH2
0ppm SDBS
100ppm SDBS
200ppm SDBS
475ppm SDBS
700ppm SDBS
800ppm SDBS

(b)


Dynamic Surface Tension (mN/m)
80
70
60
50
40
30
20
0
1
2
3
Time x 10^{-5}(s)
PWB at pH2
0ppm SDBS
100ppm SDBS
200ppm SDBS
475ppm SDBS
700ppm SDBS
800ppm SDBS

(c)

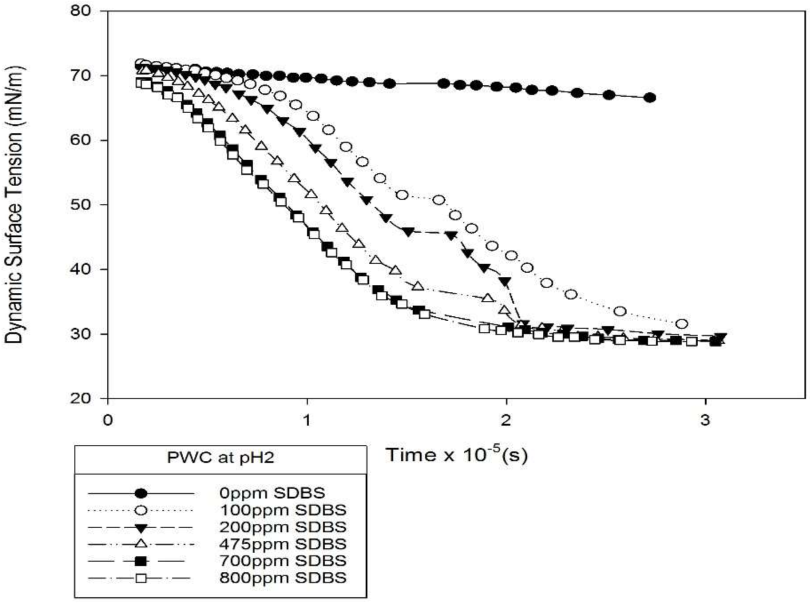
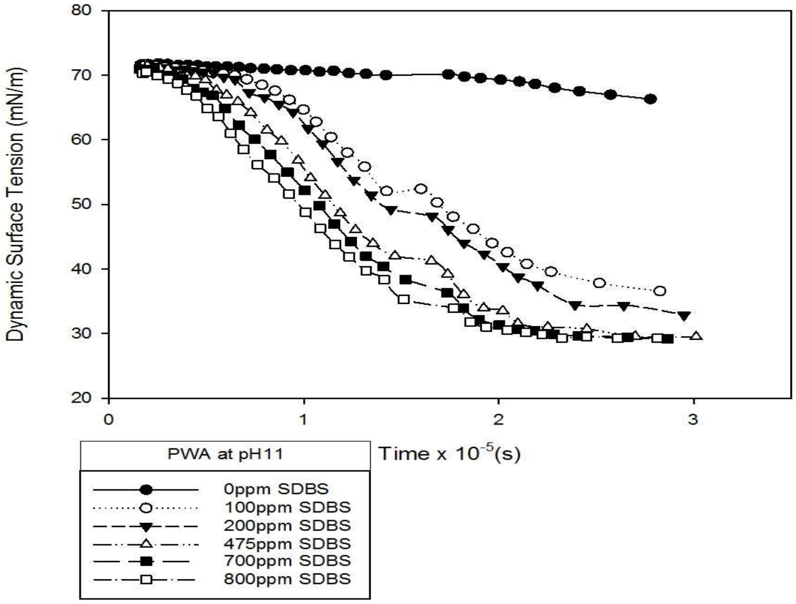
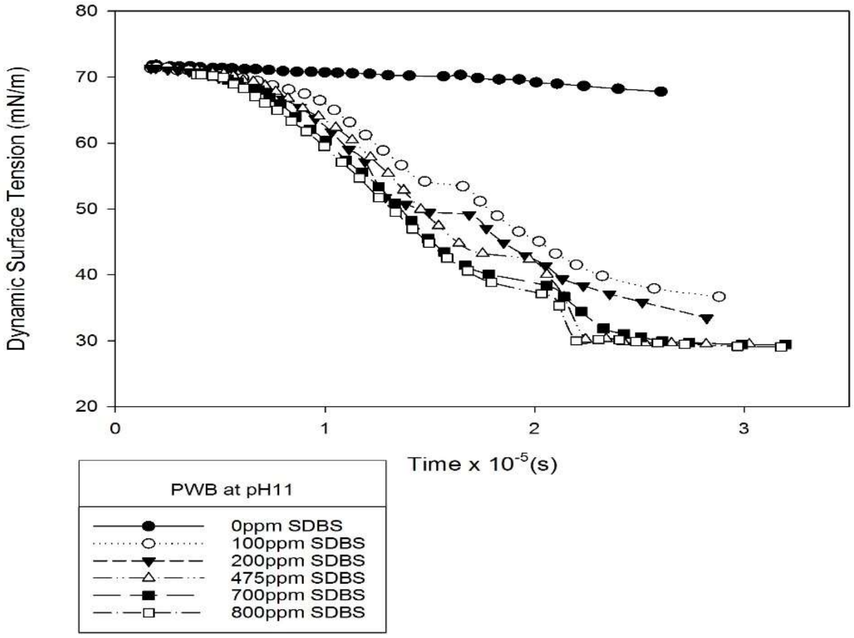


Figure 3.4 Dynamic surface tension of (a) PWA, (b) PWB and (c) PWC at different SDBS concentration at brine pH2.

3.5 (a)



(b)



(c)

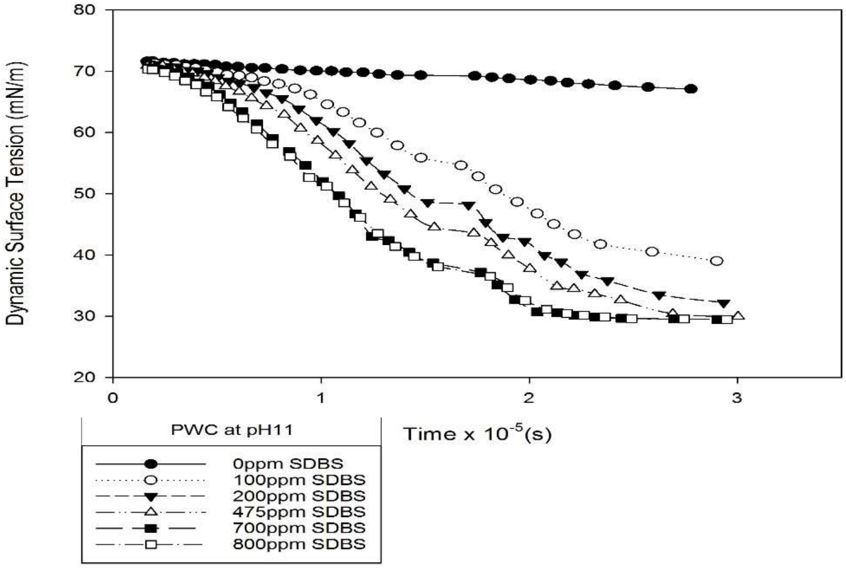


Figure 3.5 Dynamic surface tension of (a) PWA, (b) PWB and (c) PWC at different SDBS concentration at brine pH11.

3.4.3 Diffusion coefficient study:

From Diffusion co-efficient the time range can be estimated where adsorption of solute onto the newly created bubble surface is occurring solely by diffusion, not through adsorption or surface re-orientation. Equation 3.7 states that when there is a linear relationship between F and the square root of time, within the short time interval, adsorption is diffusion controlled at the interface. And here Figure 3.6 shows the linear relationships for three PW samples at a time range of 10 to 100 ms. This concludes that at air bubble; the adsorption mechanism of hydrocarbons has been totally controlled by diffusion during short time interval.

The slope of the regression lines of Figure 3.6 is $\sqrt{D}$ and the range of R^2 values is in between 0.96 and 0.99. In this figure the linear relationship has been plotted only for 100ppm SDBS concentration of each PW of brine pH6.2. Other regression lines have been also plotted in same way.

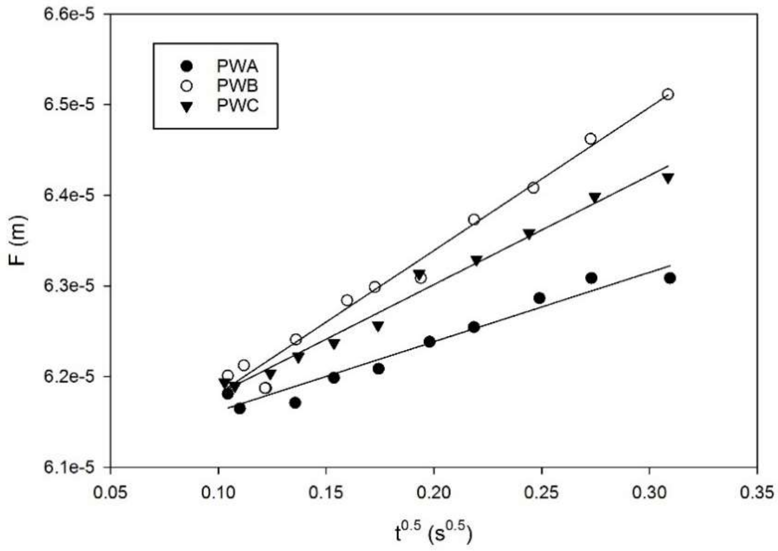


Figure 3.6 Relation between F and $\sqrt{t}$ in the short-time limit (10–100 ms) for adsorption of dissolved hydrocarbons in PWA, PWB and PWC.

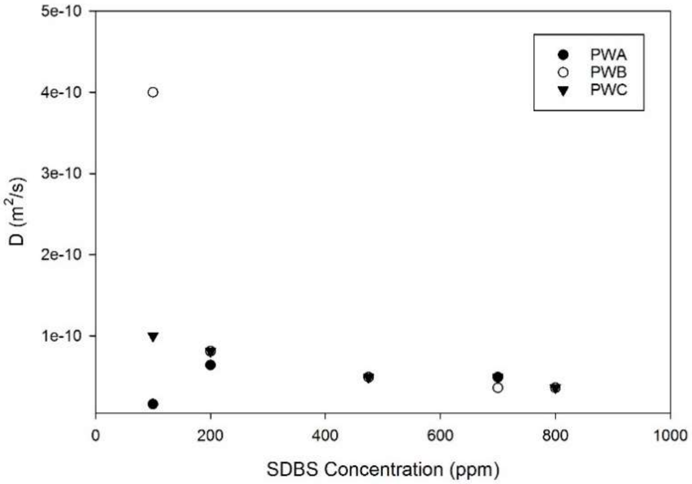


Figure 3.7 Change in D in different SDBS concentration for PWA, PWB and PWC.

Change in D with varying SDBS concentration at the bulk phase of the PWs at Brine pH 6.2 has been shown in Figure 3.7. Here initially D values increases with increased SDBS concentration in bulk follows the trend predicted by Phan et al. in 2005. Before kickoff of micelles formation with increased concentration surface active compounds travelled more and more towards the interface and value of D goes higher. After CMC the increased concentration does not affect D that much and it remains almost same.

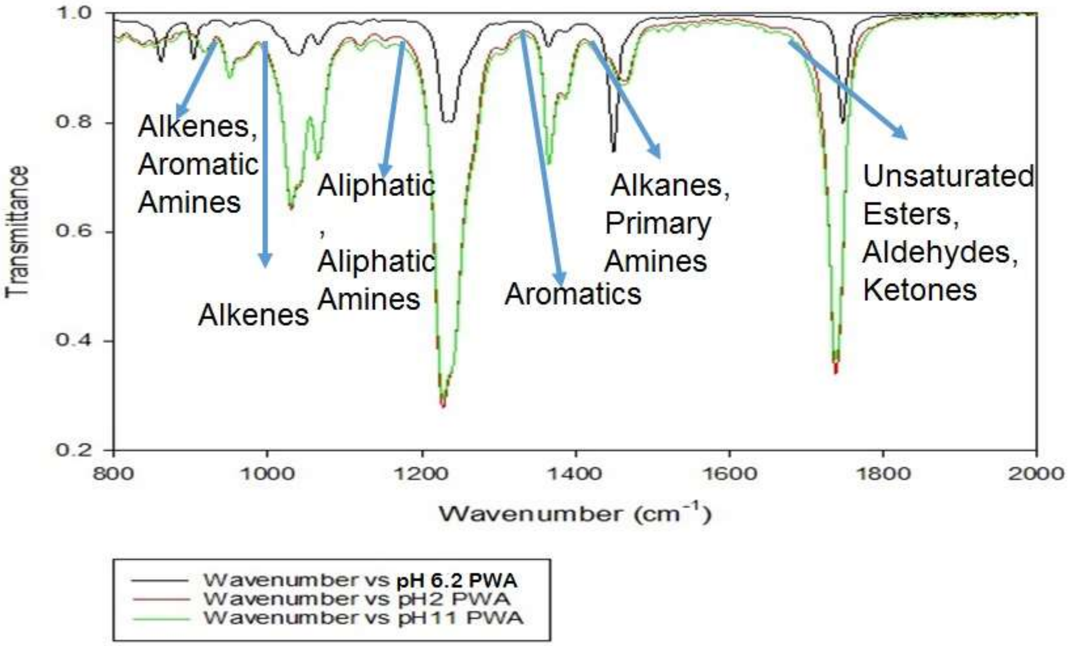


Figure 3.8 FTIR Spectra of PWA at different pH.

FTIR spectra in Figure 3.8 shows presence of different compounds in PWA at different pH. PWB and PWC also show a similar trend.

3.5 Conclusion

Initially, the air-liquid interface remains very clear when bubble is just forming. Then with prolonged time, the surface tension approaches a lower value. It makes the initial surface tension value almost same as the pure water. The process proceeds from short time interval diffusion controlled regime to the long time adsorption controlled process. PWA and PWC shows similar trends. Initial increase in brine pH hike the lowest value of surface tension for PWs. After that higher pH causes low value of surface tension.

4 Chapter 4 :

Emulsified oily-waste water: An approach to the pretreatment with inorganic salts and treatment using two indigenous membrane modules

Aims of the Chapter

Present work proposes an application of high sheared membrane modules in separating the oil and water from its emulsified form. The oil-in-water (o/w) emulsion after being treated with different electrolytes and the results from the treated feed to membrane were compared with the untreated feed as well. Two high sheared modules, called turbine flow membrane module (TFMM) and radial flow membrane module (RFMM) were compared to understand the superlative performance in removing the oil from its o/w emulsion both treated and untreated form at different temperatures as well as pressures.

4.1 Introduction

Oil is nowadays one of the acrimonious components of wastewater that is continuously polluting the water because of increased urbanisation and industrial revolution in all over the world. Furthermore, the issues with the oily wastewater manifolds, once the oil is getting mixed with the water to form a homogeneous mixture in presence of emulsifiers, called emulsion. Mainly two types of emulsion can be formed in case with the oily wastewater - one is thermodynamically stable microemulsion consisting of smaller oil droplets (radii in the range 0-100 nm) and another is kinetically stable macroemulsion having larger oil droplets (0.05-100µm) (Fletcher and Horsup, 1992, Perrechil and Chunha, 2010). Several industries produce oil contaminated emulsified wastewaters include heavy metal industries, paint industries, textile industries, refineries, petrochemical industries, food industries, chemical manufacturing industries, allied industries and many others(Zhong et al., 2011). The formation of emulsion gets increased due to the presence of contaminants like silt, metal particles, emulsifiers, cleaners, soaps, solvents, and other residues. Therefore, without proper measures if this wastewater is discharged to urban sewerage system, it ultimately conveys the water to some river or sea manifesting imbalance in aquatic flora and fauna. Moreover, the drainage of such oily wastewater populates hydrocarbons in the aquatic environment and perturbs the aquatic life by attenuating the entrance of sunlight through the surface of the water. Phenols, polyaromatic hydrocarbons (PAH) and many other components of oily wastewater that ultimately accumulated in our every day's water resources, are mutagenic as well as carcinogenic for human being (Alade et al., 2011). Hence, the discharge of such hazardous contaminants in oily wastewater needs to be prevented and taken care off.

Treatment of the oily wastewaters according to the environmental discharged standards (oil content less than 5 ppm) requires various oil treatment systems(Jegatheesan et al., 2009, Salahi et al., 2010). So far different strategies have been adopted in the treatment of oily wastewater. There are different conventional technologies adopted by several water treatment fraternities attributing to the separation of oil from oil-water emulsion. Some of these schemes are gravity separation, API oil-water separator followed by skimming, dissolved air flotation, de-emulsion coagulation and flocculation(Abbasi et al., 2010; Cheryan and Rajagopalan, 1998; Srijaroonrat et al., 1999). Gravity separation process followed by skimming is fairly effective to get rid of free oil from wastewater. API unit has been widely accepted as an effective, low cost, primary treatment step. However, these methods are not effective for removing smaller oil droplets and emulsions attributing to thermodynamically stable microemulsion. However, the oil that adheres to the surface of solid particles in contaminated oily wastewater could be effectively removed by sedimentation. Dissolved air flotation (DAF), the mostly used treatment unit for oil-water emulsion, uses air to increase the buoyancy of smaller oil droplets through continuous bubbling of air from the bottom of the tank in order to enhance the rate of oil-water separation. The influent emulsified oil of DAF is getting detached from its mixture with water, called demulsification, either chemically, or thermally, or by both together. DAF units typically employ chemicals to promote coagulation and to increase flock size to facilitate separation(Salahi et al., 2010; Cheryan and Rajagopalan, 1998)apart from relying solely on the buoyancy force. All these conventional systems based on physical and chemical principles, indeed, cannot give an absolute guarantee in effective separation attributing to an improved effluent quality. However, high consumption of chemicals in coagulation makes these processes costly and even sometimes the unutilised chemicals are also found in the final wastewaters as contaminant. Hence, the eradication of such chemicals from water becomes one of the primary challenges. Moreover, the time dependent coagulation process might attain a partial demulsification, which ultimately fails to reduce the oil contaminant from the water.

In order to mitigate such limitation with the primary treatment techniques for oily wastewater treatment, Hockenberry and Lieser(HocKenberry and Leiser, 1977) had applied membrane separation technique along with the conventional heat pretreatment to demulsify the emulsion and separating oil from water. They had applied ultrafiltration followed by the reverse osmosis process, where the separation of surfactants from oil-water interface attributes to the demulsification process. It was observed that the reverse osmosis process ultimately results almost clean oil. In the subsequent year, Salahi et al. adopted similar approach, where the oily wastewater was treated using combined ultrafiltration and reverse osmosis process manifesting almost 95-100% of oil and grease content. However, one of the limitations with any membrane separation process is membrane fouling, sometimes which is irreversible and makes the process cost intensive. Especially, with the oily wastewater the primary issue is the adsorption of oil over the membrane surface that eventually reduces the performance of the membrane along with its longevity (Panpanit and Visvanathan, 2001). However, in presence of surfactant in case of emulsion the scenario is something different. According to Panpanit and Visvanathan, with an increase of bentonite clay concentration in oil in water emulsion (o/w) the resistance over the membrane initially decreases and goes through a minimum. In a recent study, same fact was supported by Kiss et al.(László et al., 2013), where they had seen that the increased concentration of emulsifier reduces the fouling of the membrane due to oil. Moreover, the performance of the process depends on the nature of the emulsion and the materials for the membrane selected. In 2006, Shu et al.(Shu et al., 2006) had fabricated a ceramic supported polyamide/polyvinyl alcohol thin film composite membrane for the treatment of o/w microemulsion. According to them, with this fabricated membrane the fouling of the membrane can be mitigated enormously with almost 99% oil rejection even with such stable microemulsion. However, the specialised form of membrane fabrication sometimes increases the overhead cost of the process attributing to an urge for the comparatively low cost simple approach in order to combat with the fouling. One of the commonest techniques in reducing the fouling of the membrane is an increase in the shear rate over the membrane surface that ultimately reduces the fouling after sweeping away the adsorbed oil from the surface. Li et al.(Li et al., 2009) had studied the recovery of oil from o/w emulsion using rotary disk filtration system. According to their study, the rotation of a smooth membrane or the vane attached membrane removes the possibility of coalescence of oil droplets and resists the formation of bigger oil droplets. Therefore, the formation of secondary layer over the surface of the membrane could be eradicated completely by the shear enhanced membrane, especially with the vane attachment, attributing to better oil recovery. However, one of the key considerations with the shear enhanced membrane is the energy consideration that eventually increases the accumulated cost associated with the process. However, energy expenses involve the cost to rotate the membrane attributing to additional accessories' cost. In 2014, Putatunda et al.(Putatunda et al., 2014) had fabricated a high sheared membrane module, where the vanes can be rotated using the introduced feed flow energy and thus reduces the additional expenses associated with the adjoining of other machineries in order to increase shear rate over the surface.

In the present study the oily emulsified wastewater, synthesised using spent oil collected from local automobile garages amd water, has been primarily treated with four different salts, alum, sodium chloride, sodium sulphate and magnesium chloride to demulsify the oil-water emulsion. Subsequently the emulsified wastewater as well as the sodium sulphate treated wastewater, which gives better result compared to other electrolytes, has been sent to two indigenous high sheared membrane module, namely radial flow membrane module (RFMM) and turbine flow membrane module (TFMM), equipped with 25 kDa polysulfone (PSf) ultrafiltration (UF) membrane for better removal of oil with higher throughput.

4.2 Material and methods

4.2.1 Materials:

0.025 m^3 (2.5 L) of emulsified wastewater as feedstock solution was prepared after mixing spent oil with water in the ratio of 1:200) aided by an emulsifier, home detergent (1% w/v). Detergent was procured from local grocery shop, and spent mobil has been collected from local gas stations with car wash facility. Ultrapure deionised water was collected from the Arium RO unit followed by Arium 611DI ultrapure water system (Sartorius, Göttingen, Germany). Sodium chloride (NaCl) (CAS No. 7647-14-5), sodium sulphate (Na_2SO_4) (CAS No. 7757-82-65), magneseum chloride ($MgCl_2$) (CAS No. 7791-18-6) and alum (CAS No.

7784-24-9) used as electrolytes in order to destabilize the emulsion had been procured from Merck (Mumbai, India). Sodium hypochlorite (NaOCl) (CAS No. 7681-52-9), sodium hydroxide (NaOH) (CAS No. 1310-73-2) and ethanol (CAS No. 64-17-5) were also procured from Merck (Mumbai, India).

4.2.2 Destabilization of emulsion and the subsequent membrane operation:

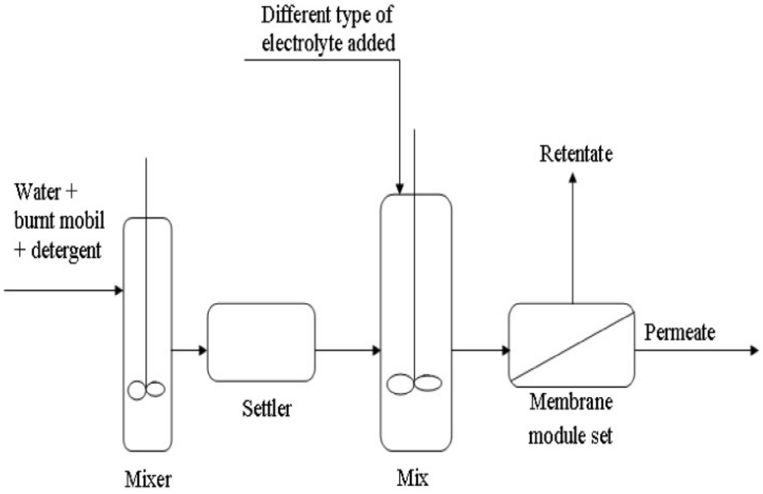


Figure 4.1 Flow diagram for the treatment of oily wastewater.

2% (w/v), 5% (w/v), 10% (w/v) and 15% (w/v) solutions for each of the electrolytes were added to the emulsified solution at ambient temperature of around 30-35°C and the solution was stirred at 100 rpm stirrer speed for 1.5 hrs. Figure 4.1. shows the schematic representation of the process for emulsified oily wastewater treatment. The demulsified feed (emulsified water treated with 15% sodium sulphate solution) was introduced in turbine flow membrane module (TFMM) and radial flow membrane module (RFMM) fitted with 25 kDa polysulfone (PSf) membrane (0.041 m effective diameter, procured from Koch Membrane, USA).

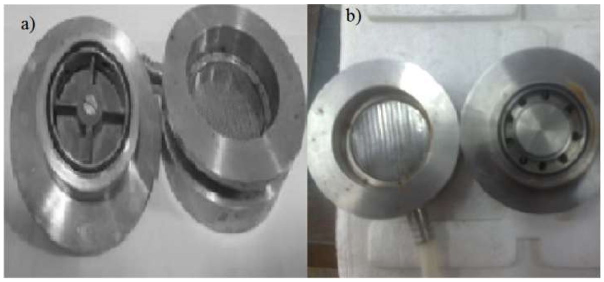


Figure 4.2 (a) Turbine flow membrane module (TFMM) (b) Radial Flow membrane module (RFMM).

Furthermore, to study the performance of the two aforesaid membrane modules in comparison to salt pretreated emulsion as a feed to the membrane module, emulsified oily wastewater without such pretreatment has been introduced in both RFMM and TFMM. However, prior to experimental runs, both the membranes were subjected to water compaction at a trans-membrane pressure (TMP) (ΔP) of 0.6 MPa, higher than that of experimental TMPs (0.3 MPa, 0.4 MPa and 0.5 MPa) in order to avoid any changes in the pores' size during the experimental runs. Compaction of the membrane was ensured after 5400 s (1.5 hrs), when the water flux became stable for a substantial period of time. Total petroleum hydrocarbon (TPH) present in emulsion has been analysed with the standard ASTM D3173-75 methods. TFMM and RFMM (Putatunda et al., 2014) (fabricated by Concept International Ltd, Kolkata, India), both the modules were constructed of SS316, has been shown in Figure 4.2(a) and 4.2(b). A plunger pump (Maker: American Sparing & Press Workshop Pvt. Ltd., Mumbai, 3 H.P.; Maximum Pressure: 400 psi) is attached with the module to withdraw the pretreated oily feed solution from a jacketed feed tank (Capacity: 0.005 m^3 or 5 L) and introduced it to the membrane module. During experiments the temperature of the feed solution had been maintained at 15, 20, 25 and 30°C. The pressure over the membrane was controlled using a back pressure regulator valve (BPRV) fitted in the retentate line.

The performance of the module was studied at a TMP of 0.3, 0.4 and 0.5 MPa. Figure4.3. shows a schematic diagram of the experimental setup used for experiment. Once an experimental run was completed, the fouling was estimated measuring the hydraulic resistance. Membrane was washed with a solution of 10% (v/v) n-hexane in water, which resulted in at least 90-95% water flux recovery. Finally, the membrane was second washed with 1(N) NaOH and 2% (w/v) NaOCl solution in order to enhanced regaining of the flux. The primary wash with n-hexane was continued for an average duration of 2 hrs until the desired flux regain was achieved, while the secondary wash cycle was continued for 1.5 hrs on average basis. After the completion of experiment, the membrane was stored with 20% (v/v) ethanol solution for subsequent use.

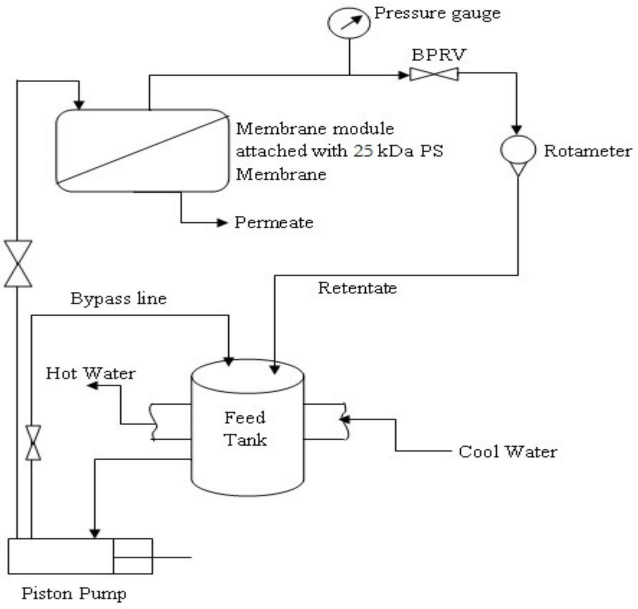


Figure 4.3 Schematic diagram for the experimental setup used in this case.

4.3 Result and Discussions

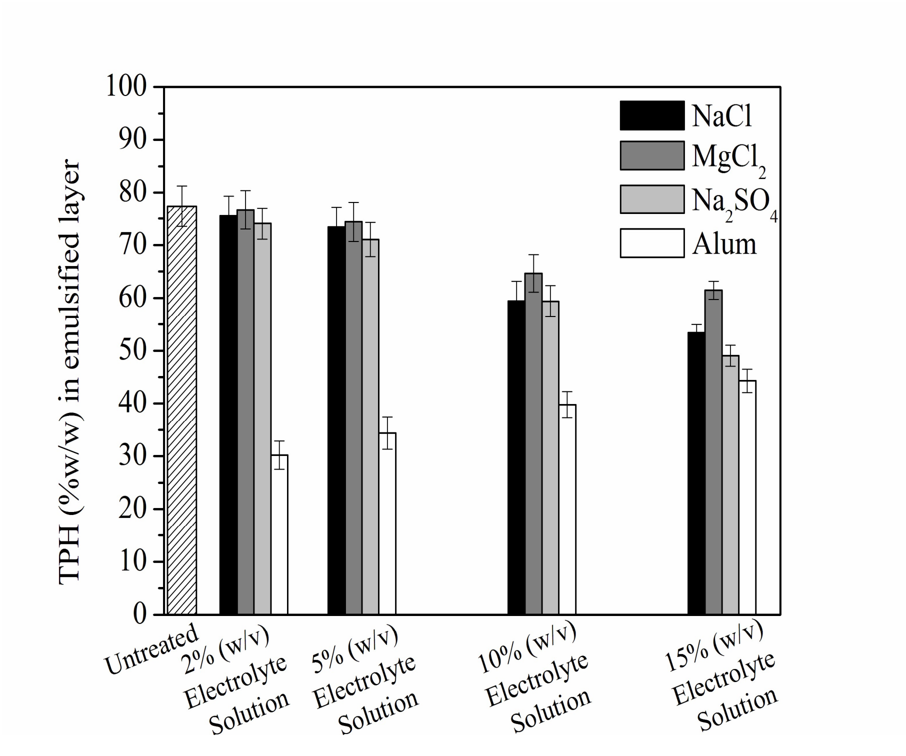


Figure 4.4 Percentage of TPH (with a S.D. of 5% error margin) in the organic phase collected from the separator after salt dosing. Data were collected after 72 h of salt dosing to the emulsified oily water.

4.3.1 Effect of different salts on emulsified wastewater:

Figure4.4 shows the variation of total petroleum hydrocarbon (TPH) from spent fuel present in the aqueous layer after addition of different salts, such as alum, sodium chloride, sodium sulphate and magnesium chloride, as electrolytes in the emulsified oil in water system. The reduction of TPH in the aqueous layer confirms the demulsification process, leading to a formation of top oily layer. From the figure it can be seen that addition of sodium chloride, sodium sulphate and magnesium chloride decreases TPH with an increase in the salt concentration, while, alum follows an opposite trend. After keeping the emulsion in bench for 72 hr with added electrolytes, three distinct layers had been observed. The top layer consists of lighter oil, the middle layer consists of rest of the emulsified oil-in-water solution and the bottom portion was the sediment of suspended solids, mainly dirts. Continuous addition of different salts with increased concentration to the emulsion altered the height of uppermost oil layer, which had been noticed visually. One of the basic concepts with the emulsion is the idea of the charge distribution over the surface of the colloidal particle that could be explained leading to a formation of electrical double layer as explained by Helmholtz in 1850. The detergent used in the present study is the domestic caustic detergent consisting of sodium and sulfonates/sulfates group.

$$u_{oil} = \frac{2gr^2(\rho_{oil} - \rho_w)}{9\mu} \qquad 4.1$$

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_0 \varepsilon_{rs} k_B T}{2000 e^2 I N_{Avogadro}}} \qquad 4.2$$

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2 \qquad 4.3$$

The addition of salts decreased the zeta potential (measured using Malvern Nano-ZS90 zeta analyzer), which ultimately leads to a coalescence of smaller oil droplets to form larger droplets. Due to increase in the droplet size, the droplets float at the top of the aqueous surface(Nour and Sothilaxmi, 2010) as lighter oily layer according to Stoke's law (Eq. 4.1). Moreover, the decrease of zeta potential compressed the electrical double layer, i.e. the Debye length (Eq.4. 2), which can be estimated after knowing the ionic strength (Eq. 4.3) of the solution with added electrolytes. Table 4.1 shows the ionic strength of the electrolytes in the o/w emulsion.

Table 4.1 Ionic strength of the dosed electrolytes with varied concentration in the emulsified oily wastewater.

Electrolytes	Concentration dosed to o/w emulsified water			
	2% (w/v)	5% (w/v)	10% (w/v)	15% (w/v)
NaCl	0.34	0.86	1.71	2.57
$MgCl_2$	0.21	0.53	1.05	1.58
Na_2SO_4	0.14	0.35	0.70	1.06
Alum	0.04	0.11	0.21	0.32

From figure 4.4, it is evident that 15% Na_2SO_4 provides maximum reduction in TPH in residual emulsion layer beneath the top oily layer. As the oil droplets are being negatively charged, therefore, the accumulation of positive ions because of the added electrolytes might compress the electrical double layer to retain electroneutrality. This leads to an increase in the Van der Waals' (Eq. 4.4)(Evan and Wennerström, 1999) force of attraction between the dispersed phases and electrolytes. After the ions being adsorbed on the oppositely charged surface of the dispersed phase in an emulsion, the ionic compressibility was getting reduced(Narayan 1979). More compression will produce more internal repulsive energy to ensure the stability of the emulsion. Addition of alumn will release Al^{3+} ion in the aqueous solvent, which is adsorbed over the charged surface of the colloidal particles and reduces the surface potential. As a result it reduces the potential barrier by charge neutralisation, and through Van der Waals forces dispersed phases will aggregate. According to Kudoh et al.(Kudoh et al., 1992), the ionic compressibility is proportional to the slope of ionic radius versus logarithm of bond strength (Z/Ɲ), and it is 0.155 x 10^{-11} m^2 N^{-1} for Al^{+3}. Moreover, with excess alumn concentration in the solvent, there is a charge reversal and the $SO4^{-2}$ ion of compressibility 5.232 x 10^{-11} m^2 N^{-1} gets attracted towards the newly formed positively charged dispersed phase. Hence, increased concentration of alumn shows less salting out destabilisation of the emulsion (Figure 4.4) as it shows more compressibility (almost 50 fold) to the emulsion system compared to the other electrolytes added. At a lowest concentration of 2% (w/v), it removes almost 39% of oil from emulsified solution.

$$V_{VDW} = -\frac{H_{121}}{12\pi h^2} \tag{4.4}$$

On the contrary, other ions' (after addition of electrolytes NaCl, $MgCl_2$ and Na_2SO_4) effect follows the principle of double layer contraction. Figure 4.5 shows the zeta potential for different electrolytes at a concentration of 15% (w/v). According to DLVO theory(Evans and Wennerström 1999), the net potential for the interaction of the droplets is given by the summed value of Van der Waals energy of attraction and doubled layer energy of repulsion. The situation can be explained by two parameters; one, with the Debye length and the other one is the ionic radius. According to Evans and Wennerström[1], the potential for maximum interactivity occurs when for the distance of separation between two droplets in an emulsion is two times of the Debye length. In a more generic way, according to Quesada-Pérez et al.(Quesada-Pérez, et al., 2009) the hydrated ionic radius of the salts would be more precise and overlapping of hydration zone will increase the possibility of coalescence. Eq. 4.5 shows the condition of interactive potential(Quesada-Pérez, et al., 2009) along with the variation of hydrated radius for different ions. This attributes to the fact that Van der Waals attraction force becomes predominant with the first condition where the charged particles coalesce and destabilise the emulsion.

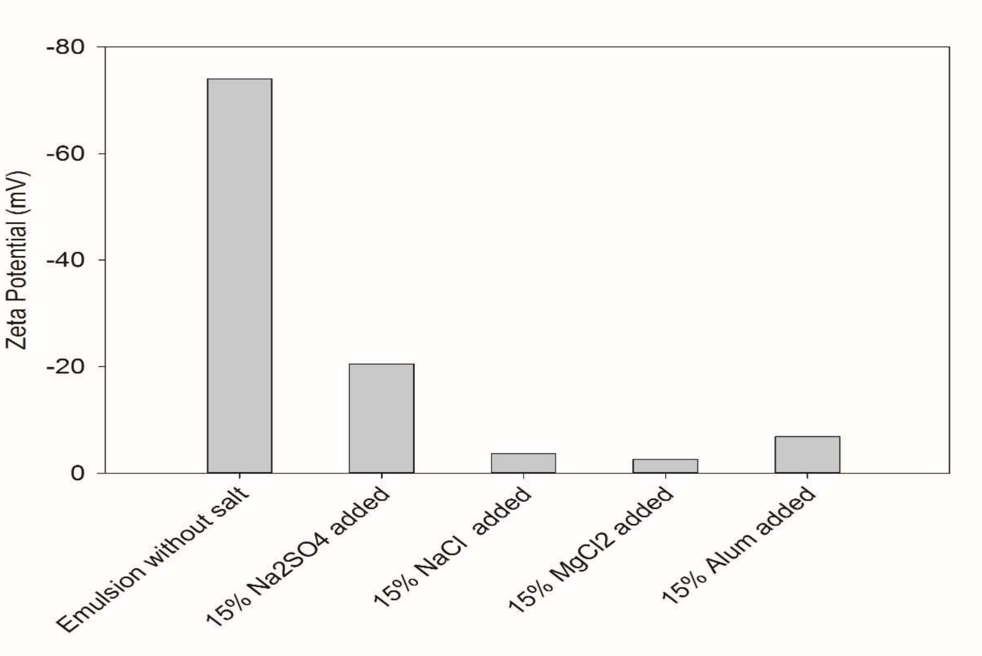


Figure 4.5 Zeta potential (mV) for different electrolytes at 15% (w/v) concentration.

$$V_{rep} = \begin{cases} 0 : h < \left(r_{hydrated} + r_{dispersed}\right) \\ \infty : h \geq \left(r_{hydrated} + r_{dispersed}\right) \end{cases} \qquad 4.5$$

Now if the dispersed phase radius is assumed to be unique for all the electrolytes apart from trivalent aluminium, the ratio $h/r_{hydrated}$ (Figure 4.6) provides an idea of desalting operation efficiency with varied electrolytes. However, the ratio depends on how the diffuse layer is affected by the electrolytes after the addition of electrolytes, which in turn depends on the hydration energy of the electrolytes. The hydration energy of added electrolytes as given below were calculated using thermodynamic Born-Haber cycle(Yoder 2005):

$MgCl_2$ (2521 kJ mol^{-1}) > Na_2SO_4 (1387.1 kJ mol^{-1}) >NaCl (771 kJ mol^{-1})

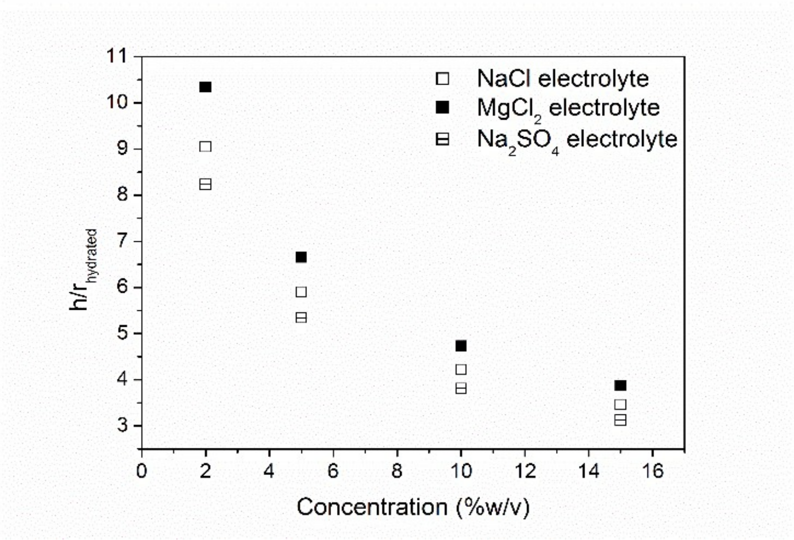


Figure 4.6 Variation of $h/r_{hydraulic}$ with the electrolytes' concentration dosed in the emulsified oily wastewater.

From the above series, it is well understood that NaCl will readily release ions as the hydration energy is much low compared to other electrolytes. Therefore, it apparently seems that more release of positive ions in this case after NaCl addition decrease the Debye length attributing to the destabilisation. However, according to Figure 4.4, good agreement on destabilisation is shown after addition of Na_2SO_4. According to Narayan(Narayan 1979), one of the reasons towards the stability of lattice also depends on the ionic compressibility. Aforesaid more ionic compressibility leads to more repulsion and therefore more stable ionised condition once the electrolytes get hydrated. The compressibility of SO_4^{2-} (5.232 x 10^{-11} m^2 N^{-1}) is almost twice of Cl^- (2.952x 10^{-11} m^2 N^{-1}), which attributes to more formation of ions from Na_2SO_4. As a result it imparts a significant contribution to the decrease of double layer followed by a coalescence of thee dispersed phase. Therefore, even at low concentration of Na_2SO_4 addition shows lower percentage of oil present in the emulsified form compared to chloride salts as shown in Figure 4.4. However, 15% (w/v) Na_2SO_4 removes around 26% of oil from their emulsified form. On the contrary, solvation energy of $MgCl_2$ is much higher compared to both salts (approximately 2-3 fold) that potentially reduce the ionisation and henceforth the performance of $MgCl_2$ in demulsification compared to other two salts.

4.3.2 Comparative study on the effect of membrane, TMP and temperature on permeate flux during ultrafiltration (UF) of emulsified oily wastewater in TFMM and RFMM:

Figure 4.7 and 4.8 shows the variation of steady state permeate flux of treated or untreated wastewater with applied TMP after 30 min run at different experimental temperatures for TFMM and RFMM module respectively. One of the primary concerns in analysing the steady state flux variation with applied TMP is to depict the pressure at which the separation shifts from pressure driven to mass transfer controlled region. Aforesaid, with membrane separation the macromolecules are getting deposited over the membrane surface that increases the concentration over the surface. Hence, reverse concentration gradient acts against the applied TMP (Eq. 4.6 and 4.7) that changes the driving force from pressure driven to mass transfer driven(Bowen and Jenner, 2005). With TFMM the permeate flux is almost 30-38% higher compared to RFMM in all possible conditions. TMP is employed over the membrane surface with the help of a flow restrictor, which is shown (Figure 4.3) as backpressure regulator valve (BPRV) fitted with the retentate line.

$$Jc = Jc_p - \left(-D\frac{dc}{dz}\right) \tag{4.6}$$

$$J = \frac{\Delta P}{\mu R} \tag{4.7}$$

Where, J is the permeate flux, c is the bulk concentration, c_p is the permeate concentration, D is the diffusivity of the solute in the solvent, z is the distance evaluated from the membrane surface to the bulk, ΔP is the TMP, μ is the viscosity of the solution and R is the total resistance over and within the membrane.

In case of TFMM, if the applied TMP is high then it will restrict the rotation of the blades that ultimately results in reducing the sweeping action over the membrane surface and hence, less removal of the solutes from the membrane surface. Hence, increased TMP will increase the possibility for the deposition of the solutes over the surface followed by sticking of oil over the surface. The phenomenon is well understood from the contact angle measurement (using Kruss Drop Shape Analyser DSA25, Kruss GmbH, Hamburg), where it can be seen that after run the contact angle is increased by almost 1.5 fold attributing to a formation of hydrophobic surface because of sticking of oil on the surface.

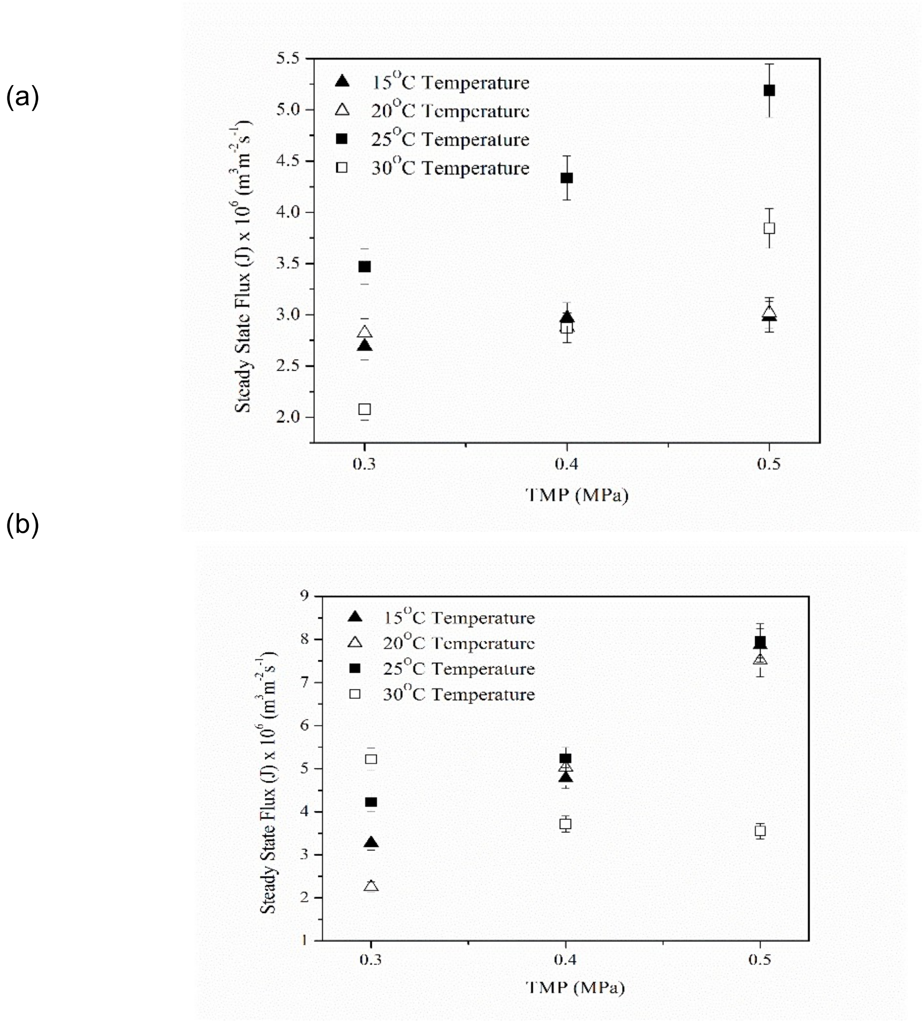
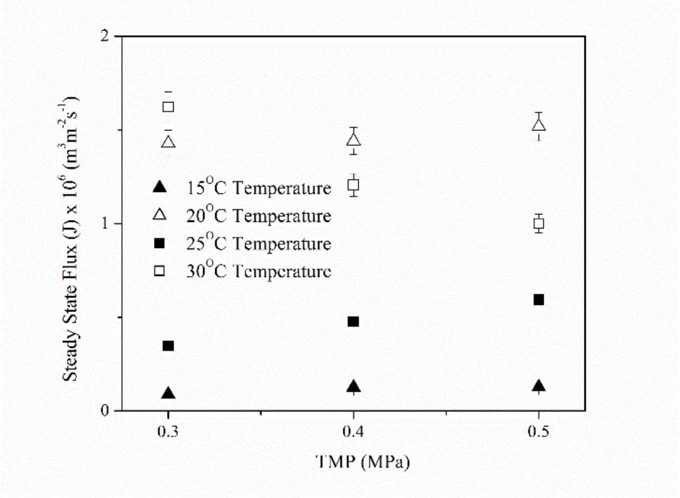


Figure 4.7 (a) Variation of steady state flux (<J>x 10^6 m^3 m^{-2} s^{-1}) from TFMM with varying TMP and feed temperature with the untreated emulsified wastewater. (b) Variation of steady state flux (<J>x 10^6 m^3 m^{-2} s^{-1}) from TFMM with varying TMP and feed temperature with the pretreated emulsified wastewater.

From Figure 4.7(a) at low temperatures (15°C and 20°C), there is practically no increase in the steady state flux with the increased TMP. It is seen from the figure that only mere 8.3% increase in the steady state flux once the applied TMP increases from 0.3 MPa to 0.5 MPa. With the applied TMP the vanes are restricted to rotate and hence, the shear force over the membrane is getting reduced. Now according to Hoshyargar et al.,(Hoshyargar et al., 2012) with increased shear stress the rate of shear is reduced with the emulsified o/w at 15°C-20°C. Hence, on the contrary low stress over the surface manifesting high shear rate attributes to an increased concentration over the membrane surface that imposes almost no slip condition over the surface. Therefore, at this temperature, the separation is limited by the mass transfer controlled region only instead of pressure driven process. However, the opposite effect was felt with the treated feed, where the oil is separated from water. With the oil without emulsified form the shear rate will increase with the shear force over the surface(Hoshyargar et al., 2012). At high TMP the shear stress is reduced over the membrane attributes to a reduced shear rate and this depicts the less momentum transfer. This manifests reduced formation of gel layer over the surface and hence, the steady state flux in increased by almost 60% to 160% with the increased TMP (Figure 4.7(b)).

(a)



(b)

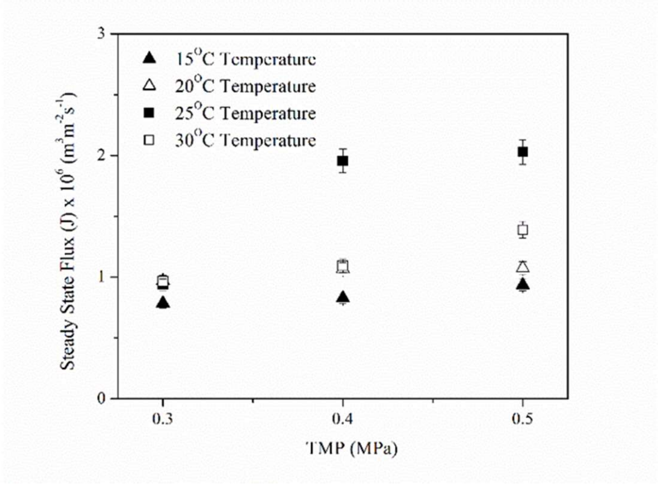


Figure 4.8 (a) Variation of steady state flux (<J>x 10^6 m^3 m^{-2} s^{-1}) from RFMM with varying TMP and feed temperature with the untreated emulsified wastewater. (b) Variation of (<J>x 10^6 m^3 m^{-2} s^{-1}) from RFMM with varying TMP and feed temperature with the pretreated emulsified wastewater.

At low temperature, where the stability of emulsion is prominent attributes to a mere 15%

increase at 0.5 MPa over the flux obtained at 0.3 MPa at low temperatures (Figure 8(a)). For both of the modules, less TMP attributes to a high flow over the membrane that eventually increases the shear over the membrane surface in order to reduce the concentration polarization over the membrane.

Furthermore, one of the primary concerns in any membrane separation process is the surface charge of the membrane that dictates the permeation along with other operating parameters. The membrane process here depends on primary four conditions that make the differences in permeation – a) membrane material b) shear environment over the membrane c) temperature of the feed and d) electrolytes' concentration. PSf membrane is hydrophobic in nature and repulses the negatively charged solutes because of the presence of strong polar sulfonated group(Gourley et al., 1998). Therefore, with the negative surface charge o/w emulsified form will be less prone to get attached with the negatively charged membrane surface. As a result, the population of counter ions gets increased over the surface. Subsequently, the osmotic pressure gradient will act in the direction away from the membrane surface to dilute the ionic strength in the mid-way between bulk and membrane surface. Hence, in case with the TFMM, at higher temperature, increase in TMP led to a substantial increase in permeation through the membrane by counteracting the reversed osmotic pressure developed. However, in case with RFMM, at high temperature (30°C) the flux gets reduced with increased pressure. With increase in temperature the electrophoretic mobility of the charged particles will increase, while there is no change with the zeta potential(Arroyo et al.,1999) . The charged dispersed phase with positive charges (Na^+) surrounding it (Stern layer) gets adsorbed over the negatively charged membrane surface increasing the resistance over the surface. In case of TFMM there is a tangential force over the membrane surface by the blades of the vanes that swept away the adsorbed solutes and hence reduce the polarization. While, in RFMM the mode of transport is because of the eddy transport and eddy ruptures under increased TMP. Therefore, ultimately after release, charged solutes settle down over the surface and increase the concentration polarization.

Aforesaid, with the increase in temperature, the electrophoretic mobility of the charged particle will increase while keeping zeta potential constant. This manifests more ionic concentration between bulk and membrane surfaces followed by an increase in the osmotic pressure. In this case, at 30°C and 0.3 MPa, with TFMM the steady state flux is lowest. Adsorption and hence back diffusion along with the strong upward osmotic pressure restrict the permeation. While, in case with RFMM this mobility gets disrupted because of the strong turbulence created over the membrane surface. This makes the steady state flux at this condition superior compared to the others. However, with increased TMP, this turbulence gets reduced along with the rupture of eddies and increases the mobility. In case with the

TFMM highest permeate flux has been obtained for 25°C while this has been obtained at 20°C in case of RFMM. At 25°C the mobility gets increased, which might increase the osmotic pressure and at the same time the adsorbed layers' résistance, which can be taken care off by tangential shear by TFMM but not by eddies in RFMM. On the contrary, in RFMM at 25°C the steady state flux at different TMPs is lower than at 30°C with the untreated o/w emulsion. However, in this case the increased mobility is accompanied by the turbulence created within the module over the membrane. Possibly, turbulence imparts an additional force in conjunction with the inertia force due to mobility to the charged dispersed phase that is enough to overcome the repulsive force because of the double layer and ultimately helps to coalesce(Chakraborty 2008). This coalescence results in the floatation of oil and reduces the possibilities polarization.

4.3.3 Comparative study on the effect of membrane, TMP and temperature on permeate flux during ultrafiltration (UF) of 15% (w/v) Na_2SO_4 treated emulsified oily wastewater in TFMM and RFMM:

Figure 4.7(b) and 4.8(b) illustrate the steady state flux after 30min run with wastewater, after being treated with 15% (w/v) Na_2SO_4, at different temperatures and TMPs using both TFMM and RFMM respectively. In case with the salt treated wastewater the o/w emulsion breaks and the oil becomes free from water. Hence, colloid type charge distribution becomes neutralised that restricts the oil to stick over the membrane surface through electrostatic attraction. However, the oil shows an impermeable layer over the membrane surface that forms a secondary layer on the membrane surface. In case with RFMM, as seen with the untreated emulsion, at 25°C, the steady state flux is higher compare to the flux at 30°C attributing to an increased electrophoretic mobility leading to the adsorption of the solutes over the membrane through electrostatic attraction. However, at lower TMP the fluxes obtained at all the temperatures are equal. Here the maximum steady state flux obtained at 30°C is almost 33% higher compared to the steady state flux obtained at 15°C and 0.5 MPa TMP for untreated wastewater. On the contrary, TFMM shows higher permeate flux for the treated emulsion, almost 45% higher than that of in the untreated one. One of the important observations here is that almost the same steady state flux was obtained at 30°C and 0.5 MPa pressure in case with the modules for both treated and untreated emulsified form. However, in case with the TFMM, at 30°C the steady state flux decreases with the increase in TMP. Apart from the electrophoretic mobility, one of the possible reasons might be because of less tangential shear due to increased back pressure on the blades. Hence, the secondary layer over the membrane surface due to oil can't be alleviated. This restricts the permeation through the membrane. Figure 4.9 and 4.10 shows a comparative statement between TFMM and RFMM for the required pump energy to have 1ml of permeate collected across unit area of the membrane. According to Putatunda et al. the equation for the fold increase is given by Eq. 4.8. It can be seen from the figures that with the untreated one (Figure 4.9), RFMM required much energy compared to TFMM in order to obtain one ml of permeate across unit area of the membrane at 15^{O}C and 0.3 MPa. However, with the increase in TMP, the energy consumption by RFMM gets reduced. On the contrary, an opposite could be observed in case with the treated feed (Figure 4.10). As said before, the shear rate is decreasing with the increase in the stress in case of emulsion. Now, with the increase in TMP, as the stress component in TFMM was reduced followed by an increase in the rate, the energy requirement will be more compared to RFMM, where the energy is associated only with the eddy transport. Moreover, one of the substantial advantages with the RFMM is the rupture of the large eddies at high TMP that eventually releases energy in addition to the pump energy. Although the energy consumption is much higher in RFMM compared to TFMM with the untreated feed because of the presence of large colloidal droplets in case with the emulsion. In case with the treated feed at 30^{o}C, due to the combined effect of less stress at 0.5 MPa TMP and the electrophoretic mobility, the energy requirement by the TFMM is much higher compared to RFMM. However, like untreated one, with the treated feed also, the energy consumption of RFMM is higher than that of TFMM manifesting TFMM's low energy consumption ability. Figure 4.11 shows the FTIR spectra for the retentate obtained after the emulsified oily water being treated with the membrane modules at 15^{o}C and 0.5 MPa. The figure shows flattened peak in the vicinity of 3200 cm^{-1} is because of the stretching vibration in –OH due to hydrogen bonding of water with the electronegative oxygen atom in –C=O of acids. In the vicinity of 1720 cm^{-1} the peak for –C=O is observed because of the stretching vibration. However, there is a peak shift .for –C=O on the right side in the spectrum attributing to H-bonding with electronegative oxygen atom. Peak around 2840 cm^{-1} is because of stretching vibration in aldehyde's sp^{3} hybridised state. Under radical environment the aldehyde groups are continuously morphed into its vinyl form attributing to a loss in such sp^{3} hybridisation state(Mills and White, 1987). Hence, the peak for such vibration is absent in case with the untreated emulsion. In the vicinity of 1100 cm^{-1} spectrum shows the peak for symmetric stretching vibration for S=O, which is primarily because of the detergent added contain SDS.

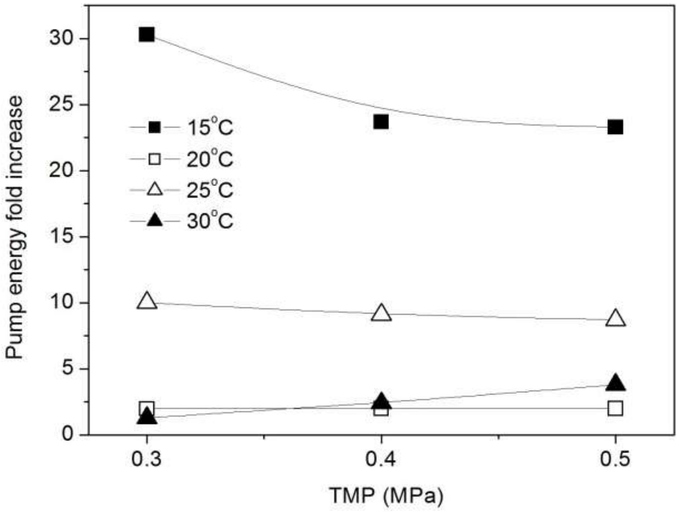


Figure 4.9 Pump energy required per ml of permeate across unit area of the membrane for RFMM over TFMM at different untreated feed temperatures.

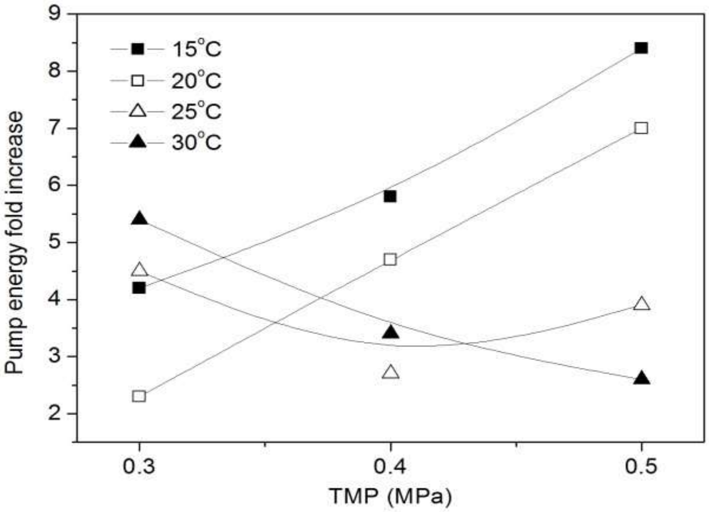


Figure 4.10 Pump energy required per ml of permeate across unit area of the membrane for RFMM over TFMM at different treated feed temperatures.

However, salt treated feed to RFMM shows low transmittance compared to TFMM attributes to the more presence of SDS on the retentate side that are supposed to be permitted through the membrane because of low molecular weight.

$$\text{Pump energy fold increase} = \frac{E_{RFMM}}{E_{TFMM}} \qquad 4.8$$

Where, E_{RFMM} is the pump energy required per ml of permeate collected across unit area of the membrane in RFMM; E_{TFMM} is the pump energy required per ml of permeate collected across unit area of the membrane in TFMM.

This manifests more secondary layer formation in case of RFMM compared to TFMM, which is at par with the steady state data obtained for both the modules. On the contrary, the band is absent in case of untreated emulsified form. The stretching vibration for S=O is sensitive to local environment changes(Thorstenson et al., 1993)). Stretching vibration has been diminished because of its attachment with the polar aqueous environment manifesting the stable emulsion. Peaks in the range of 2300-2400 cm^{-1} are because of stretching vibration in linear coordination of CO_2 (Gougousi et al., 2003; Yasin et al., 2014). With the untreated emulsion presence of acidic CO_2 attributes to a strong peak in this range. However, addition of Na^{+2} salt shows strong affinity for CO_3^{-2} leading to neutralisation. Hence, with the salt treated emulsified system these peaks are absent. However, in case with the untreated TFMM the absorption is more compared to RFMM manifests less neutralisation. With the emulsified form TFMM was found more productive in restricting the gel layer formation and hence, maximum salt ions can pass through the membrane. This attributes to less neutralisation showing more absorption of energy to have stretching vibration in CO_2 dissolved in the system.

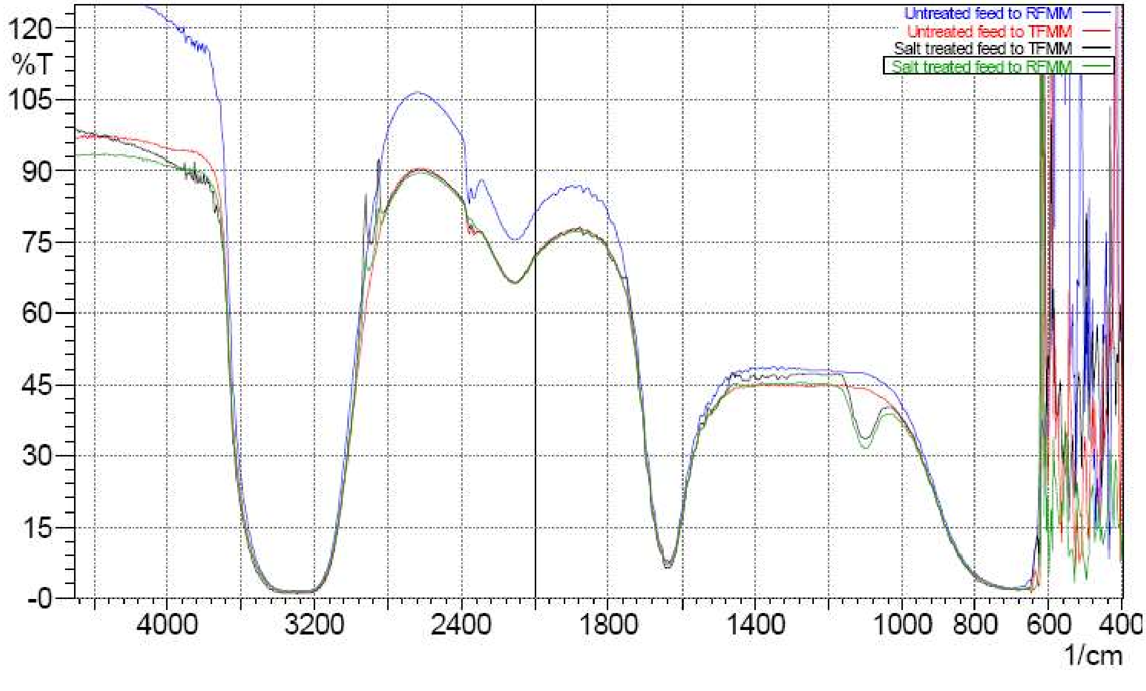


Figure 4.11 FTIR chromatogram of retentate from TFMM at 15°C and 0.5 MPa.

4.3.4 Significance test towards understanding the pretreatment of emulsified oily wastewater using analysis of variance (ANOVA):

To understand the effect of salts and concentration on the demulsification procedure, a two factor ANOVA test was carried out based on null hypothesis. Table 4.2 shows the result of the ANOVA test. The significance test was done considering 5% confidence interval. The analysis shows that the F- value for different salts is 12.723, which is greater than the critical value with degrees of freedom 4.

Table 4.2 ANOVA analysis on the effect of different salts and their concentration on demulsification followed by separation.

Source of Variation	SS	df	MS	F	P-value	Fcrit
Salts	2573.6	3	857.868	12.7238	0.00138	3.86255
Concentration of the salts dosed	412.499	3	137.5	2.03937	0.17889	3.86255
Error	606.802	9	67.4225			
Total	3592.91	15				

**SS: Sum squared error; df: degrees of freedom; MS: Mean square error*

Therefore, it can be said that, the variation in the extent of demulsification between different salts is larger than the variation at different concentration level, for the same salts. While, on the contrary at different concentration level the variation is smaller than the variation obtained because of differences in the salts' chemical nature. From Table 4.2 it can be seen that for the variation of salts, p-value (probability of making type-I error) is 0.001 (<0.05) that attributes to a significant effect on demulsification with the variation in salts. However, concentration of dosed salts shows p-value 0.18 (>0.05) manifesting less significant effect on demulsification. Therefore, based on the analysis it can be said that the selection of electrolytes is much crucial issue in effective demulsification compared to the variation in concentration.

Table 4.3 (a) ANOVA analysis on the effect of temperature on the salting out pretreatment and subsequent flux from TFMM at different TMPs and (b) ANOVA analysis on the effect of TMP on the salting out pretreatment and subsequent flux from TFMM at different temperatures.

Source of Variation	SS	df	MS	F	P-value	Fcrit
(a) Salting out treatment	19.1876	1	19.1876	12.3181	0.011	5.99
Temperature (^{O}C)	8.9178	6	1.4863	0.641	0.696	2.74
TMP (MPa)	37.0903	16	2.3181			
Total	65.1957	23				
(b) Salting out treatment	19.1876	1	19.1876	3.736	0.125	7.71
TMP (MPa)	20.5459	4	5.1365	3.631	0.024	2.93
Temperature (^{O}C)	25.4622	18	1.4146			
Total	65.1957	23				

Table 4.3 and 4.4 shows the significance test analyzing the effect of electrolyte treatment; temperature and TMPs on the steady state permeate flux obtained for both TFMM and RFMM respectively. In table 4.3(a) and 4.3(b), the F-values (Eq. 4.9 and 4.10) show that for TFMM the variation in the steady state flux because of different temperatures is much prominent compared to the electrolytic treatment employed to destabilize the emulsion, while effect of TMP is at par with the treatment (as the F-value is very close to the critical F-value). The later might be due to the osmotic pressure that depends on the ionic strength of the charged dispersed phase (with positively charged stern layer) and the negative environment of the PSf membrane surface. However, in case with TFMM the treatment is much important to the flux compared to the temperature variation of the feed solution as F (=12.32) > Fcritical (=5.9) (Table 4.3(a)). Moreover, the effect of TMP is much significant compared to the treatment of the oily water. However, comparing the effect of temperature variation over the TMP variation, RFMM shows (F(=11.6)>Fcritical(=2.7)) that temperature variation is much significant to the flux compared to TFMM (F(=0.6)<Fcritical(=2.7)).

Table 4.4 (a) ANOVA analysis on the effect of temperature on the salting out pretreatment and subsequent flux from RFMM at different TMPs and (b) ANOVA analysis on the effect of TMP on the salting out pretreatment and subsequent flux from RFMM at different temperatures.

Source of Variation	SS	df	MS	F	P-value	Fcrit
(a) Salting out treatment	0.6836	1	0.6836	0.864	0.389	5.99
Temperature (^{O}C)	4.7485	6	0.7914	11.560	0.000	2.74
TMP (MPa)	1.0954	16	0.0685			
Total	6.5276	23				
(b) Salting out treatment	0.6836	1	0.6836	6.391	0.065	7.71
TMP (MPa)	0.4278	4	0.1070	0.355	0.837	2.93
Temperature (^{O}C)	5.4161	18	0.3009			
Total	6.5276	23				

$$F=\frac{\begin{array}{l}\text{Variation of the steady state flux because of the treatment}\\ \text{of emulsified oily waste water}\end{array}}{\begin{array}{l}\text{Variation of the steady state flux because of the variation}\\ \text{in temperature of emulsified oily waste water}\end{array}} \qquad 4.9$$

$$F=\frac{\begin{array}{l}\text{Variation of the steady state flux because of the treatment}\\ \text{of emulsified oily waste water}\end{array}}{\begin{array}{l}\text{Variation of the steady state flux because of the variation}\\ \text{in TMP of emulsified oily waste water}\end{array}} \qquad 4.10$$

4.4 Conclusion

The present inspection depicts a contingent study on the application of two indigenous membrane modules RFMM and TFMM equipped with 25 kDa PSf membrane, for the treatment of emulsified oily wastewater (O/W emulsion) generated in automobile industry. One of the primary challenges with the emulsified form is the electrical double layer that may arises electrostatic adsorption of the charged phase onto the membrane surface, leading to a development of an osmotic pressure gradient and hence, repulsion. In addition, even after destabilization of the emulsion, after introducing the feed to the membrane module, the permeation depends on the presence of ions, their compressibility followed by the arrival of

Van der Waals force. Here, TFMM gives around 3 fold increase in the permeate flux compared to RFMM with untreated emulsion and almost 4 fold increase with respect to the treated one. In another sense, one of the disadvantages with RFMM, especially with the treated feed is the quick shifting from pressure controlled process to mass driven process at any temperature. Hence, TFMM shows almost 53% increase in the steady state flux for treated feed over the untreated feed at 25°C. Moreover, with TFMM the maximum flux was found for the pretreated feed at 15°C, while energy requirement ratio is almost eight times for the RFMM compared to TFMM and this ensures the suitability of TFMM over RFMM in terms of lowest energy involvement to separate oil from water.

5 Chapter 5:

Comparative study on bioremediation strategy for remediating spent oil contaminated waste stream

Aims of the Chapter

Bioremediation is an intricate treatment procedures which can provide an effective, efficient and economic strategy to enhance the removal of hydrocarbons from the waste stream. In this present study an attempt was made to bioremediate the spent oil from waste stream, by two oil degrading bacteria, "A_3" and "A_4", isolated from contaminated waterways using *enrichment culture* process. The efficacy of the more potent strain A_3 in degradation of spent oil in emulsion form has also been monitored.

5.1 Introduction

Industries, like lubricant, paint, rubber chemical, heavy metal, petrochemical, automobile etc., produce oily wastewater that typically include phenols, polyaromatic and petroleum hydrocarbonsin varied range of concentrations (Zhong et al., 2003). Once, this contaminated wastewater flows into the flowing stream, specifically as run-offs from different sources, will contaminate large aquatic water body. Along with increasing the biological and chemical oxygen demand, the oily wastewater will develop a light impervious layer at the top of the water surface restricting the sunlight to pass through perturbing the aquatic flora and fauna. Furthermore, the polyaromatics as run-offs manifests increase in the toxicity level of the aquatic region, which will cause an epidemic during the consumption of sea foods (Bande et al., 2008). Hence, proper treatment of this wastewater is desired before it is being disposed off to the aquatic region. A substantial effort has been made so far in developing different techniques to deal with the oily wastewater, especially where the oil becomes miscible in water forming emulsion because of the presence of surfactants. In general, this huge emulsified wastewater, called ‘produced water’, is a major issue near the oil wells and requires a considerable effort to alleviate the problem. However, urban wastewater may also comprise of emulsified form because of the dust and detergent contaminations with the run-off from local garages and automobile shops.

Wastewater coming out from automobile industries’ car washing facilities consists of oil sludge comprising of diesel oil, used motor oil, grease, tar and other different cuts of hydrocarbons in a varied concentration. Oil and grease in wastewater found in several forms; free, dispersed or emulsied (Rhee et al., 1987). In oil-water mixture, free oil is exist with droplet sizes greater than 150 μm, dispersed oil lies in a size range of 20±150 μm and the size of emulsied oil is less than 20 μm. Many technologies have helped to find solution to oily waste stream treatment, trying to meet up the the environmental discharged standards of oil content of less than 5 ppm in the treated effluent stream (Jegatheesan et al., 2009, Salahi et al., 2010). Conventional approaches to treat oily wastewaters include gravity separation, API unit and skimming, dissolved air flotation, demulsification, electro-coagulation and flocculation, membrane separation (Cheryan et al., 1998, Abbasi et al., 2010, Srijaroonrat et al., 1999, Salahi et al., 2009). Gravity separation followed by skimming is effective in removing free oil from wastewater. API separators and its variations could be used in combination with other processes as an effective, economical primary treatment technique. Both gravity and API separators are not adequate for removal of smaller oil droplets and emulsions. Oil that attached to the surface of solid particles can be efficiently removed through sedimentation in a primary clarifier. In dissolved air flotation, air is used to increase the buoyancy of smaller oil droplets and enhance separation. Dissolved air flotation can be used in combination with chemical coagulants to increase the floc size ensuring better separation (Cheryan and Rajagopalan, 1998). However, membrane separation is efficient to remove oil from water and produce cleaner effluent, economic viability and short life of membrane restricts its application (Salahi et al., 2009). Use of chemicals leads to production of hazardous effluent from electrocoagulation and flocculation, inhibit uses of these applications.

Bioremediation of oil-contaminated wastewater using microbial metabolism is one of the most lucrative way-out for researchers in recent days due to its eco-friendly impact. Bioremediation techniques, take advantage of microbial degradation of organic compounds, as these processes use microorganisms (generally bacteria) to remove pollutants. The bioremediation process, offers countless advantages in comparison to previously mentioned conventional treatment processes (Gogoi et al., 2003, Demnerová et al., 2005, Ghazali et al., 2004). However, bioremediations are comparatively slow processes and the biodegradation of hydrocarbons in wastewater depends on various factors, including microorganism species, nutrients, pH, temperature, moisture, oxygen and contaminant concentration (Walter et al., 2005, Semple et al., 2001, Bardi et al., 2000, Sabaté et al., 2004). Oil degrading strains are generally present in the waste stream to be treated and uses the oily sludge as their nutrient carbon source. Some reported strains having ability of oil degradation are *Pseudomonus sp., Rhodococcus sp., Seratia sp., Gordonia sp., Bacillus sp., Achromobactor sp., Enterobactorsp.* etc (Obayori et al., 2014). Not only the free oil but the emulsified oil also can be demulsified by demulsifying bacteria, such as, *Ochrobacterum anthropi* RIPI5-1 (Mohebali et al., 2015).

In this present study, bacterial strains have been isolated from the wastewater samples collected from different location nearby Kolkata, West Bengal, India followed by its characterization and growth kinetics study. However, the key objectives are to evaluate the efficiency of the isolated strains and an understanding its oil degradation potential, when the oil is being completely mixed with water as oil-in-water (o/w) coarse emulsion.

5.2 Material and Methods

5.2.1 Materials:

Bushnell Haas and nutrient agar broth/media compositions were used in this study according to the guidelines of Hi-Media Laboratories Pvt. Ltd. Sodium sulphate (Na_2SO_4) (CAS no: 7757-82-6),chloroform ($CHCl_3$) (CAS no: 67-66-3), n-hexane ($CH_3(CH_2)_4CH_3$) (CAS no: 110-54-3) and ethanol (CH_3CH_2OH) (CAS no: 64-17-5)were purchased from Merck Chemicals Ltd.

5.2.2 Isolation of bacteria:

Local automobile shops' wastewater, which was collected from two different locations (one near to Ruby Hospital, Kolkata, West Bengal, India, 22.5135° N, 88.4019° E and Amtala, S. 24 parganas, West Bengal, India, 23.9310° N, 88.4477° E) for isolation of bacterial strain. The samples were preserved at 4°C after collection. The samples were inoculated in Bushnell-Haas (BH broth) media (Bushnell and Haas, 1941)with spent oil as single carbon source (Sterilised through 0.2 µm filter),purchased from local automobile service center. 5ml sample water and 1 ml spent used spent oil was added to 50 ml BH broth. The mixed media was incubated in BOD incubator and-shaker at 120 rpm and 35°C temperature for 7 days. After 7 days, the media was withdrawn from the incubator and diluted to 1000 folds. 0.1 ml of diluted inoculums was dispersed over a sterile petridish holding Bushnell-Hass agar media (BH agar media). 100 µl spent oil was and spread over the surface of the plate followed by an spent oil addition of inoculums. The plates were incubated at 35°C for 5 days in non-inverted position (Mandri and Lin 2007). . Single colonies that grow on BH agar media supplemented with spent oil as single carbon source are then purified by streak plate technique until pure single colony was obtained. Pure isolates were then inoculated at nutrient agar slant in test tubes and incubated at 35°C for 72 h and preserved at 4°C as pure slant culture. Among all pure isolates, two of the prompt oil degrading strains (said as A_3 and A_4) were selected by screening of their degradation and growth potential in oil supplemented solid BH media.

5.2.3 Study on the effect of growth parameters on purified bacterial strains (A_3 and A_4):

The pH and temperature of the purified strains inoculated with the BH media and used oil were variedfrom5 to 10 and 25 to 40°C respectively. The bacterial growth was estimated after measuring the turbidity of the broth culture, which is directly proportional to the number of microorganisms populated. Thus increased turbidity of the broth media manifests the increase in the microbial cellular mass.

5.2.4 Study of biodegradation of spent oil:

Previously isolated pure strains (A_3 and A_4)were pre-cultured separately in 50 ml nutrient broth media. A loop of single colony bacterial culture was transferred to the stock media aseptically in a laminar air flow chamber and was given under shaking condition at 100 rpm and at 35˚C for 24 h. Then, 1% (v/v) freshly pre-cultured broth was transferred to each of the four different conical flasks containing 60 ml of BH liquid media along with each strain. Then 2% (v/v) spent oil (sp. gravity 0.93) was added to all conical flasks containing 60 ml broth media and given to shaker-incubator at 120 rpm and at 35˚C for 30 days. The optical density for microbial growth was measured at 600 nm for both of the strains. The samples were collected at a particular interval of days in order to analyze the percentage degradation through studying the growth of the strain. To study the degradation with A_3 strain a pH 8 was maintained with acetate buffer and with A_4 strain a pH 6 was maintained with glycine – NaOH buffer. Growth was terminated by adding 10% (v/v), 1/20 diluted concentrated HCl acid to reduce the pH to 3±0.05 in order to cease the activity of bacterial enzyme. To assess the residual oil, gravimetric analysis had been carried out. Residual oil in the system was extracted through liquid-liquid solvent extraction process using chloroform, n-hexane and ethanol as the ternary solvent system in a ratio of 2:2:1(v/v) (“http://www.cyberlipid.org/extract/extr0001.htm”). Solvent containing spent oil separated carefully and the spent oil and extraction was carried out twice to ensure complete recovery of oil.

$$\%\ \text{Consumption} = \frac{\text{Final weight-Initial weight}}{\text{Initial weight}} \times 100\% \qquad 5.1$$

$$\%\ \text{Degradation} = \frac{\text{Amount of spent oil degraded}}{\text{Amount of spent oil added in the media}} \times 100\% \qquad 5.2$$

5.2.5 Biochemical tests of the bacteria:

Several biochemical tests were done such as, gram staining, catalase test, motility test, Indole test, starch hydrolysis test and colony morphology test as per standard protocol of Bergey's Manual of Determinative Bacteriology and protocol of Smibert and Krieg (Holt et al., 1994; Smibert and Krieg, 1994).

5.2.6 Preparation of o/w emulsion as carbon source to strain A_3:

Simulated emulsion of used spent oil was prepared according to the method described by Putatunda et al., 2015. 250 ml emulsion containing 2%(v/v) of used spent oil with respect to 50 ml BH broth media was prepared and 1% (v/v) inoculums of strain A_3 with respect to media were added to the system. After 7 days the biodegradation at 35°C and pH 8, the degradation of emulsion was compared with free oil degradation.

5.2.7 Biodegradation kinetics study:

One of the key concerns of any biodegradation process is an understanding of microorganisms' growth with time, which inherently shows the consumption of substrate rich with the carbon sources. In this study, the rate of consumption of the petroleum hydrocarbons was considered proportional to the growth of the concerned strain A_3, which may be expressed as the population density function given by Eq. 3.3 (Yeung *et al.* 1997). However, the primary challenges lie in finding out the degradation constant is the variability of hydrocarbons present in the spent oil and thus show a range of values for the constant. It is evident that the lighter hydrocarbons degrades faster compared to the heavier ones and thus show higher value of the constant

$$Y = Y_0 \exp\left(-k_d t\right) \qquad 5.3$$

Where, 'Y' is the residual hydrocarbon content, 'Y_0' is the initial hydrocarbon content, 'k_d' is the biodegradation rate constant, and 't' is degradation time. Rearranging Eq. 5.3, it can be written as,

$$\ln(a) = -k_d t \qquad 5.4$$

Now, in order to calculate its biological half life, $a = \left(Y \middle/ Y_0 \right)$ becomes 0.5, which evaluates the time, called half life, to degrade the hydrocarbon at its exactly half of its original quantity once the strain was allowed to grow within the medium consisting of the said hydrocarbon. However, in the study as the hydrocarbon comprises of several molecular weights from lighter to heavier fractions, hence the half life here depicts the time required to degrade the maximally heavier hydrocarbons present. The biomass growth rate yield coefficient ($y_{x/s}$) is defined as the net gain in the biomass weight per unit amount of substrate consumed (Eq. 5.3).

$$y_{x/s} = \frac{\left(X_m - X_0\right)}{\left(S_0 - S\right)} \qquad 5.5$$

Where, 'X_m' is maximum biomass concentration in g/l, 'X_o' is initial biomass concentration in g/l, S_o is initial substrate concentration in g/l, S is final substrate concentration and $y_{x/s}$ is yield coefficient.

Inheriting the Monod kinetics, the time period for maximum biomass production is given as,

$$t_d = \frac{\ln(2)}{\mu_{max}} \qquad 5.6$$

Where t_d is cell mass doubling time (d), μ_{max} is the maximum specific growth rate (d^{-1}).

5.3 Results and Discussion

5.3.1 Identification of bacteria:

Both the strains, A_3 and A_4 were identified through a study on their phenotypic characteristics. The results from gram staining of both the strains are shown in table 5.1, that depicts gram-positive semi rod shaped bacterial strain. Strains responded negatively to the Indole test, and starch hydrolysis test, manifesting that they are unable to hydrolyze tryptophan and starch. Negative catalase test proves that both the strains were unable to produce catalase enzyme, while negative motility test indicates that both the bacteria are lacking flagella for movement.

Table 5.1 Biochemical test study.

Strain	Gram staining	Catalase test	Starch hydrolysis test	Motility test	Indole test
A_3	Positive	negative	negative	negative	negative
A_4	Positive	negative	negative	negative	negative

Table 5.2 Colony morphology study.

Strain	Colour	Type	Form	Elevation	Margin	Texture
A_3	Red	Opaque	Circular	Pulvinate	Entire	Buttery
A_4	Orange	Opaque	Circular	Pulvinate	Entire	Viscous

Both the microorganisms were grown on nutrient agar medium that is appropriate for all mesophilic bacteria. Strain A_3 was further identified on the basis of the partial sequencing of 16srRNA gene sequence (analyzed at MTCC Chandigarh). The most probable closest match was found with *Gordonia terrae* (Strain name: NBRC100016 (T), Acc no. BAFD01000032), where the pair wise similarity was found 98.63% for 834-1426 bp and 98.48% for 29-556 bp of the gene.

5.3.2 Optimization of growth parameters:

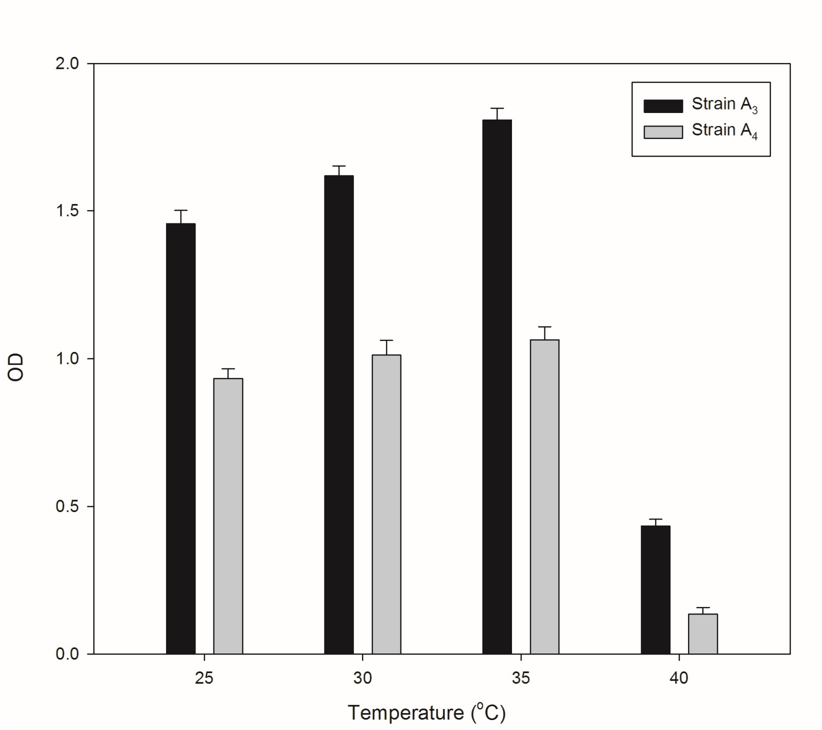


Figure 5.1 Temperature optimization of strain A_3 and A_4 at pH 7.

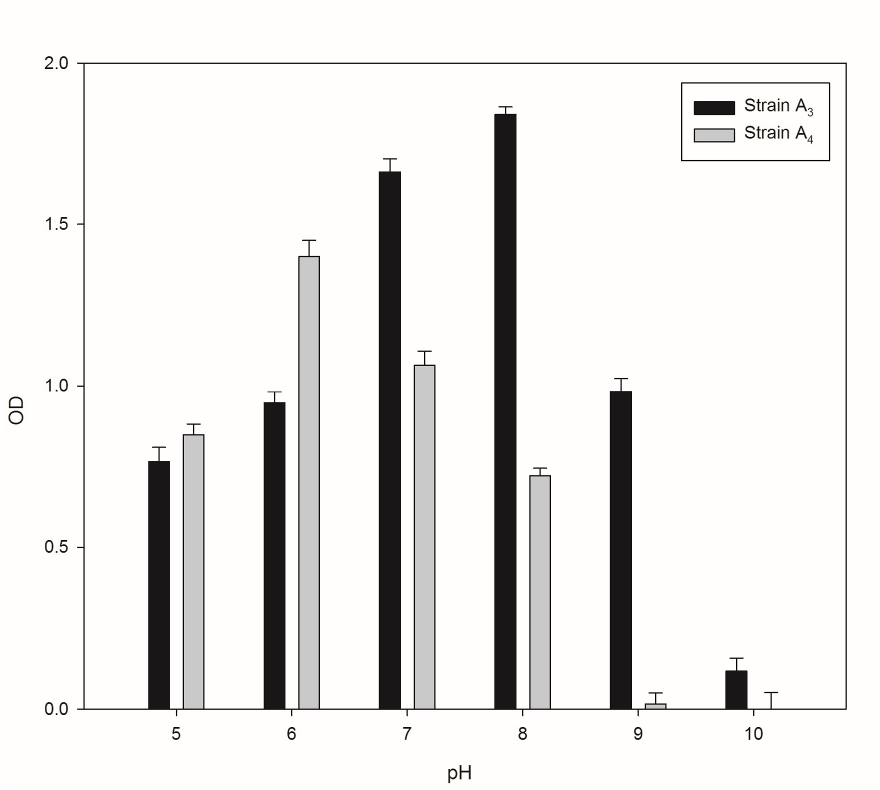


Figure 5.2 pH optimization of strain $A_3$and A_4 at 35°C temperature.

Figure 5.1 and 5.2 show the growth of the identified microbial strain A_3 and A_4 at different temperature and pH. Temperature and pH play a key role in the regulation of protein synthesis, enzymatic activity and other cellular functions of any living organism. At pH 7 and at temperature 35°C, A_3 shows 50% more growth compared to A_4 (Figure 5.1). At neutral pH, in a temperature range from 25°C to 40°C, A_4 strain shows much less growth compared to A_3. On the contrary, if the acidic condition of the medium is increased, at 35°C A_4 shows marginally increased value of growth compared to A_3. In Figure 5.2, A_4 shows around 46% and 14% more growth compared to A_3 as the pH of the system is decreased to 6 and 5 respectively. This attributes to the fact that under acidic condition and at 35°C, strain A_4 shows more growth compared to the other. As we are increasing the pH, the growth rate for both A_3 and A_4 decreases at a temperature of 35°C as observed from Figure 5.2. While, Figure 5.1 shows that at pH 7 and within a temperature range, the growth of A_4 shows a comparable result and the growth rate was suddenly decreased when the temperature was increased to 40°C. A_3 shows a bell-shaped profile for the entire temperature range with a peak value at 35°C. Figure 5.2 also shows a bell shaped profile both for A_3 and A_4, when the peak value for growth of A_3 was seen at pH 8 and for A_4 it was at pH 6. Table 5.3 shows the significance of variations for both A_3 and A_4. From the table, it is observed that RSD for A_3 strain shows around 17% increase with varying pH (fixed temperature at 35°C) compared to the varying temperature (fixed pH at 7). While strain A_4 shows 59.6% increase in the RSD manifesting that A_4 is more sensitive to pH compared to temperature.

Table 5.3 Standard deviation analysis of Temperature and pH study.

Strain	pH: 7, 25°C – 40°C			35°C, pH: 5-10			Percentage change in RSD
	Average OD	SD	Relative SD (RSD_1)	Average OD	SD	Relative SD (RSD_2)	
A_3	1.33	0.61	0.46	1.06	0.58	0.54	17.4
A_4	0.8	0.42	0.52	0.68	0.57	0.83	59.6

5.3.3 Effect of individual strains in biodegradation of spent oil:

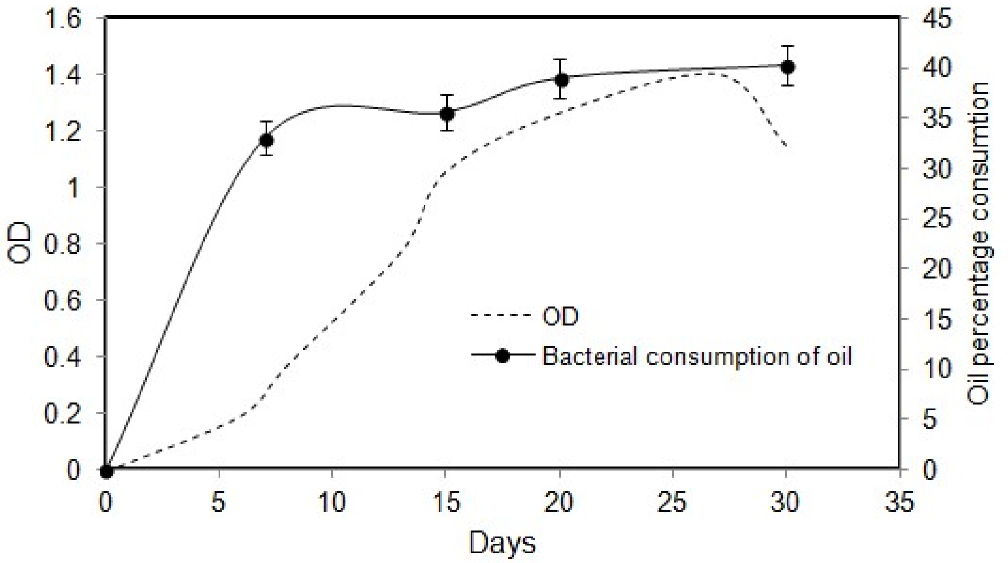


Figure 5.3 Growth curve of strain A_3 and the corresponding percentage consumption of oil.

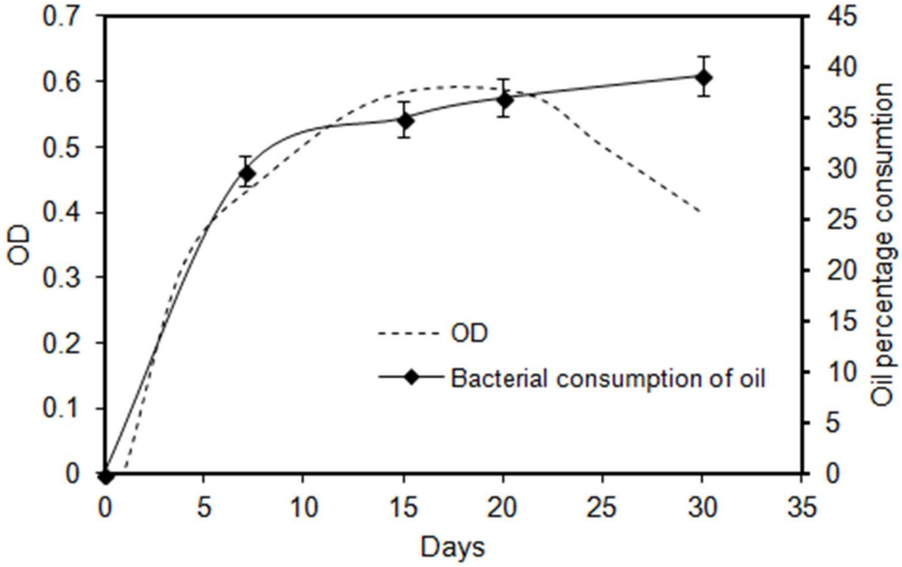


Figure 5.4 Growth curve of strain A_4 and the corresponding percentage consumption of oil.

Figure 5.3 and 5.4 shows the growth curve for strains A_3 and A_4. From figure 5.4 it is evident that first 1-2 days were the initial lag phase and 3-15 days were the log or exponential phase for A_3. However, the stationary phase remains from 20-25th day followed by death phase after 25th day. In comparison, for strain A_4, 1-2 days were the initial lag phase, 3-14 days were the log or exponential phase and 15-20 days were the stationary phase. All the phase behaviours for both the strains that are observed from the figures are compared to the hydrocarbon consumption during their growth. It was observed that the maximum consumption rate of spent oil during the first 7 days, when the microbial growth was in the exponential phase. After that, when the stationary growth phase reached, the spent oil reduction rate was decreased. After 4 weeks around 41% of used spent oil was degraded by the strain A_3 and 39% of oil with strain A_4. Usually, spent oil is composed of multiple persistent pollutants that are non-biodegradable. During the growth of the bacterial strain, the less persistent pollutant primarily degrades, while the higher persistent compounds retains in the medium. From the figure, it is seen that for both the strains, during the death phase the consumption is almost invariant with time. With A_4 strain, the percentage increase in the oil consumption is around 10% and with A_3, there is almost no variation in the consumption. This might attribute to the fact that at this stage, less persistent compounds are maximally exhausted and hence, the residual strains are no longer capable of consuming the hydrocarbons. Moreover, with the hydrocarbon consumption, the compounds like catechol might be released which increases the acidity of the medium. With the increase in the acidity, the growth rate of strain A_4 is also enhanced manifesting a slight increase in the hydrocarbon consumption.

Maximum growth rate μ_{max} was determined from the slope values calculated from the bacterial growth curve (Figure 5.3 and 5.4). It is seen that strain A_3 shows μ_{max} is equal to 0.079 d^{-1}, while for strain A_4 it is 0.0624 d^{-1}. From equation 5.6, the mass doubling period attributing to exponential growth phase of biological strains were enumerated. The value of mass doubling time for strain A_3 was 14 days, while for A_4 it is 7 days. The value of mass doubling time for strain A_3 is twice than that of strain A_4, though the rate constant values are almost same for both A_3 and A_4 viz. 0.017 d^{-1} and 0.016 d^{-1} respectively. As the biomass creation here is proportional to the consumption of hydrocarbons, the two fold value of mass doubling period for strain A_3 compared to A_4 manifests maximum hydrocarbon consumption at the exponential phase. Hence, it is observed that the oil percentage consumption shows a steep curve for A_3 compared to A_4 (Figure 5.3 and 5.4). The biomass yield was 0.53 for strain A_3 and 0.57 for Strain A_4. Figure 5.5 and 5.6 shows first order kinetic model of strain A_3 and A_4 subsequently, where higher R^2 value (0.9674 for strain A_3 and 0.9664 for strain A_4) suggests good fit to the model.

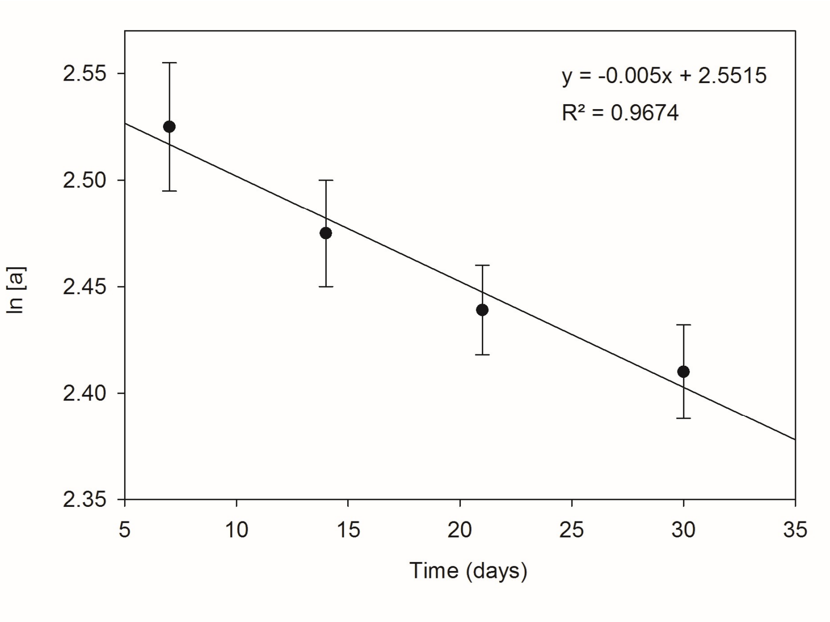


Figure 5.5 First-order kinetic model of strain A_3.

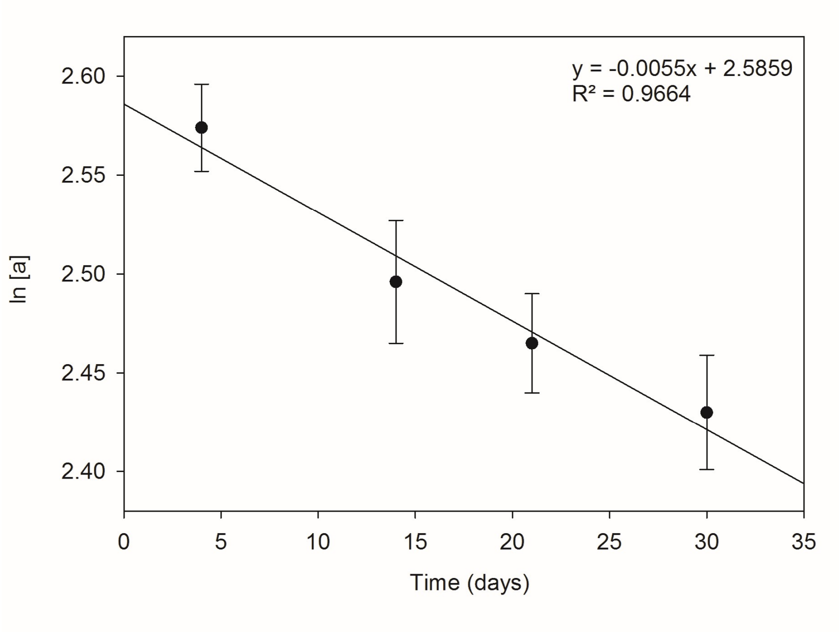


Figure 5.6 First-order kinetic model of strain A_4.

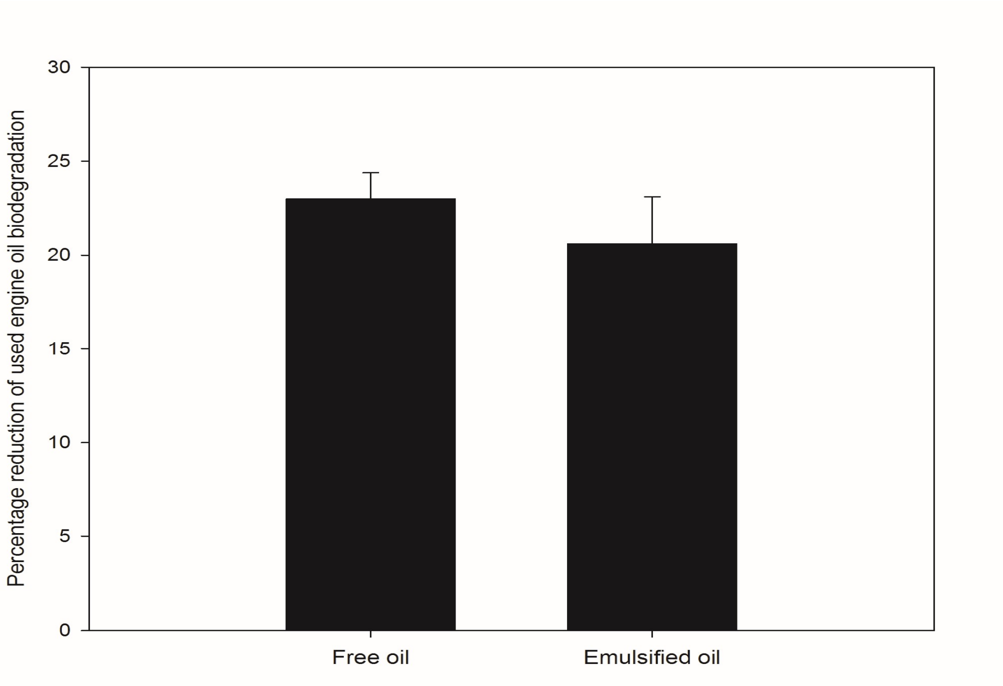


Figure 5.7 Percentage reduction of free oil and emulsified oil by strain A_3.

Figure 5.7 shows the variation in percentage of spent oil degradation by strain A_3 from free oil and emulsion enriched medium. In both the cases, the removal percentage was 21-23%. In o/w emulsion the primary resistance to the oil intake by the bacterial strain might be because of zeta potential barrier and the diffusion through water phase towards the bacterial wall. However, in this case the strain A_3 was found effective in compensating those two resistances.

5.4 Conclusion

The present study illustrates the bioremediation study of spent oil by strain A_3 and A_4, which had been isolated from waste stream coming out of an automobile shop. From the growth it was seen that strain A_4 was pH sensitive and showed substantial growth nature at acidic condition. Both the strains used the spent oil as their carbon nutrients source to grow. Maximum growth of strain A_3 was seen at 35°C temperature and pH 8, while strain A_4 found to exhibit the highest growth at 35°C temperature and pH 6. Here amongst both the strains A_3 comes to be the potent one with 41% removal of free spent oil (30 days incubation) and 21% removal of oil from o/w emulsion (7 days incubation) at optimum growth condition evaluated.

6 Chapter 6:

Conclusion and Future Scope

Aims of the chapter

Present chapter provides an overall conclusion that can be drawn on the entire thesis work. This chapter aims to make some conclusive remarks on the technology that can be adopted to perform oil contaminated wastewater management. Finally, this chapter states the future scope of the present work to extend the ideas removal of oil from oil wastewater streams.

6.1 Conclusion

Present work mainly focuses on the oil contaminated wastewater management. In that respect produced water and the oil contaminated wastewater stream coming out from the automobile industrial premises has been opted as the treatment of concern. In the study of effect of SDBS in produced water the process proceeds from short time interval diffusion controlled regime to the long time adsorption controlled process, when surfactant is added to different produced water. The effect of SDBS much prominent in lower pH values. While studying the efficacy of two indigenous membrane modules RFMM and TFMM, for the treatment of emulsified oily wastewater (O/W emulsion) generated in automobile industry. TFMM gives around 3 fold increase in the permeate flux compared to RFMM with raw untreated emulsion. When the pretreatment process prior to the membrane technology is provided, 15% Sodium sulfate is efficiently demulsifying the emulsified oil contaminated water stream through the reduction in total petroleum hydrocarbon in the emulsified layer. TFMM gives almost 53% increase in the steady state flux for treated feed over the untreated feed at 25°C. The maximum flux was found for the pretreated feed at 15°C for TFMM. Almost eight times energy requirement ratio for the RFMM compared to TFMM and this ensures the suitability of TFMM over RFMM in terms of energy consumption to separate oil from water. In the bioremediation study of used engine oil experimented strain A_3 provides effective biodegradation of free oil as well as the emulsified form of the oil. While studying bioremediation of spent oil, strain A_3 and A_4 , isolated from waste stream coming out of an automobile shop, uses the spent oil as their carbon nutrients source to grow. Here amongst both the strains A_3 comes to be the potent one with 41% removal of free spent oil, prevailing at its optimum growth condition, where strain. Strain A_3 was also found to remove 21% of spent oil from its emulsified form in 7 days.

6.2 Future scope of the work

Economically viable potential technology must be developed for reclamation of oil-contaminated wastewater. Especially treatment of tough to break o/w emulsion of liquid waste stream can be studied further. The designed indigenous membrane assisted EC-EF module in the appendix, can be applied in treatment of oily wastewater for a simultaneous emulsion destabilization and oil separation to produce clarified water. The module can be studied without the membrane, replacing the membrane disk by a stirrer, to sweep away the accumulated mass from the vicinity of electrodes. The module could be served as an electrochemical cell followed an enzyme immobilized membrane reactor. It will provide glycerol, a value added product in biodiesel, from oil after hydrolyzation of glycerides in oil being by enzyme over the membrane surface.

7 Appendix

Aims of the chapter

This appendix is comprising of an indigenous membrane assisted electrocoagulation-electroflotation module preparation to add a future scope of this thesis research which will ensure an unique effective process technology providing simultaneous destabilization and separation of oil to have clarified water from oily waste streams.

7.1 Field of invention

Several process industries produce large amount of wastewater containing several pollutants from their usual processes that compels present world to fight with geminate catastrophe of water dearth and environmental debasement. With the urbanization and therefore, the industrial revolution imparts a significant amount of several pollutants of which oil is the key component that attributes to a complex treatment procedure in order to obtain purified water. Many of these contain different size of oil droplets, metals and biodegradable components that leads to an increase in the BOD(Stephenson, 1992). Especially, the prime concerns revolve around the urban wastewater management, where the wastewater from different small and large scale industries are being drained to cities' sewerage system that ultimately conveys the water to common aquatic region. Thus the drainage of such oily wastewater without proper processing, will eventually lead to an accretion in pollution load of water resources. Presence of oil over the water surface disrupts the aquatic environment as it restricts the avenue of sunlight through water surface, which finally constrains the aquatic life. Moreover, sustainable water reclamation attributes to the reuse and conservation of usable water for future need.

Oily wastewaters generally contain oil in form of free oil and in form of emulsion. Free oil is simply mixed with the aqueous phase floating over the water surface, while the emulsions are stably dispersed throughout the aqueous phase. However, in case of free state, the oil and water are mostly immiscible attributing to a low cost separation processes. The extent of difficulties is higher when the proportion of oil in a wastewater is in a very small amount leading to a formation of tiny oil droplet surrounded by the water molecules after being linked with different emulsifiers present in the wastewater. However, conventional approaches such as dissolved air flotation, chemical coagulation-flocculation, centrifugation to treat such emulsified oily wastewater might not ensure proper separation of oil from water (Cheryan et al., 1998, Abbasi et al., 2010, Srijaroonrat et al., 1999, Salahi et al., 2009).

An indigenous membrane assisted electrocoagulation(EC)/electroflotation(EF) set up has been fabricated to incorporate membrane facility with EC and EF to treat the oil contaminated wastewater, to ensure well extent of separation of oil from oily wastewater simultaneously after demulsification of the waste stream through EC EF. The electrochemical cell will ensure the separation of different size of oil droplets as well as other suspended unwanted particles (silt), through flotation followed by coagulation and settling, while coagulation will reduce the possibility of secondary layer formation over the membrane surface and thereby will enhance the life and reusability of membrane reducing the chances of membrane fouling. As the set up is consisted of UF membrane the treated permeate will be much more purified than the treated water collected from only EC/EF module. The membrane attachment will be equipped with a motor to provide a mild rotation to the membrane disk creating an enhanced shear near the membrane surface to ameliorate the deposition over the membrane and thus the fouling.

7.2 Objective of the module

Objective of the present invention is to cater an indigenous embodiment, where the membrane and the electrochemical arrangements will accommodate in the same module to reduce the possibility of emulsion regeneration during the transport of the oil free water after electrochemical process to the membrane module for further clarification. Henceforth, it will provide a simultaneous destabilization and separation of oil to have clarified water.

A further objective of the present invention is to providing a rotating disk membrane system for filtration involving slow rotation of the membrane, to generate mild tortional shear over the membrane surface and thereby to reducing the possibility of secondary layer formation over the membrane surface.

A still further object is the module could be used with or without the membrane as per requirement. In case while the cell is operating without membrane, the membrane disk would be replaced by a stirrer, which will sweep away the accumulated mass from the vicinity of electrodes.

7.3 Future Scope

The module could be served as an electrochemical cell followed an enzyme immobilized membrane reactor. It will provide glycerol, a value added product in biodiesel, from oil after hydrolyzation of glycerides in oil being by enzyme over the membrane surface.

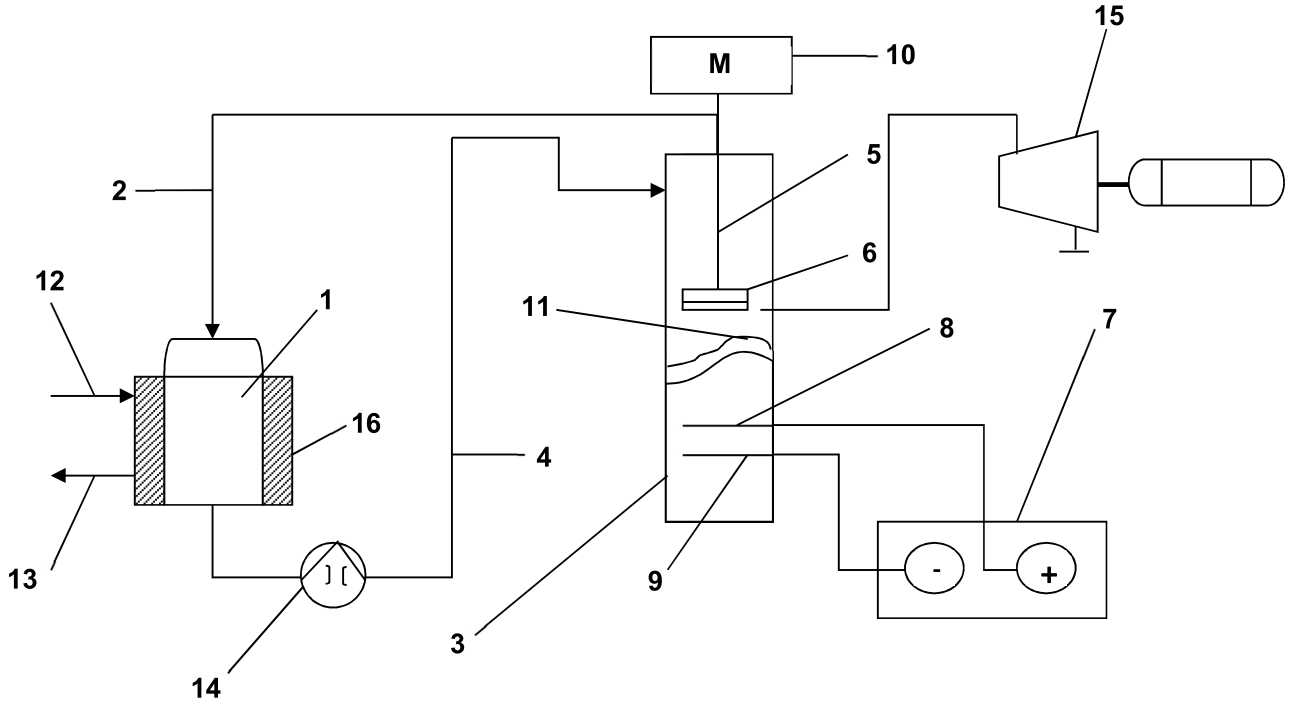


Figure 7.1 Schematic diagram of the membrane assisted ECF set-up 1. feed tank, 2. Recirculation line, 3. ECF embodiment, 4. pipeline, 5. hollow shaft, 6.membrane unit, 7. DC source, 8. Aluminium anode, 9. Stainless steel cathode, 10. motor, 11.floating oil surface at ECF embodiment, 12.water inlet port if feed tank jacket, 13.water outlet port of feed tank jacket, 14.magmnetic pump, 15.air compressor, 16. jacket coil of feed tank.

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