AN INVESTIGATION OF DYE-SURFACTANT INTERACTIONS IN AQUEOUS SOLUTIONS FOR ELUCIDATING THE MECHANISMS OF ULTRAFILTRATION

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ABSTRACT

AN INVESTIGATION OF DYE-SURFACTANT INTERACTIONS IN AQUEOUS SOLUTIONS FOR ELUCIDATING THE MECHANISMS OF ULTRAFILTRATION

Low Molecular Weight Contaminants (LMWCs) in waters are serious environmental concern due to removal problems with classical techniques such as chemical coagulation, biological treatments and adsorption. LMWCs are usually co-present with surface active agents in contaminated waters. Though such advanced removal techniques as ultrafiltration and micelle enhanced ultrafiltration are said to perform better, no systematic study is present for elucidating how the contaminant-surfactants interactions affect removal efficiency.

In this study, methylene blue (MB), a dye widely employed in textile, paper and chemical industries, was chosen as the model contaminant. Surfactants selected were anionic sodium dodecyl sulfate (SDS), cationic hexadecyltrimethyl ammonium bromide (CTAB) and non-ionic ethoxylated octylphenol (TX-100). Surface tension, size, charge and contact angle measurements were conducted to investigate dye-surfactant interactions. Cellulose nitrate filters were employed to determine the effect of these interactions in filtration efficiency.

It was found that significant amount of MB was removed from solution since it attached on the negatively charged cellulose nitrate filter. Though presence of surfactants generally decreased MB removal efficiency, MB-SDS interaction created large-loose aggregates at low SDS concentrations which cannot pass the filter paper. The MB-CTAB/TX-100 interactions created positively charged MB-surfactant pairs which can attach to the filter surface causing a decrease in the removal.

At concentrations above Critical Micelle Concentration (CMC), the efficiency of MB removal is low due to the formation of surfactant-micelles that are smaller than the pores of the filter. Detailed size distribution experiments suggest that MB molecules are within the micelles structure, not in the core as believed in literature and do not increase the size of the micelle.

ÖZET

SULU ÇÖZELTİLERDE BOYA-SÜRFAKTAN ETKİLEŞİMLERİNİN
ULTRAFİLTRASYON MEKANİZMASININ AYDINLATILMASI
AMACIYLA İNCELENMESİ

Sularda bulunan düşük moleküler ağırlığa sahip kontaminantlar kimyasal koagülasyon, biyolojik arıtma, adsorpsiyon gibi klasik yöntemler ile arıtılmaları konusunda zorluklara sahip olmaları sebebiyle çevre için önemli bir sorun teşkil etmektedir. Düşük moleküler ağırlığa sahip kontaminantlar genellikle kirli sularda yüzey aktif maddeler ile birlikte bulunmaktadırlar. Ultrafiltrasyon ve misellar ultrafiltrasyon gibi gelişmiş arıtma tekniklerinin daha yüksek performansa sahip olduğu söylensede, kontaminant-sürfactan etkileşiminin giderme verimliliğini nasıl etkilediğini açıklığa kavuşturacak sistematik bir çalışma bulunmamaktadır.

Bu çalışmada, tekstil, kağıt ve kimya gibi endüstrinin birçok dalında yaygınca kullanılan metilen mavisi (MB) model kirletici seçilmiştir. Sürfaktan olarak, sodyum dodesil sülfat (SDS), heksadesil trimetil-ammonyum bromid (CTAB) ve etoksile oktil fenol (TX-100) kullanılmıştır. Boya-sürfaktan etkileşimin incelenmesi için yüzey gerilim, boyut, yük ve kontak açısı ölçümleri yapılmıştır. Bu etkileşimin filtrasyon verimine etkisini belirlemek amacıyla selüloz nitrat filtre kullanılmıştır.

Sonuçlar incelendiğinde, metilen mavisinin negatif yüklü selüloz nitrat filtreye tutunmasından dolayı çözeltiden önemli miktarda uzaklaştırıldığı görülmüştür. Sürfaktan bulunması durumunda metilen mavisinin uzaklaştırılma verimliliğinin azaldığı, düşük SDS konsantrasyonlarında metilen mavisi-sürfaktan etkileşiminin filtre kağıdından geçemeyecek büyüklükte gevşek agregatlar oluşturduğu gözlemlenmiştir. Metilen mavisi-CTAB/TX-100 etkileşimlerinin pozitif yüklü metilen mavisi-sürfaktan çiftleri oluşturarak, boyanın uzaklaştırılma verimini düşürecek şekilde filtre yüzeyine bağlandığı sonucuna varılmıştır.

Kritik misel konsantrasyonunun üstünde, sürfaktan-misel oluşumları filtrenin gözenek boyutlarına kıyasla küçük olmasından dolayı MB uzaklaştırılma veriminin düşük olduğu görülmüştür. Detaylı boyut dağılım sonuçlarına göre, MB molekülleri literatürde düşünüldüğü gibi misellerin çekirdeğinde değil, yapısında bulunmaktadır.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1. Statement of the Problem: Low Molecular Weight Contaminants (LMWCs)

Contaminants could be any substance which present in elevated concentrations in the environment above the natural background level and contaminants are the main problems for the environment. They are most of the time generated by human activities and some examples are food, chemical, mining industries, household consumptions. In addition contaminants of human origin come in very wide spectrum such as metallic species, toxic gases and LMWCs. There are many sources for LMWCs in wastewater such as metal-plating industries, circuit-board manufacturing process, photo graphic and photo-processing industries, refineries and metal-tailing leachate (Choi et al., 1998). The pollution of nation harbors, waterways and ground water resources with these organics has reached critical proportions, and might also have hazardous influence on human health (Hurter and Hatton, 1992). LMWCs have molecular weight less than 800 Dalton and some examples of LMWCs can be seen from Table 1.1. Some of them are the products and some are input. For instance Polycyclic Aromatic Hydrocarbons (PAH) appear as a result of incomplete burning of organic compounds and they are toxic and have cancerogenic effects while methylene blue (MB) has many uses in a range of different fields, such as biology and chemistry as a dye, redox indicator.

LMWCs are big problem for environment because not only they can be detected in air, water and soil, but also they can be easily transferred between these environments. Because of being human-origin contaminants, the highest concentrations are found in urban areas and the difficulty of removing is associated with its low molecular weight.

Table 1.1. Molecular weights of LMWCs.

LMWCs	Molecular weight (D)
Polycyclic (2 or 3 fused rings) aromatic hydrocarbons (PAHs)	152-178
Acid anhydrides	100-218
Methylene Blue (MB)	374
Cyclonite	222
Atrazine	216
2,4-Dichlorophenol	163
Eosin dye	692

1.2. Commonly Used Removal Methods for LMWCs and MB

As it was mentioned before LMWCs have big implications for environment they are widely generated, hence they have widespread presence in air, water and soil and they have large concentration in urban areas. Due to their small molecular weight they easily transfer between different environments. Therefore, treatment of these contaminants in wastewater has big importance. Wastewater treatment consists some steps 1) pretreatment to do sedimentation and equalization, then primary treatment to stabilize wastewater (Gupta and Suhas, 2009). 2) Biological treatment (Kasprzyk-Hordern et al., 2003) which is impossible because of toxic pollutants in treated water although it can be thought to be economic and applicable. 3) Physical-chemical treatment process and there are lots of tertiary treatment methods to remove LMWCs from water such as adsorption, chemical oxidation, ozonation, membrane separations (Gupta and Suhas, 2009). Treatment of wastewater which contains dye is difficult because dyes are resistant to aerobic digestion and are stable to light, heat and oxidizing agents (Sun and Yang, 2003). In the world, more than 10,000 tones/year dye is consumed in the textile industry and discharge into water streams is approximately 5-10 % of production (Yagub et al., 2012). MB is the most common soluble dye in water which is used in cotton, medical, paint, printing industries. Adsorption which is applied by which contaminants held on the surface and pores of adsorbent is used widely as a treatment method for MB and other dyes. The method has simplicity of design, ability to treat dyes more concentrated from other techniques. Activated carbon is a commonly used sorbent which is effective to remove a large number of organic/inorganic metal

ions but not selective, ineffective against dispersed dyes and it has high cost which limits the usage of the method (Yagub et al., 2012). Coagulation, conventional oxidation methods by oxidizing agent (ozone) are classified as chemical treatment methods. Ozone is used widely because of its high oxidation and disinfection potential but it has some disadvantages such as being low solubility and stability in water, high cost of ozone production and formation of biodegradable organic matter. Chemical coagulation is also another chemical method which is used for treatment. Fine solid particles can be dispersed and dispersed particles can be destabilized by the method. The advantage of the method is that higher overflow rates can be applied and greater removal efficiencies can be achieved. On the other hand, increased operational cost and mass of primary sludge are disadvantages of the method. All the chemical methods cause secondary pollution because of the excessive chemical used and the other reasons for not being effective treatment method are high energy demand and requiring high cost. Filtration is one of the seperation process which can be defined as the separation of two or more componenets from a fluid stream based on size differences. It usually used to seperate solid immiscible particles from liquid and gaseous streams and membranes act as a selective barrier. Membrane filtration process is one of the physical methods for the treatment of dyes just as adsorption. Membrane process removes many types of large molecules and ions from solutions by applying pressure to the solution when it is on side of the selective membrane. There are lots of reasons why membrane separations are being used more and more frequently. First of all, membrane process can be easily included in the whole process in the wastewater treatment and the use of the membrane separation in the wastewater treatment containing toxic inorganic is an attractive and suitable technique. Membrane separation processes do not require phase change to make separation as a result energy requirement will be low. In addition, membrane process has no complex control schemes compared to many other treatment processes with very simple flow sheet thus this process has low maintenance process option. Moreover, membrane process can be preferred because of the low energy and space requirement and better for the environment since the membrane treatment require the use of relatively simple and non-harmful materials (Bohdziewicz et al., 1999). Nanofiltration, ultrafiltration and reverse osmosis are some types of membrane process. Table 1.2 shows the main membrane processes.

Table 1.2. Main membrane processes.

Process	Driving fore	Retentate	Permeate
Osmosis	Chemical potential	Solutes, water	Water
Dialysis	Concentration difference	Large molecules, water	Small molecules, water
Microfiltration (MF)	Pressure	Suspended particles, water	Dissolved solids, water
Ultrafiltration (UF)	Pressure	Large molecules, water	Small molecules, water
Nanofiltration (NF)	Pressure	Small molecules, divalebt salts, dissociated acids, water	Monovalent ions, undissociated acids, water
Reverse osmosis (RO)	Pressure	All solutes, water	Water

Osmosis can be defined as the transport of solvent through a semipermeable membrane from the dilute solution side to the concentrated solution side of the membrane. Reverse osmosis (has filter pore size around 0.0001 micron) is used widely to treat dye wastewater though this method has low permeability and requiring high operating pressures like as nanofiltration (Purkait et al., 2004). Reverse osmosis retains all components other than the solvent. Dialysis process is used to purify macromolecules by using concentration difference of the permeable species between the solution in the dialysis bag and outside the bag. Microfiltration, ultrafiltration, nanofiltration and reverse osmosis are pressure-driven membrane process and they are applicaltion of hydraulic pressure to speed up the transport process. All membrane processes have different separation molecule sizes. Surface water and fresh ground water which contains low total dissolved solid can be treated by nanofiltration with a membrane which have pore size typically about 1 nanometer. Nanofiltration is applied as an intermediate process between ultrafiltration and reverse osmosis (Ong et al., 2014). Ultrafiltration can separate particles smaller than 0.001-0.02 μm. Microfiltration have suspended particles in the range of 0.1 μm to about 5 μm. In microfilration and ultrafiltration, the pressure gradient across the membrane would force solvent and smaller species through the pores of the membrane, while the larger molecules/particles would be retained. The retained stream is called as retentate will be enriched int he retained macromolecules and permeate is the stream which is going through the membrane. Pressure required is low for ultrafiltration because of separating large molecules than reverse osmosis and nanofiltration. In addition, smaller molecules can be treated by ultrafiltration than microfiltration. Thus, ultrafiltration is most applicable

membrane process with low pressure requirement, low energy consumption and low operating cost (Cheryan, 1998). The modified ultrafiltration process is MEUF which combines high selectivity of reverse osmosis and high flux of ultrafiltration (Baek et al., 2003). Schematic form of membrane process can be seen from Figure 1.1.
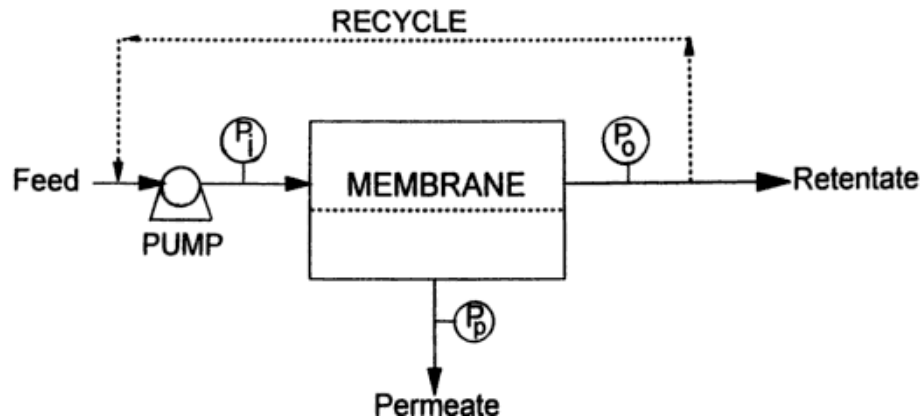
Figure 1.1. Membrane process.

Ultrafiltration membranes can be made from both organic (polymer) and inorganic materials. There are several polymers used for membranes and polymer is chosen as a membrane material according to some properties such as molecular weight, chain flexibility, chain interaction. Polysulfone, polyethersulfone, sulfonated polysulfone, polyvinylidene fluoride, polyacrylonitrile, cellulosics, polyimide, polyetherimide, aliphatic polyamides, and polyetherketone are some of the organic membrane materials while alumina and zirconia are used as inorganic membrane material (Wenten and Ganesha, 1996).

As a summary of the treatment methods, advantages and disadvantages can be seen from Table 1.3. Although there are different treatment methods, all have some shortcomings. For example, they are not very successful for low molecular weight components and they are not applicable at relatively low contaminant concentrations. Also, they are usually expensive and require high pressures.

Table 1.3. Commonly used treatment technologies for dyes.
(Source: Crini, 2006)

Technology	Advantages	Disadvantages
Coagulation	Simple, economically feasible	High sludge production, handling and disposal problems
Biological treatment	Economically attractive, applicable	Not suitable for toxic wastewaters, slow process, necessary to create an optimal favorable environment
Activated carbon adsorption	Simple design, the most effective adsorbent, great, capacity, produce a high-quality treated effluent	Ineffective against disperse, expensive regeneration and results in loss of the adsorbent, non-destructive process
Oxidation	Rapid and efficient process	Low solubility in water, high energy cost, chemicals required
Membrane separations	Removes all dye types, low space requirement, produce a high-quality treated effluent	Fouling, high operating pressures, expensive, effective on small volumes of water

1.3. Micellar Enhanced Ultrafiltration (MEUF)

MEUF is a surfactant-based separation process which is effective for removing many contaminants such as heavy metals (i.e. lead, cadmium), LMWCs (i.e. MB, Reactive Black 5 and Orange 16, Eosin dye, Direct Blue 71) and toxic organic materials (i.e. Phenol, Di-butyl Phosphate (DBP), Tri-Butyl Phosphate (TBP)) from wastewater (Ruzitah and Sharifah, 2011; Zaghbani et al., 2007). It combines the benefits of surface active agents and ultrafiltration membranes and based on the following principles: Attaching LMWC to a surfactant molecule, forming larger micelles from loaded surfactant molecules and separating the micelles from water using a membrane (Scamehorn et al., 1982). Ultrafiltration membrane which has lower pore size than contaminants can be used but, as LMWC are very small molecules, to be successful with very small pore size with high flow rates, high pressures have to be applied. By having larger size with micelles, the system can work at low pressures with low energy consumption. To sum up the advantages of MEUF, LMWCs can be captured efficiently even at low contaminant concentrations. The other advantage is that it can employ

anisotropic membranes in wide range of pore sizes. Moreover, the system requires low pressure hence lower energy consumption. By using these advantages, it can provide higher flow rates (Ruzitah and Sharifah, 2011). However, the mechanism of how MEUF actually works is not clear (Lee et al., 2005). Studies on the solubilization of aqueous MB in surfactant using MEUF (Purkait et al., 2005) have shown that, the micelle is made up of the inner core (constituted by hydrophobic groups), palisade layer (constituted by CH_2 groups) and outer layer (constituted by hydrophilic groups). The organic matters get embedded in the micelles via ''like dissolves like'' principle while heavy metal ions are adsorbed on the opposite-charged micelles via electro-static interaction. Ionic surfactants have higher CMC value than nonionic surfactants and cationic surfactants have higher cost values than nonionic surfactants. The monomeric surfactants permeating through the membrane can cause secondary pollution. To solve those problems mixed surfactant systems can be applied. Decrease in charge density and electrical potential can be observed when nonionic surfactant is added into the ionic surfactant solution because hydrophilic part of nonionic surfactant balances the charge of ionic hydrophilic groups. Decreasing electrical potential and electrical repulsion results as formation micelles with lower CMC as a results of decreasing charge density (Lee et al., 2005). In the literature studies, MEUF is classified into four categories which are MEUF using cationic surfactant, MEUF using anionic surfactant, MEUF using nonionic surfactant and MEUF using mixed surfactant (Ruzitah and Sharifah, 2011).

Bielska and Szymanowski claim that MB can be solubilized in the micelles of anionic surfactants due to their positive charge (Bielska and Szymanowski, 2006) and Luo showed larger hydrodynamic diameters of micelles in the presence of micelles (Luo et al., 2010).

According to Huang et al (2012) most of the MB molecules were adsorbed on the ultrafiltration membrane without surfactant and the retentate MB concentration increased with increasing SDS concentration. Permeate and retentate MB concentrations increased with increasing MB concentration because of more MB molecules in water and retentate MB concentration increased with increasing feed SDS concentration due to more aggregated micelles (Huang et al., 2012). When surfactant concentration increased, the absorbance of monomer and dimer increased because of two different processes which are formation of SDS premicelles taking up dye molecules and attribution to the suppression of electrostatic interaction between dye

molecules by more surfactant monomers. In addition, at the CMC value of the SDS, all dye molecules are solubilizes into normal micelles as monomeric molecules. Variation of absorbance of MB as a function of cationic (CTAB) and neutral (TX-100) surfactant concentrations did not show any change on the absorbance of MB when the concentrations of surfactant TX-100 and CTAB varied on both sides of CMC because of the variation in the absorbance of MB with SDS is due mainly to an electrostatic interaction and MB retention was feasible only in the presence of the anionic surfactant because of the opposite charge of the components. Moreover, there is no retention of MB in the presence of CTAB and the electrostatic interaction between MB and surfactants plays an important role in the retention. According to Zaghbani et al (2007), MB molecules are much smaller than the membrane pores the retention could be attributed to the adsorption of dye at the surface or in the pores of membrane and since the dye is solubilized on the surfactant micelles, which are held by the ultrafiltration membrane. Energy of repulsion between charged head group of micelles which concludes a decrease in the CMC and an increase in the aggregation number of micelles decreases with increasing ionic strength and the free counter ion concentration (Zaghbani et al., 2007).

Misra et al (2009) claimed that metal anions/cations are captured by micelles are having cationic/anionic heads while dissolved organic or non-polar organic matters in the aqueous solutions are absorbed by the tail of micelles. They found that there is no metal ions in the retention with the surfactant which was added less than its CMC concentration (Misra et al., 2009). Retention rates for the MEUF process were higher than that for the UF and dye molecules are solubilized within the surfactant micelles which are retained by membrane. For example, while the dye retention is less than 30 % in the surfactant free system, the retention increased to 96.5 % in the presence of CTAB surfactant at the same pressure and time conditions (Zaghbani et al., 2009).

Bielska et al (2009) said that premicellar surfactant aggregation and enhanced dye dimerization with more surfactant monomers present in the solution can be explained by increasing intensity of absorption bands at 660 and 612 nm with increasing SDS concentration. Moreover, as there is more stronger repulsion forces between the same charged dye and surfactant than the hydrophobic and Van der Waals interaction, there is no visible spectra of the dye and new band in the CTAB experiments (Bielska et al., 2009). Polyethersulfone (PES), cellulose (CQ) and polyvinylidene fluoride (PVDF) membranes which have static wetting angles are equal to 53.8, 54.8 and 66.1,

respectively, were used and similar fluxes were obtained for each membrane (Majewska-Nowak et al., 1997). Dynamic wetting angle can depend on the permeate flow and static angle is not significant parameter to differentiate membranes. The retention depended on the type of membrane and surfactant. Hydrophilic membrane made of cellulose and SDS solution gave the best retention results (above 94%) while the worst results (36.2 %) was obtained for oxyethylated coconut fatty acid methyl esters (OMC-10) used alone could not form the ion pair with the dye (Bielska and Szymanowski, 2006).

1.4. Scope of the Study

Low molecular weight contaminants are difficult to remove from waters. Hence, more advanced removal strategies such as ultrafiltration and micelle enhanced ultrafiltration are being developed to improve removal efficiency. Presence of surface active agents which have a potential to bind the contaminant molecules only make the system more complicated. Hence, before utilizing such advanced removal technologies, a systematic characterization of the surfactant-contaminant system should be carried out to determine the potential success and the window of operation of these techniques.

The scope of the study is to investigate the interactions between a model contaminant (methylene blue) in the presence of anionic, cationic and non-ionic surface active agents in aqueous solutions and their effect on ultrafiltration performance. Hence, the study is focused towards understanding the behavior of methylene blue and surfactant molecules individually and together in aqueous systems. The specific objectives of the study are;

1. Characterization of the morphology and physicochemical properties of various anionic, cationic and non-ionic surfactants in the absence and presence of MB. For this purpose, surface energy, size and charge measurements were carried out in surfactant solutions of varying concentrations to shed light on association behavior of surfactant molecules within themselves (micelles) and with MB.

2. Evaluation of the influence of morphology and physico-chemical properties of the surfactants and surfactant-MB pairs on ultrafiltration (removal) efficiency.

CHAPTER 2

METHYLENE BLUE AND SURFACTANTS

2.1. Methylene Blue (MB)

Chemical compounds that can attach themselves to surface or fabrics for the aim of transmit color are called as dyes. Dyes are very stable compounds with their aromatic structures and they are durable to chemical or biological degradation. Because of this reason, it has challenge to treat the dye from wastewaters. Annual production of dye is more than $7x10^5$ tones/year and more than 100 commercial dyes can be achieved (Aguayo-Villarreal et al., 2014). Dyes have an importance in chemicals with usage of different areas such as paper, textiles, plastic. Dyes, even in low concentrations, are visually detected and meanwhile affect the aquatic life. Dyes are classified according to their structure, color, application methods and their particle charge upon dissolution in aqueous applications. Cationic dye (all basic dyes), anionic dye (direct, acid, and reactive dyes) and non-ionic dye (dispersed dyes) are types of dyes based on their particle charge (Clarke and Anliker, 1980). Anionic dyes are used widely with their bright colors and less toxicity than other dyes and they have problems such as having high hydrolyzing tendency and high tinctorial value (Auta and Hameed, 2011). Anionic dyes have a net negative charge because of the presence of sulphonate (SO_3) groups and cationic dyes have net positive charge due to presence of protonated amine or sulfur containing groups (Netpradit et al., 2004). Human-being focused on removing cationic dyes such as MB that is because cationic dyes are highly toxic by comparison with anionic and non-ionic dyes. MB is most common cationic dye consisting of dark green crystals or crystalline powder which has wide application areas such as coloring paper, temporary hair colorant, oxidization-reduction process dyeing cottons, wool and coating for paper stocks, microbiology and surgery. MB is heterocyclic aromatic compound with molecular formula ($C_{16}H_{18}ClN_3S$, $3H_2O$). Some physical properties and molecular structure of MB can be seen from Table 2.1 and Figure 2.1, respectively. The chemical name of MB is 3, 7-bis (dimethylamino)-phenazathionium chloride tetramethylthionine

chloride. MB is UV-visible chemical compound. It is soluble in water and it has a deep blue color in water (Lo et al., 2014).

Table 2.1. Physical properties of MB.
(Source: Chen et al., 2012)

Chemical	Molecular mass, g/mol	Characteristic wavelenght, λ/nm
Methylene Blue (MB)	320	665

While the dye is not classified as highly toxic, it has many dangerous effects on human and animals (Hassan et al., 2014). It can cause some specific harmful effects in humans such as heartbeat increase, vomiting, shocks, cyanosis, jaundice, and tissue necrosis even its low toxicity (Aksu et al., 2010). It can affect the photosynthetic activity in aquatic life due to decreased light penetration and can be toxic to some aquatic life (Yagub et al., 2014). Both biological and chemical treatment methods are applied to remove MB from water however, MB is non-biodegradable as most of the dye and not affected from these methods successfully (Gürses et al., 2014).
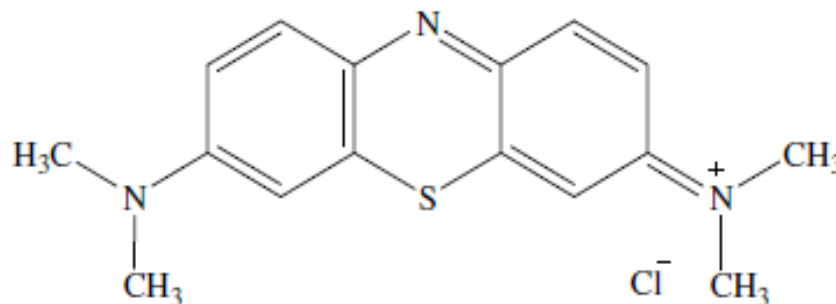
Figure 2.1. Molecular structure of MB.

MB is considered as a contaminant and the ministry of environment and urban planning regulation limits for this chemical only for different water classes are given in Table 2.2. They classified the water according to its constituent limits in four groups which are high quality, low contaminated, contaminated, and highly contaminated water. The first one can be used as a drinking water after disinfection while second one can be used household use, and the third one is suitable for industrial applications.

Table 2.2. Regulation limits for MB.

	High quality water, I	Low contaminated water, II	Contaminated water , III	Highly contaminated water, IV
Can be used for	Drinking water (after disinfection)	Household use (washing, swimming)	Industrial use (except food, textile)	Water contaminated above I,II and III
Methylene blue (mg/L)	0.05	0.2	1	>1.5

2.2. Surfactants and Micellar Structures

Surfactants are short for surface active agents which are chemicals that adsorb at surfaces/interfaces due to their dual structures: hydrophilic and hydrophobic part in one molecule. These chemicals lower the surface tension of a liquid, increasing the contact between the liquid and another substance. Working principle of surfactants is known as adsorption. They tend to be on the surface of liquid and creating film which lowers the surface tension. Surfactant molecules involve two main parts. The first part is water-liking group which is called as hydrophilic and the other part is water-hating part which can be described as hydrophobic or lipophilic. There is many type of hydrophilic and hydrophobic part and combination of these hydrophilic and hydrophobic groups form a great number of different surfactant types. Hydrophilic part can be sulfate, carboxylate, phosphate, betaines, sucrose, polypeptide while hydrophobic part can be formed by paraffin, olefins, polyoxypropylenes, fluorocarbons, alcohols. Hydrophobic part is hydrocarbon chain and surfactant is classified according their hydrophilic part as anionic, cationic, amphoteric and nonionic. Nonionic surfactants have no charge on their hydrophilic part and hence does not dissociate into ions. However, some nonionic surfactants such as tertiary amine oxides are able to have charge depending on the pH value. Moreover, polyethylene oxides can exist in cationic form under acidic conditions while long-chain carboxylic acids are non-ionic under neutral and acidic conditions and anionic under basic conditions. Consequently, definition of nonionic surfactant depends on working range of pH (Möbius et al., 2001). Compatibility with all other types of surfactants is one of the advantage of nonionic surfactants. In addition they can be made

resistant to hard water and they are soluble in water and organic solvents. Anionic surfactants consist of negatively charged group in their hydrophilic part like a sulphonate, sulphate and carboxylate. Dispersing ability, high foaming, sensivity to water hardness are most characteristic properties of anionic surfactant. If the surface-active portion bears a positive charge, it can be classified as cationic. According to the chemical structure, cationic surfactants are subdivided into the following main classes: alkyl amines, ethoxylated amines, alkyl imidazolines, and quaternaries. Cationic surfactants do not generally provide effective cleaning and therefore, they are not used in general-purpose detergents. The surface-active which is amphoteric (zwitterionic) portion bears both charges. This means that they can act as anionic surfactant in an alkalic solution or cationic surfactant in an acidic solution. They show both anionic and cationic properties in dependent of the pH. Long chain amino acid salts and betaines can be given as an example (Laughlin, 1994). Zwitterionic surfactants have advantages such as compatibility with all other types of surfactants, less irritating properties to skin and eyes and ability of adsorbing onto both negatively and positively surfaces without forming hydrophobic film. On the other hand, they are generally insoluble in most organic solvents. Schematic form of surfactant structure can be seen from Figure 2.2.
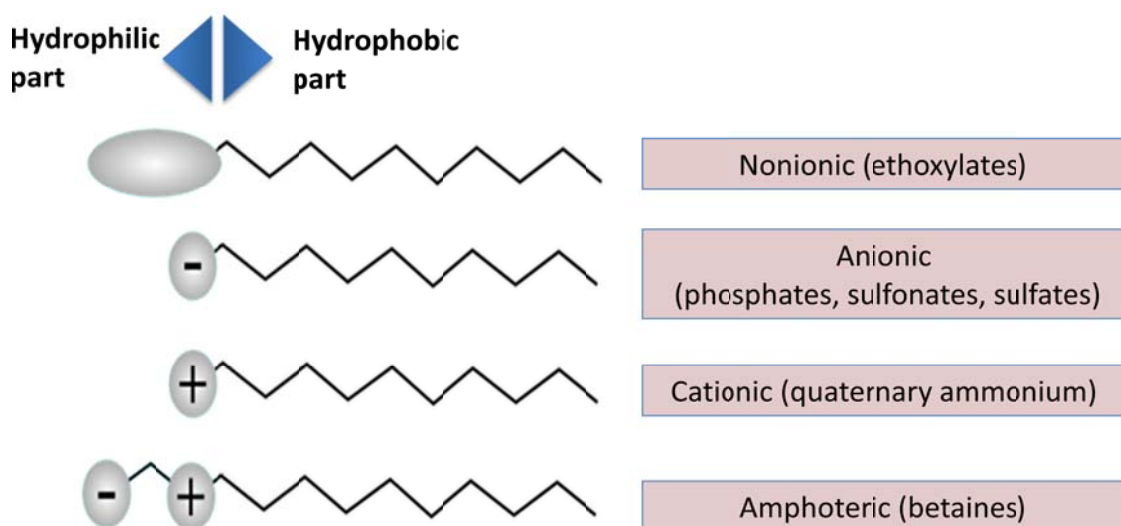

Figure 2.2. Schematic form of surfactant structure.

The attraction between the liquid's molecules by intermolecular forces creates surface tension. In the bulk of the liquid, each molecule is pulled equally in every direction by neighboring liquid molecules, resulting in a net force of zero. At the surface of the liquid, the molecules are pulled inwards by other molecules deeper inside

13

the liquid and are not attracted as intensely by the molecules in the neighboring medium. Therefore, all of the molecules at the surface are subject to an inward force of molecular attraction. When a molecule with amphipathic molecular structure which means it has lyophobic and lyophilic in one molecule dissolved in a solvent, it results in increasing free energy of the system and minimizing contact angle between lyophobic group and the solvent. As the same result, when a surfactant molecule dissolved in aqueous medium, hydrophobic part breaks hydrogen bonds between water and some of the molecules sent to interfaces of the system with their hydrophobic groups oriented so as to minimize contact angles with the water molecules. Single layer of surfactant molecules covers the surface of the water with their hydrophobic groups oriented towards the air. As air molecules are nonpolar like hydrophobic parts, surface tension of water decreases as a result of decrease in the dissimilarity of the two phases contacting each other. Hydrophilic part prevents the surfactants from being expelled from the solvent as a separate phase.

Adsorption at interfaces and aggregation in the solution bulk are significant behavior of surfactants. Adsorbing at interfaces and forming micelles, surfactants play an important role in wetting, dispersing, foaming, solubilizing and a great number of other phenomena (Möbius et al., 2001). Surfactants mainly do not exist in nature; they are manufactured by chemical reaction. Surfactant molecules have higher potential energies than those in the bulk because they interact more strongly with the molecules in the interior of the substance than they do with the widely spaced gas molecules above it. To bring a molecule from the interior to the surface, work is required.

Cationic surfactants can be used to have hydrophobic surface. They adsorb onto the surface with positively charged hydrophilic head group to negatively charged surface because of electrostatic attractions and the hydrophobic group oriented away from the surface. In addition, anionic surfactants make the surface hydrophobic. Nonionic surfactants adsorb onto surface according to surface properties. If polar groups capable of H bonding with the hydrophilic group of surfactant are present on the surface, the surfactants can adsorbed with its hydrophilic group toward the surface, making the surface more hydrophobic. If such groups are absent from the surface, the surfactants will be oriented with its hydrophobic group towards the surface to make the surface more hydrophilic. Zwitterionics can absorb onto both negatively and positively charged surfaces without changing the charge of surface. While adsorption of a cationic onto a negatively charged surface can reverse the surface to a positive charge,

adsorption of an anionic onto a positively charged surface can make the surface negatively charged. Figure 2.3 show the surfactants in bulk and surface as a single molecule and micelle.
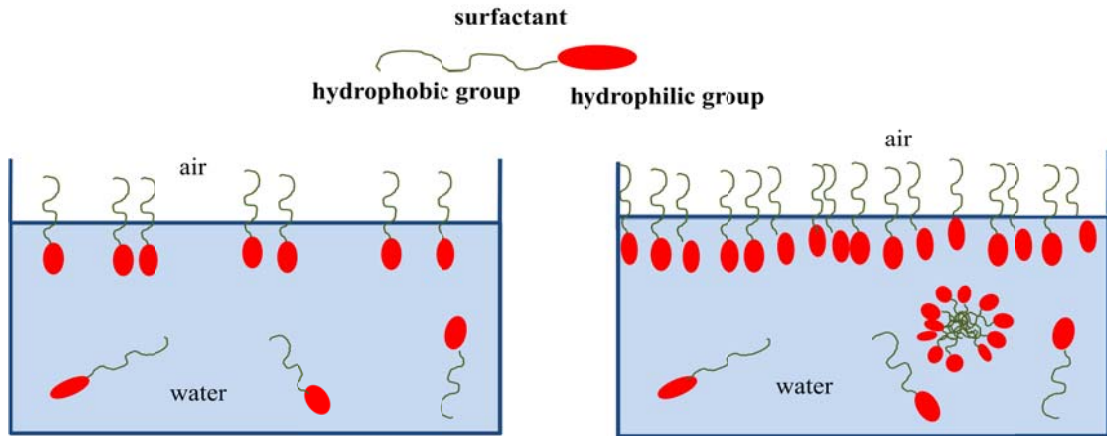

Figure 2.3. Surfactants in bulk and surface.

When surfactants adsorb at liquid/gas interface they change the surface tension of liquid significantly. At very low concentrations the molecules lie along the interface between water and the surface. As the concentration increases they gradually align up as available space is filled, until a complete monomolecular layer is formed. When surfactants are added to solution, surface tension starts to be reduced and decreases up to the CMC. At this point the surface is full of surfactant. If the surfactants are added after this point, surfactants start to aggregate to form micelles which are surfactant aggregate and the surface tension remain constant because there is no change at the surface.

Langmuir-type isotherm is observed in adsorption from solutions of surfactants if the absorbent is homogeneous, both solute and solvent have equal molar surface area, both surface and bulk phases exhibit ideal behavior (no solute-solute or solute-solvent interactions and the adsorption film is monomolecular. The formulation for Langmuir adsorption isotherm can be seen below;

$$\Gamma_1 = \frac{\Gamma_m c_1}{c_1 + \alpha} \tag{2.1}$$

where Γ_1: the surface concentration of the surfactant, in mol/cm^2, at monolayer adsorption

15

c_1: the concentration of the surfactant in the liquid phase at adsorption equilibrium, in mol/L

α: a constant (α=55.3 $e^{\Delta G^O/RT}$), in mol/L, at absolute temperature T, in the room temperature and ΔG^0 is free energy of adsorption at infinite dilution.

Krafft temperature is the temperature at which surfactant solubility equals the CMC. Above the Krafft temperature surfactants form micellar dispersions; below the Krafft temperature the surfactant crystallizes out of solution as crystallizes out of solution as hydrated crystals. Shape of micelles and their characteristics depend on their molecular structures which are nonpolar tail, polar head group and counter-ion and it can change with conditions such as solvent medium, temperature, ionic strength and pH. The shape of micelles can have hexagonal, cubic, lamellar or reverse micelles structures as can be seen form Figure 2.4.
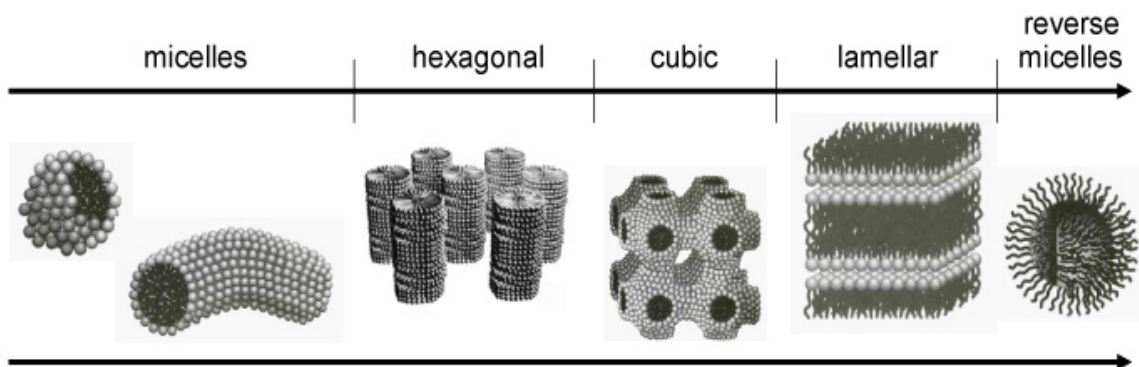

Figure 2.4. Shapes of micelles.

Micellar growth is associated with electrostatic and hydrophobic interaction between surfactant and additive. If the additives weakly polar and sparingly soluble substances such as medium chain alcohols, amines and phenols electrostatic interaction decreases the surface area of the head group which allows micallar growth (Singh et al., 2013). On the other hand, highly polar substances like short chain alcohols and amides disintegrate micelles (Patel et al., 2014).

Micelles are important in several applications such as textile, environment, food, cosmetic, so formation of micelles is important.

Figure 2.5 shows the plot which use surface tension and surface concentration data of surfactant solution. It is seen that at the low surfactant concentration, surface tension has the highest value.
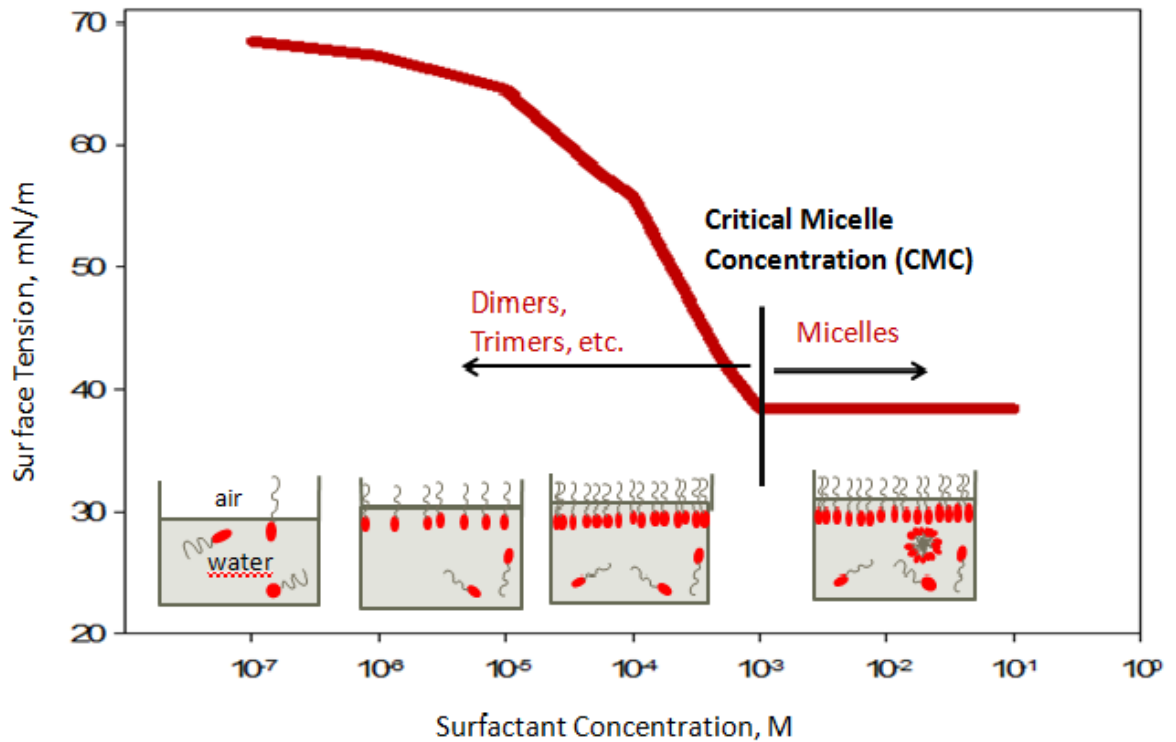
Figure 2.5. Surface tension change with surfactant concentration.

2.3. Micellar Enhanced Ultrafiltration (MEUF)

MEUF is one of the separation technology in separating LMWCs (Reactive Black 5 and Orange 16, eosin dye and MB), heavy metals (lead, zinc), toxic organic materials (phenol), Di-Butyl Phosphate (DBP), Tri-Butyl Phosphate (TBP) from wastewater by combining benefits of surface active agents and ultrafiltration membranes. MEUF is based on the following principles:

1. Attaching LMWC to a surfactant molecule
2. Forming larger micelles from loaded surfactant molecules
3. Separating the micelles from water using a membrane

Although Reverse Osmosis (RO) and Nanofiltration (NF) are recognized as better technique for separation of some inorganic and organic compound, permeability of RO membranes is very low and requires high operating pressures to get desired amounts. Moreover, traditional treatment methods such as adsorption, biological treatment, oxidation, coagulation have some difficulties such as not being successful for low molecular weight components, applicable at relatively high concentrations, expensive and requiring high pressures. Because of the shortcomings, MEUF method

was developed (Purkait et al., 2006). The advantages of MEUF can be seen from Table 2.3.

Table 2.3. Advantages of MEUF.

Advantages of MEUF
Efficient for capturing LMWCs
Can employ anisotropic membranes in wide range of pore sizes (1 to 10 nm)
Can provide higher flow rates
Effective for low contaminant concentrations
Requires low pressures; hence lower energy consumption

To apply MEUF, surfactants are added into the aqueous stream containing contaminants or solute above its CMC. When the surfactant concentration exceeding the CMC value, the surfactant monomers will assemble and aggregate to form large micelles having diameter larger than the pore of ultrafiltration membrane. During this process the contaminants are caught in micelles if they tend to attached by micelle. While micelles having solubilized contaminants with larger diameter than membrane pore size will be rejected by membrane during ultrafiltration leaving only water (Ruzitah and Sharifah, 2011). The schematic form of MEUF can be seen from Figure 2.6.
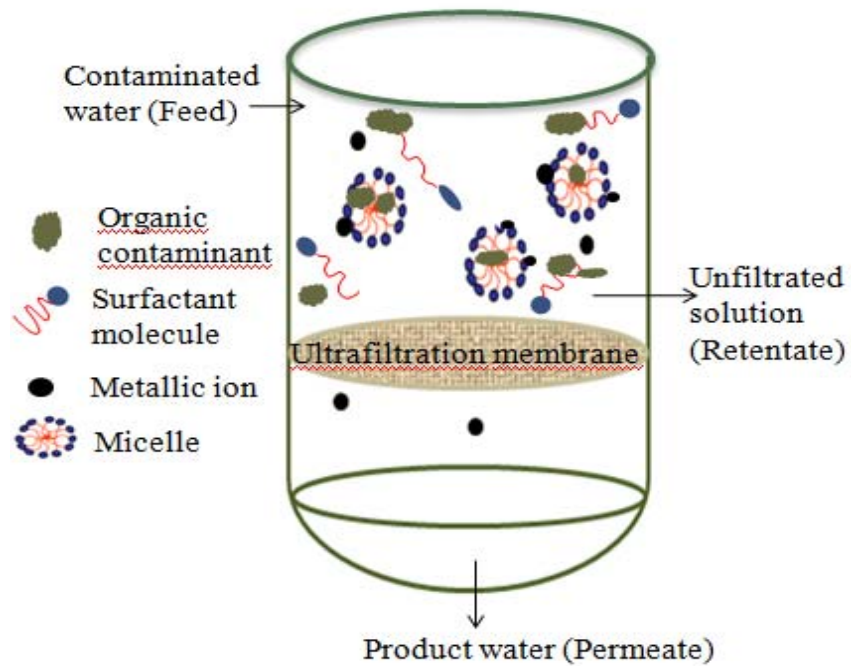
Figure 2.6. Representation of MEUF process.

The characteristics of solute and membrane designate the solute rejection and permeate flux. The increased hydrodynamic size of the solutes enables their rejection by polymeric ultrafiltration membrane (Baek et al., 2003). During the MEUF process unsolubilized contaminants, unbounded ions and surfactant monomers stay in permeate stream as seen from Figure 2.7.
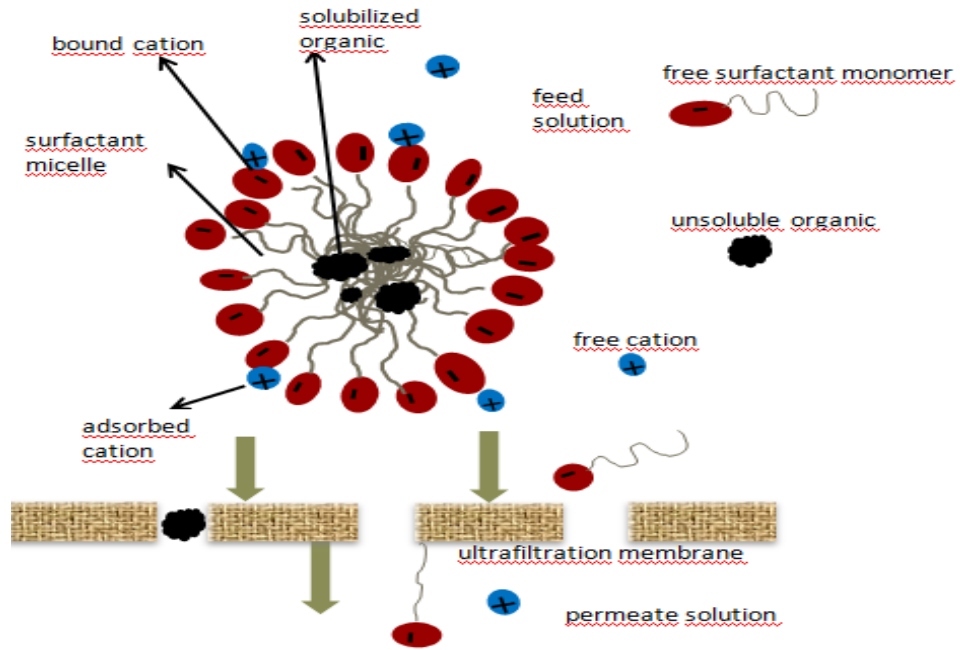
Figure 2.7. Contaminants captured by micelles and ultrafiltration membrane.

The most important parameter for MEUF is CMC where surfactants start to form micelles. The aggregation number of micelles is depends on the type of surfactant. The non-ionic surfactants normally constitute clusters of 1000 or more molecules while ionic surfactants generally only manage to create clusters of 10-100 molecules, because their charges create electrostatic repulsions between head-groups which tend to break the particles apart.
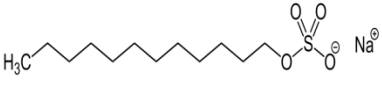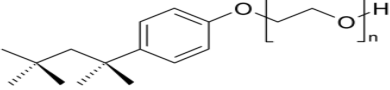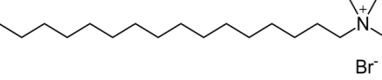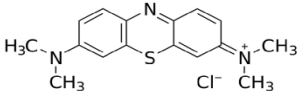
CHAPTER 3

MATERIALS AND EXPERIMENTAL METHODS

3.1. Materials

All three surfactants (anionic sodium dodecyl sulfate, cationic hexadecyl trimethylammonium bromide and non-ionic ethoxyleted octyl phenol) and the model contaminant (MB) were obtained from Sigma-Aldrich, United States (Table 3.1). Dimensions of a single methylene blue molecule is 1.43 x 0.61 x 0.4 nm which gives a molecular volume of around 0.35 nm^3 (Pelekani and Snoeyink, 2000). Cellulose nitrate membrane filters with pore size of 0.45 µm and 0.2 µm were supplied by Sartorius Stedim Biotech, Germany (Figure 3.1). Chemical structures and some selected properties of surfactants used are given in Table 3.1.

Table 3.1. Some selected properties of surfactants used.

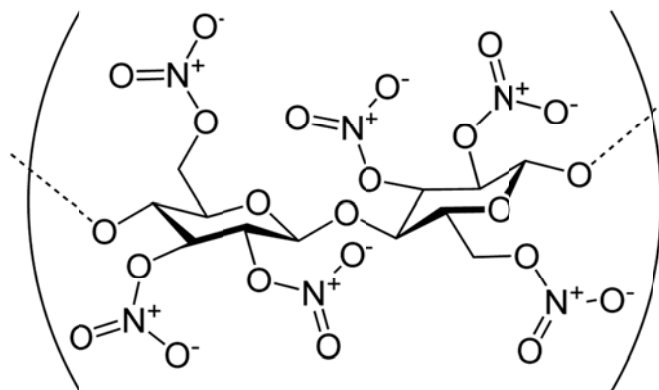| Compound name	MW (Dalton)	Chemical structure	Explanation
Sodium Dodecyl Sulfate (SDS)	288		Anionic Surfactant
Ethoxylated Octyl Phenol (TX-100)	628		Nonionic Surfactant
Hexadecyl Trimethyl-Ammonium Bromide (CTAB)	364		Cationic Surfactant
Methylene Blue (MB)	320		Organic Contaminant

Figure 3.1. The structure of cellulose nitrate filter paper used for ultrafiltration.

3.2. Methods

The methodology of this study is given in Figure 3.2. Surfactant solutions were prepared with surfactant and water. Then surface energy measurement, size measurement and charge measurements were applied to surfactant solution to characterize the surfactant molecules. After examined the micellar behaviors according to characterization results the same study were done presence of methylene blue to obtain micellar behavior of surfactant solution with methylene blue. Then ultrafiltration was applied to surfactant solutions which include methylene blue as a contaminant. By using UV-spectrometer analysis, MB concentrations were obtained. The mechanism of removal was examined by combining all the results and information. The details of all the experiments conducted and the methods used in this study will be summarized in the following paragraphs.
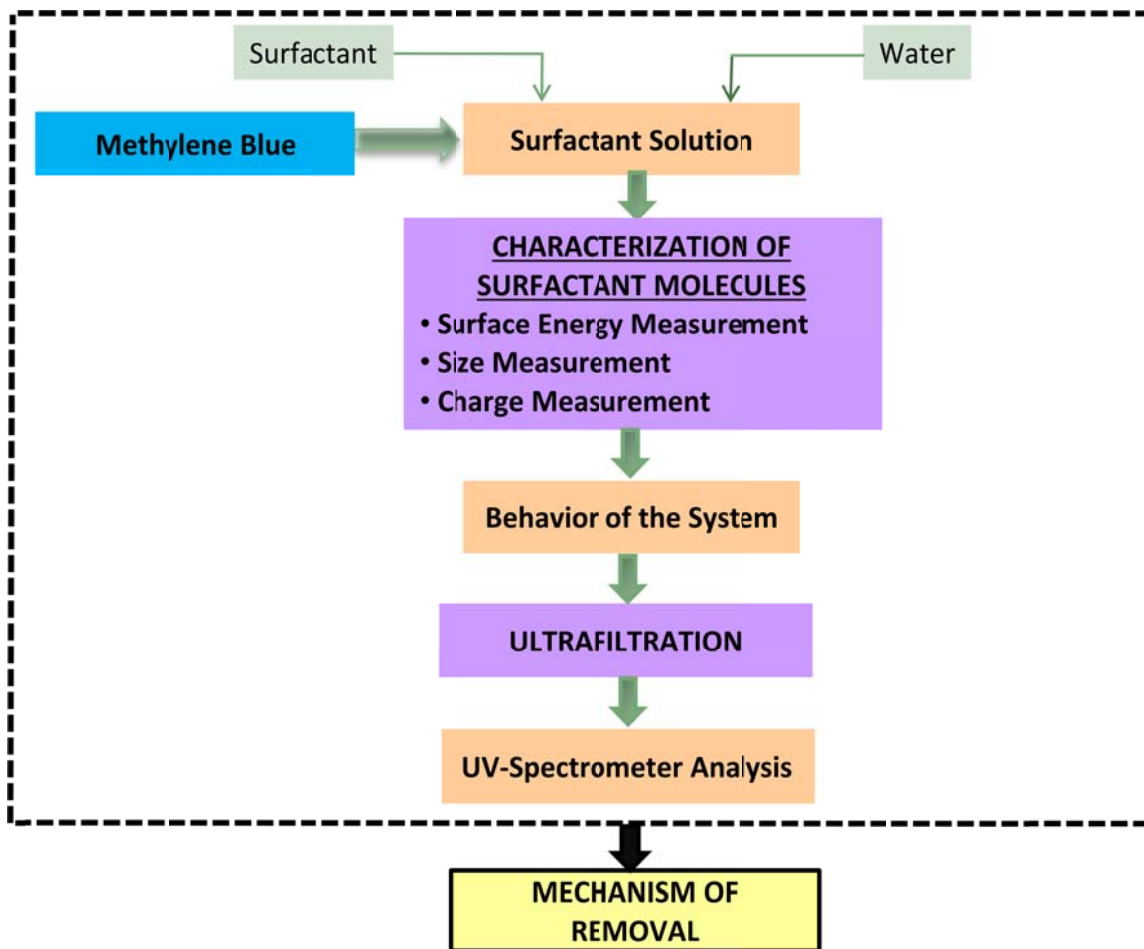
Figure 3.2. The methodology employed in this study.

3.2.1. Surface Tension Measurements

Surface tension measurements were conducted with SDS, TX-100 and CTAB as simple anionic, nonionic and cationic surfactants at different concentrations of 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6} M. For this purpose a Kruss Model Digital Tensiometer (K10ST) with the Du-Noüy Ring method was used (Figure 3.3). The ring is usually made up of platinum or platinum-iridium alloy of a radius (R) of 2-3 cm. The measuring device is a vertically suspended ring with a precise geometry. When the ring is brought into contact with the liquid, the liquid "jumps" to the ring and pulls it into the liquid. The force caused by this wetting is measured by pulling the ring up to the level of the liquid surface (Adamson, 1997). The surface tension of the liquid is determined from the measured force using the equation:

$$Y = \frac{F}{pCosQ\,f} \qquad (3.1)$$

where Y is the surface tension, F is the maximum force, p is the perimeter of the three-phase contact line is equal to twice the circumference of the ring: p = 4pR and f is a correction factor due to additional volume of liquid is lifted during the detachment of the ring from the interface and is contact angle measured for the liquid meniscus in contact with the ring surface (Drelich et al., 2002).
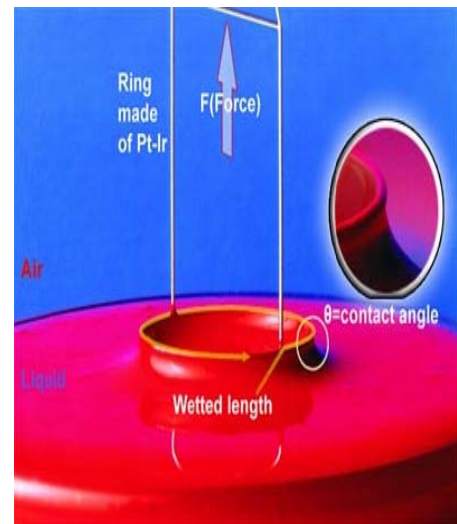

Figure 3.3. A Kruss model digital tensiometer (K10ST) used for surface tension measurements.

3.2.2. Size and Charge Measurements

Zeta potential measurements were applied to MB (2 ppm)-surfactant (SDS, CTAB, TX-100) solutions to observe the effect of surfactant concentration on MB. Size measurements were done only for TX-100 because other surfactants were small for our measurement device. Size and zeta potential measurements of molecules and micelles were carried out using Malvern Zeta Sizer Nano ZS. The device employs a combination of laser Doppler velocimetry and Phase Analysis Light Scattering (PALS). Malvern Zeta Sizer uses dynamic light scattering method and working principle based on the fact that spatial distribution of scattered light is a function of the particle size of the analyzed sample. Size of particles which are measured by the method is inversely proportional to angle seen after the particles scatter light. In other words, small particles scatter light at small angles while large particles scatter light at small angles relative to the laser beam. These particles pass through a focused laser beam during the laser diffraction measurement. A series of photosensitive detectors are used to get the angular intensity of scattered light. Particle size is calculated by using the map of scattering intensity versus angle. Particles are moving because of Brownian motion which is due to random collision with the molecules of the liquid that surrounds the particle. Stokes-Einstein equation defines the relationship between size of particle and its speed due to Brownian motion and Zeta Sizer uses the relationship to obtain size. There are some specialties to prefer Laser diffraction technique such as wide dynamic range, repeatability, rapid measurements, instant feedback, high sample throughput, no need to calibration (Figure 3.4).
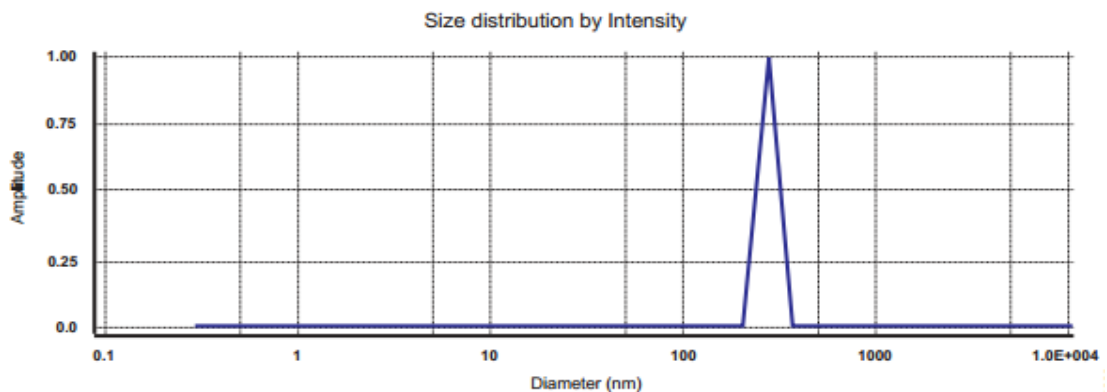

Figure 3.4. General size distribution graph.

Surface charge of nanoparticles or the potential that is at particle surface is called as Zeta potential. Malvern Zeta Sizer Nano ZS (Figure 3.5) is used to obtain zeta potential by using Henry equation. Henry equation is:

$$UE = \frac{(2 \, \epsilon \, z \, f \, (ka))}{3\eta} \qquad (3.2)$$

where z : Zeta potential

UE : Electrophoretic mobility

ϵ : Dielectric constant

η : Viscosity

f(Ka) : Henrys function

f (Ka) value generally used as 1.5 or 1.0.

Potential stability of the colloidal system can be understood by the magnitude of the zeta potential. Particles can come together and flocculating if the particles have low zeta potential values. On the contrary, if all the particles have a large negative or positive zeta potential, they will repel each other and they cannot flocculate. pH is the most important factor which affects zeta potential. The effect can be seen from Figure 3.6.
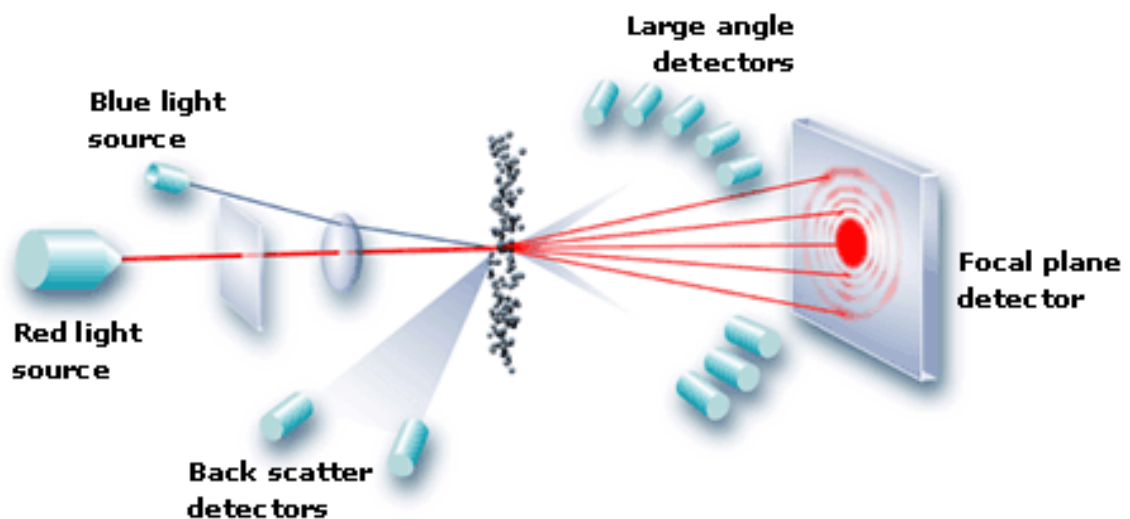

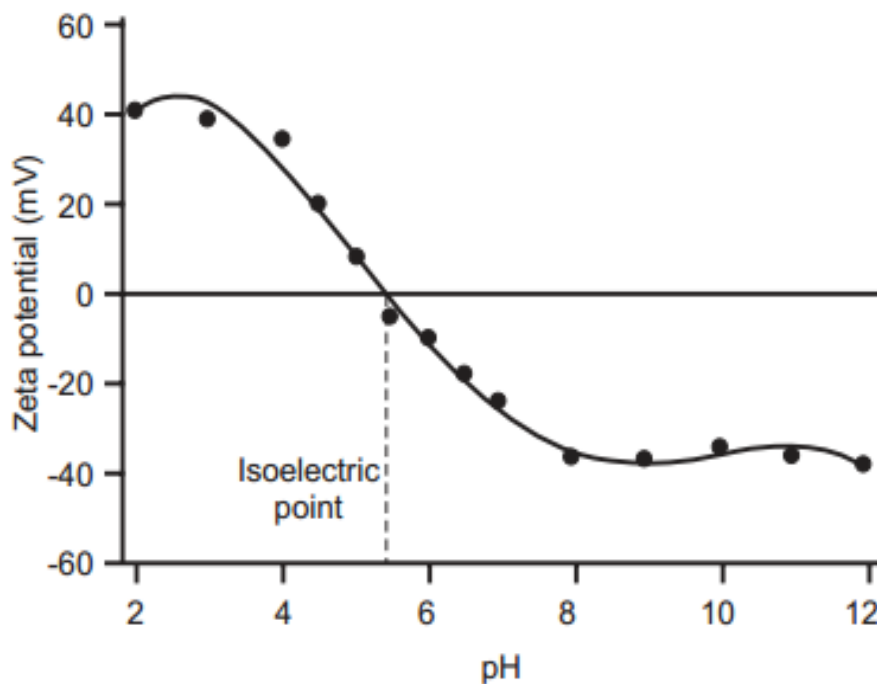Figure 3.5. Malvern Mastersizer 2000 Laser Diffraction.

Figure 3.6. Typical plot of zeta potential versus pH.

3.2.3. Determination of the Association of Surfactant Molecules and CMC

Surface tension data were plotted as a function of surfactant concentrations and the concentration regions where the slope of the curve is different were marked. These regions were evaluated and the effect of surfactant type and the environmental conditions on these regions were determined. A picture that gives a general behavior of a surfactant is given in Figure 2.5. As it is seen there should be different concentration regions where surfactant molecules have different forms. These plots were also used to obtain the critical concentrations where micelles start to form. As can be seen from the plot, at low concentrations of surfactants, there are single surfactant molecules with highest surface tension value. When surfactants were added to the solution surface tension decreases up to critical micelle concentration. After this point, surface is full of surfactant hence, surfactants starts to aggregate to form micelles and surface tension remains constant.

3.2.4. Ultrafiltration and Ultraviolet–Visible Spectroscopy (UV) Measurements

Ultrafiltration (UF) is a type of membrane filtration which is pressure-driven process. UF process removes emulsified oils, metal hydroxides, colloids, emulsions, dispersed material, suspended solids and other large molecular weight materials from water and other solutions. UF uses hollow fibers of membrane material and the feed water flows either inside the shell or in the lumen of the fibers. Suspended solids and solutes of high molecular weight are retained while water and low molecular weight solutes pass through the membrane. Size of molecule, the concentration, the pressure difference across the membrane and the affinity of the component for the membrane material determines the rate at which a particular component moves through the membrane. Ultrafiltration membranes have pore diameters in the range of 10 to 100 nm. Membranes are categorized according their Molecular-Weight Cut-Off (MWCO) which is defined as a molecular size of dextran being 90 % rejected by the membrane. For example, a membrane that removes dissolved solids with molecular weights of 10 kDa and higher has a MWCO of 10 kDa which means different membranes even with the same molecular-weight cut-off can have different pore size distribution. Ultrafiltration setup can be seen from Figure 3.7. To observe the effect of surfactant on MB removal, ultrafiltration was applied to MB-surfactant (SDS, CTAB, TX-100) solutions at various surfactant concentrations from 10^{-2} to 10^{-6} M.

Figure 3.7. Ultrafiltration setup.

UV uses light in the visible and adjacent ranges and measures the amount of light that a sample absorbs (Figure 3.8). Color of chemicals affects the absorption of the light. First of all, the intensity (number of photons per second) of light (I_0) passing through a blank which does not contain sample is measured. Then, the intensity of light (I) passing through the sample solution is measured. By using those data and absorption law, transmittance and absorbance is calculated. Beer-Lambert Law explains absorption law. According to Beer's law, absorption is proportional to the number of absorbing molecules and Lambert's law tells that the fraction of radiation absorbed is independent of intensity of the radiation. Beer-Lambert Law is: I_0

$$\log \frac{I_0}{I} = \varepsilon lc \qquad (3.3)$$

$$T = \frac{I_0}{I} \qquad (3.4)$$

where T: transmittance

I_0 : the intensity of the incident radiation

I : the intensity of the transmitted radiation

ε : a constant for each absorbing material, known as the molar absorption coefficient (called the molar extinction coefficient in older texts) and having the units mol^{-1} dm^3 cm^{-1}, but by convention the units are not quoted

l : the path length of the absorbing solution in cm

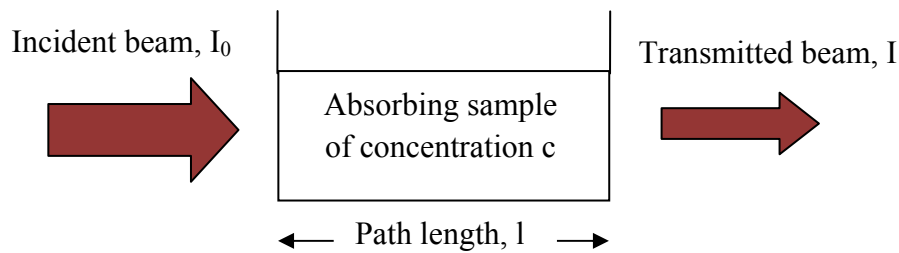c : the concentration of the absorbing species in $mol\ dm^{-3}$

Figure 3.8. Working principle of UV.

UV can be used for determination of metal and organic non-metal analyses in water such as nitrates, phosphates, MB, chemical oxygen demand, phenols. Also it can be used in petrochemical studies and food and beverage industries due to being suitable for phosphorus in gasoline, hydrogen sulfide in fuel oils, purity of olive oil, wine color and intensity and carotene content. In this study, Perkin Elmer Lambda 45 UV/Vis spectroscopy was used to determine MB concentrations in solution after UF in the absence and presence of surfactants. For this purpose a calibration curve was obtained using some MB solutions with known concentrations as standards (Figure 3.9) and used to determine unknown concentrations of MB. As it is seen the absorbance–concentration relation is linear. Then these values are used and removal percentages were calculated using equation 3.5.
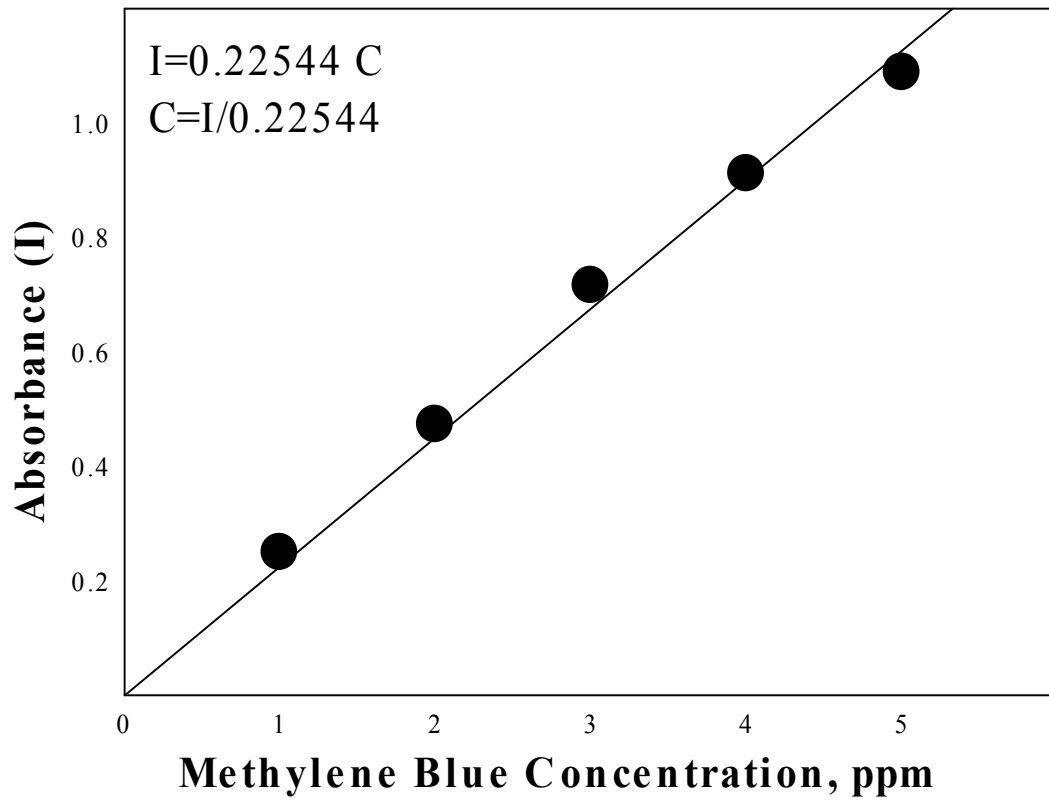
Figure 3.9. Calibration curve obtained for MB.

$$R(\%) = \frac{C_O - C_t}{C_t} \times 100 \qquad\qquad (3.5)$$

where R : Removal percent

C_o : Initial concentration of MB in ppm

C_t : Final concentration of MB in ppm

CHAPTER 4

RESULTS AND DISCUSSION

4.1. The Forms of Surfactant Molecules in Aqueous Solutions in the Absence and Presence of MB: Surface Tension Measurements

The forms of surfactant molecules in aqueous solutions vary with their concentration. Therefore surface tension measurements were performed as a function of surfactant concentration and presented Figure 4.1. As seen, increasing surfactant concentration reduces the surface tension depending on surfactant type up to a certain concentration. That is, surface tension reaches a constant value, CMC, which does not vary with a further increase in surfactant concentration. The values obtained from these measurements are about $9x10^{-4}$ M, $8x10^{-3}$ M and $3x10^{-4}$ M for CTAB, SDS and TX-100, respectively. All values agree with the ones reported in literature as $9.15x10^{-4}$ M, $8x10^{-3}$ M and $2.4x10^{-4}$ M for CTAB, SDS and TX-100, respectively (Mukerjee, 1972; Szymczyk and Jańczuk, 2007; Tofani et al., 2004).

The surface tension decreased from an initial value of 72 mN/m for the no surfactant case to a value of about 33 mN/m at a surfactant concentration of 10^{-2} M. Based on the results given above, a schematic representation of the changes in surface tension as a function of surfactant concentration is given in Figure 4.2. The surface tension behavior for surfactants could be divided into three concentration regions marked as Regions I, II and III. Region I is believed to consist principally of monomers whereas Region III involves fully developed micelles. Region II is a region where surfactant molecules are still in their monomer form but the decrease in surface tension is linear. The adsorption density may be calculated from this part of surface tension data by using the Gibbs equation.

$$\Gamma = -\frac{1}{RT}\left(\frac{d\gamma}{d\ln C}\right) \qquad (4.1)$$

where Γ and C are the surface excess and the bulk concentration of the surfactant component. The area per molecule at the interface, A, can be calculated as:

$$A = \frac{1}{\Gamma \, N_{av}} \qquad\qquad (4.2)$$

where Γ is the surface excess concentration at monolayer coverage and N_{av} is the Avogadro's number. The area calculated provides information on the degree of packing and the orientation of the adsorbed molecule.
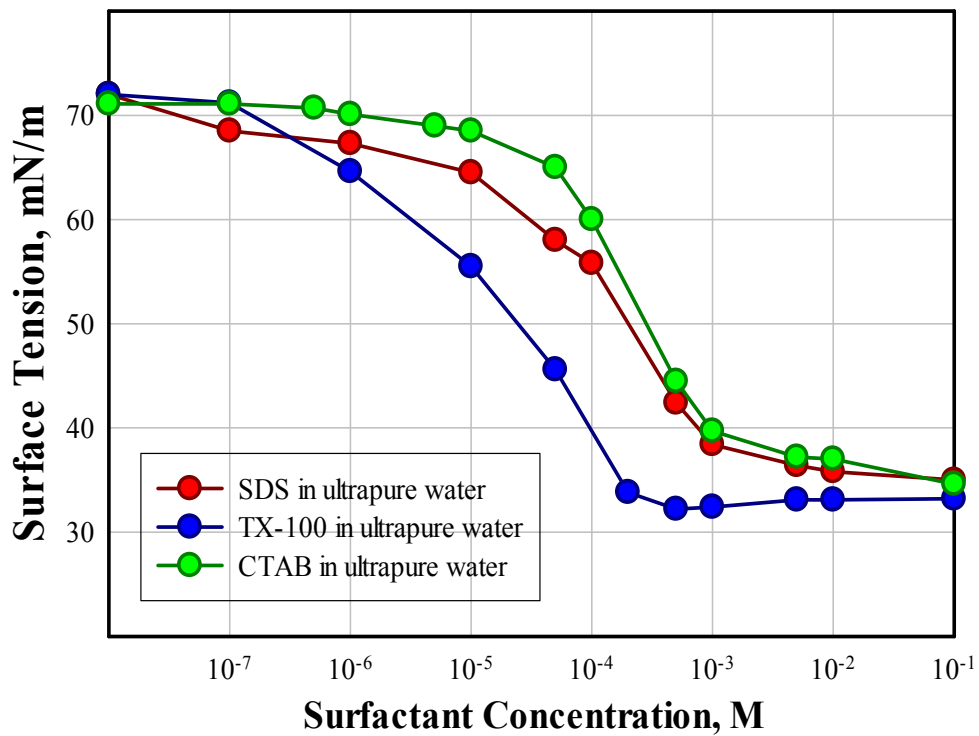

Figure 4.1. Surface tension results of SDS, CTAB and TX-100.
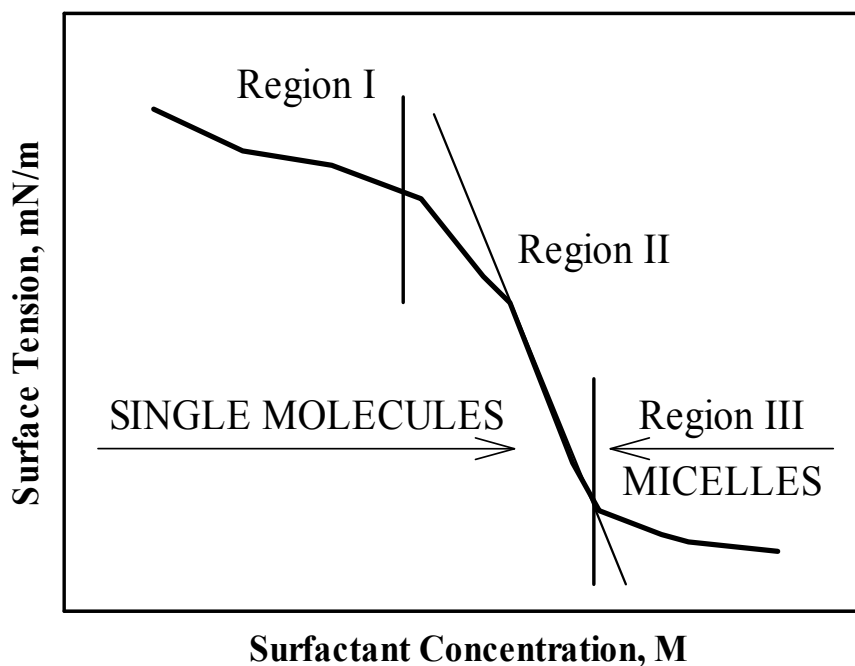
Surfactant Concentration, M

Figure 4.2. A schematic representation of the changes in surface tension as a function of surfactant concentration.

From the surface tension measurements given in the above paragraphs, the adsorption density was calculated to be 3.36×10^{-2} moles/cm^2, 3.4×10^{-2} moles/cm^2 and 3.44×10^{-2} moles/cm^2 for SDS, CTAB and TX-100 respectively. This corresponds to a parking area of about 0.4941, 0.49 and 0.4833 nm^2 per molecule of SDS, CTAB and TX-100 respectively. Since the increasing molecular weight did not affect the slope of the curve in this region significantly, the area per molecule, approximately 0.50 nm^2 at monolayer coverage, should be very similar for all the three surfactants. Based on these results, one may conclude that only a fraction of the hydrophobic groups, which is similar for the three surfactants, anchors to the surface and the rest of the hydrophobic groups remain in air or water. At a fixed concentration, said 10^{-5} M, the difference in the surface tension values of these surfactants was attributed to their different surface activity characteristics. The lower value was obtained with TX-100 with a larger molecular weight which is expected to be more surface active.

Surface tension measurements were also conducted in the presence of MB (2 ppm) for all the surfactant concentrations. These results are presented in Figure 4.3. As it is seen the surface tension values are even lower in the presence of MB in the case of ionic surfactants. In the case of TX-100, on the other hand, there was not any change in the surface tension values. This result shows the formation of MB-ionic surfactant pairs

34

and indicates that the MB-ionic surfactant pairs are more surface active compare to the MB-non-ionic surfactant pairs. That is MB-nonionic surfactant pairs do not change the effect of surfactant. It was also seen that these pairs form due to the hydrophobic attraction between the hydrophobic tail of a cationic surfactant or nonionic surfactant and hydrophobic part of the MB. In the case of oppositely charged ionic surfactant, on the other hand, this interaction is mostly due to the electrostatic attraction between the head groups of MB and anionic surfactant.
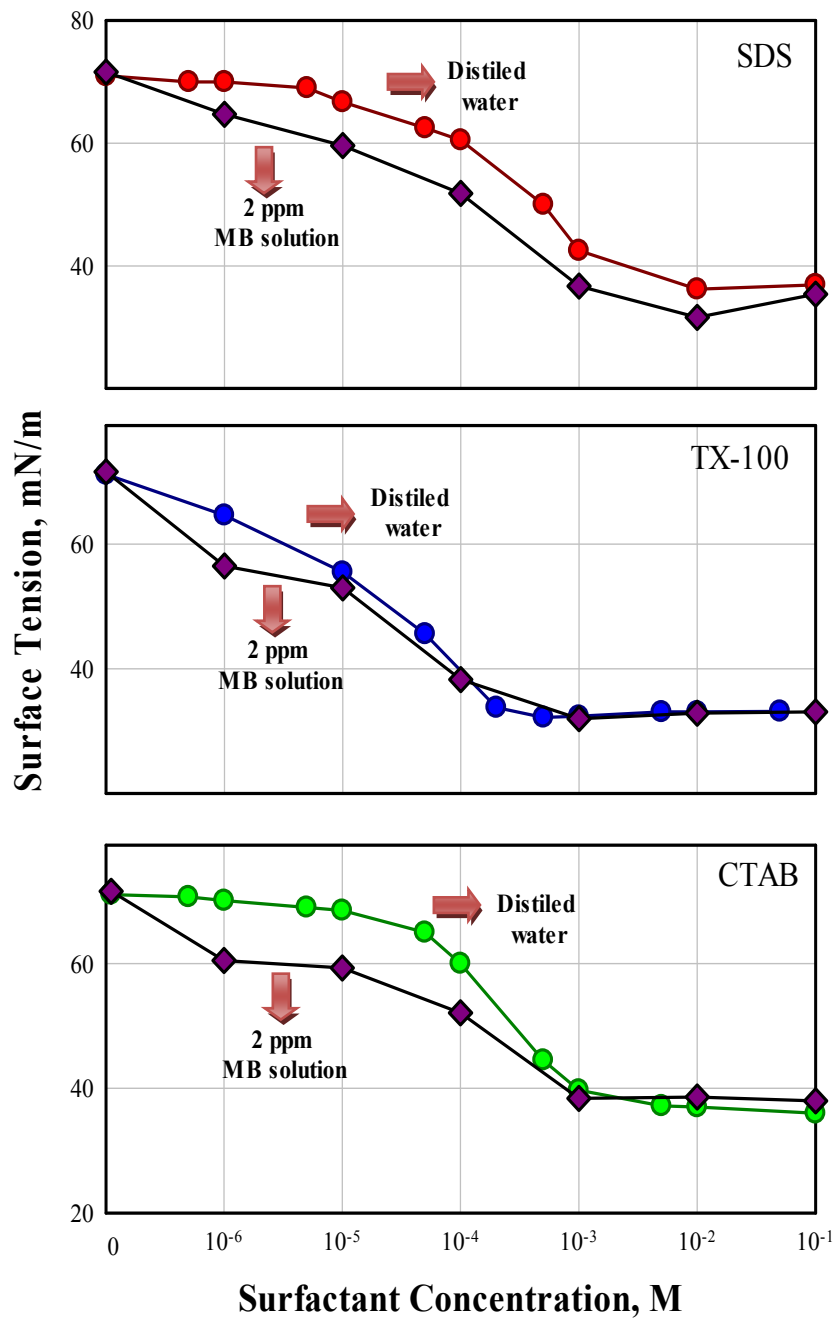

Figure 4.3. Change in surface tension with surfactant concentration (SDS, CTAB and TX-100) in the absence (upper line) and in the presence of MB (lower line).

4.2. Charge of MB-Surfactant Pairs

This part of the study was design to determine the charge of MB and surfactant pairs to understand the interactions of filter paper, surfactant and MB molecules. MB was found to be positive in the case of natural pH (that is around 7.0) conditions. As it is seen from the figures that in the presence of charged surfactants (SDS and CTAB) MB becomes more and more charged with increasing concentration (Figure 4.4). For example, if anionic SDS was added, MB surfactant pair becomes negatively charged at high concentrations of SDS. On the other hand, when cationic CTAB was added, MB surfactant pair becomes positively charged at high CTAB concentrations. In the case of nonionic surfactant, on the other hand, the charge of these pairs is negligible. All these results indicate there is an interaction between MB molecules and all type of surfactant molecules (positive, negative or no charge) in the solution. This interaction could be due to 1) *electrostatic attraction* (between polar head groups) as in the case of negatively charged surfactant and positively charged MB or 2) *hydrophobic attraction* (between hydrophobic tail groups) as in the case of positively charged surfactant and positively charged MB or hydrophobic tail groups as in the case nonionic TX-100 and positively charged MB. Hence MB and surfactant molecules interact to some degree depending on the type and concentration of surfactant molecules present before filtration. That is the result of filtration (filtration performance) is expected to depend on the interactions of these MB-surfactant pairs with filter paper. Filter paper used in this work was dominantly negatively charged and therefore is expected to interact with the positive sides of the MB-surfactant pairs. That is there will be no interaction in the case of MB-SDS pairs, strong interaction in the case of MB-CTAB pairs and some interaction in the case of MB-TX-100 pairs. The effects of these interactions on the filtration, however, could be complex. Some other conditions may affect the interactions and filtration process. All these will be discussed in the following paragraphs after presentation of filtration results.
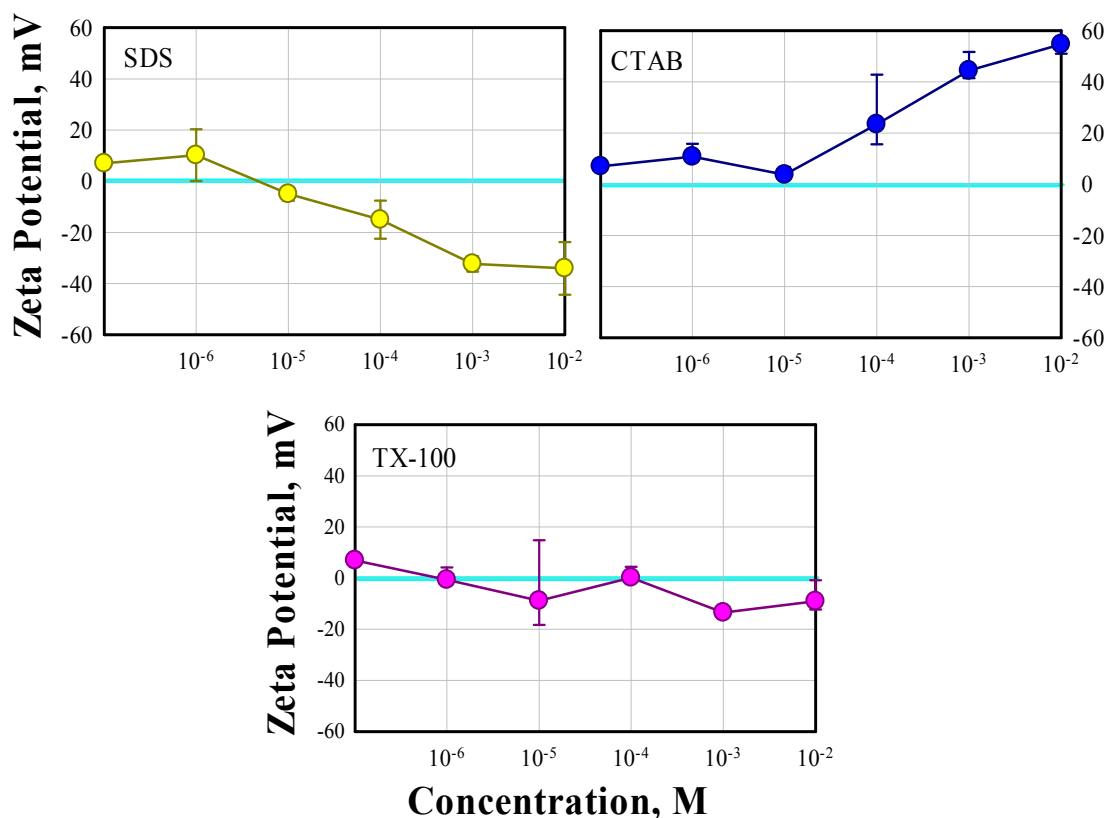
Figure 4.4. Charge of MB-surfactant pairs (10^{-5} M MB).

4.3. UV Absorbance of SDS, CTAB, TX-100 Surfactant Solutions

Prior to ultrafiltration experiments, the following UV-analyses were conducted to test and understand the effect of surfactants on the UV-absorbance of MB. These results are presented in Figures 4.5-4.8 to show these effects. Figure 4.5 gives the absorbance versus wavelength (nm) graphics for all the surfactants and the methylene blue alone at different concentrations. As it is seen there is no change in the absorbance in the case of cationic surfactant, CTAB and nonionic surfactant, TX-100. That is the presence of CTAB and TX-100 does not show any effect on the absorbance value so they do not affect the measurements of MB. However, this is not the case in the presence of negatively charged an anionic surfactant, SDS. In this case, the change of absorbance was depending on surfactant concentration.
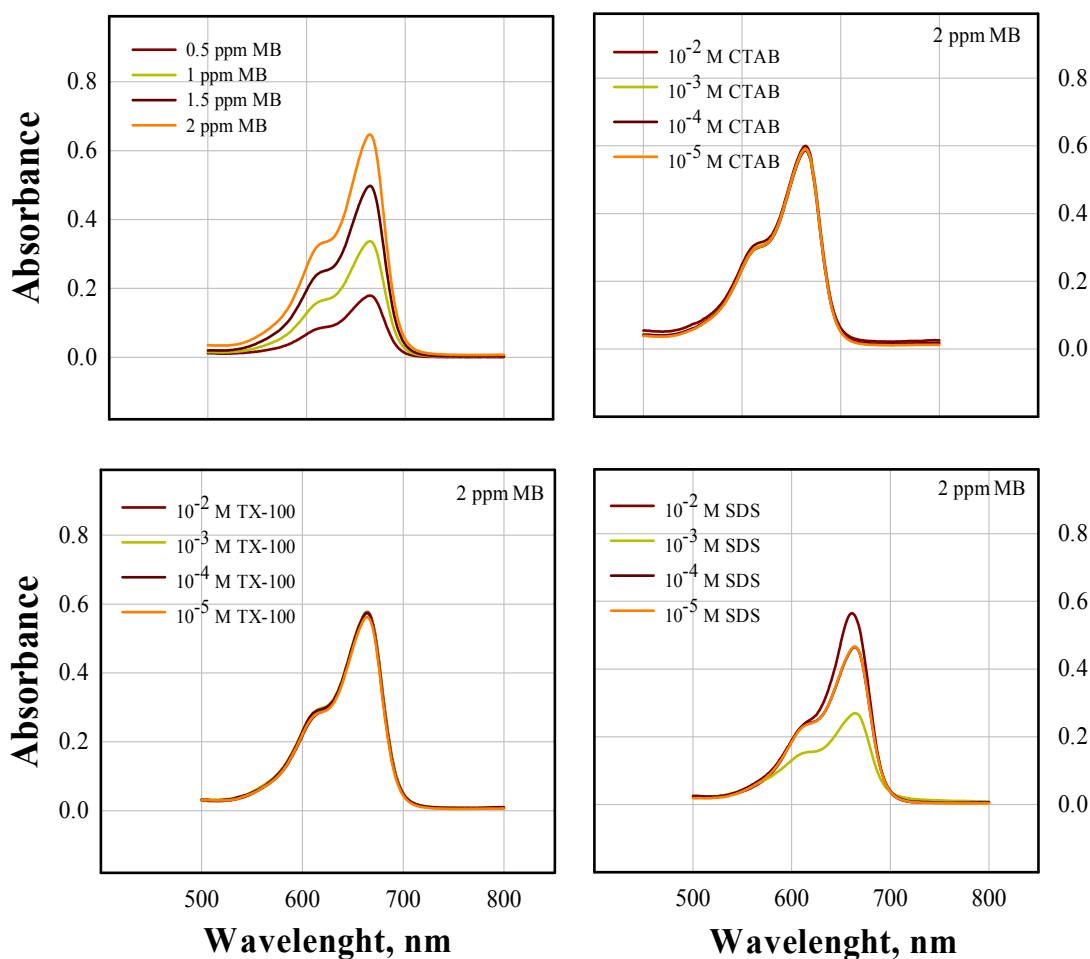
Figure 4.5. UV-absorbance of MB in the presence of SDS/CTAB/TX-100 and the absence of surfactant.

Therefore, two other types of graphs were also created to explain the effect of surfactant concentration as a function of MB concentration on the absorbance better and presented in Figures 4.6-4.8. One graph gives the maximum MB absorbance values as a function of surfactant concentration and the other gives the changes in the maximum MB absorbance as a function of MB concentration and surfactant concentration as three dimensional. Figure 4.6 shows the effect of SDS concentration on the maximum absorbance that is changing especially around CMC concentration (8×10^{-3} M), as a function of MB concentration. That is this effect seems to change as a function of MB concentration significantly. It is increasing and becoming significant at high MB concentrations. However, at the MB concentrations (2 ppm MB) used in this study, this effect does not look very significant. Therefore, UV-absorbance method was able to use to determine the MB concentrations in the presence of SDS at all the concentrations in this work. After the CMC concentration, however, the effect of surfactant on the

absorbance disappears. This is really interesting and cannot be explained with the results of present experiments therefore it needs to be investigated with a detailed work.
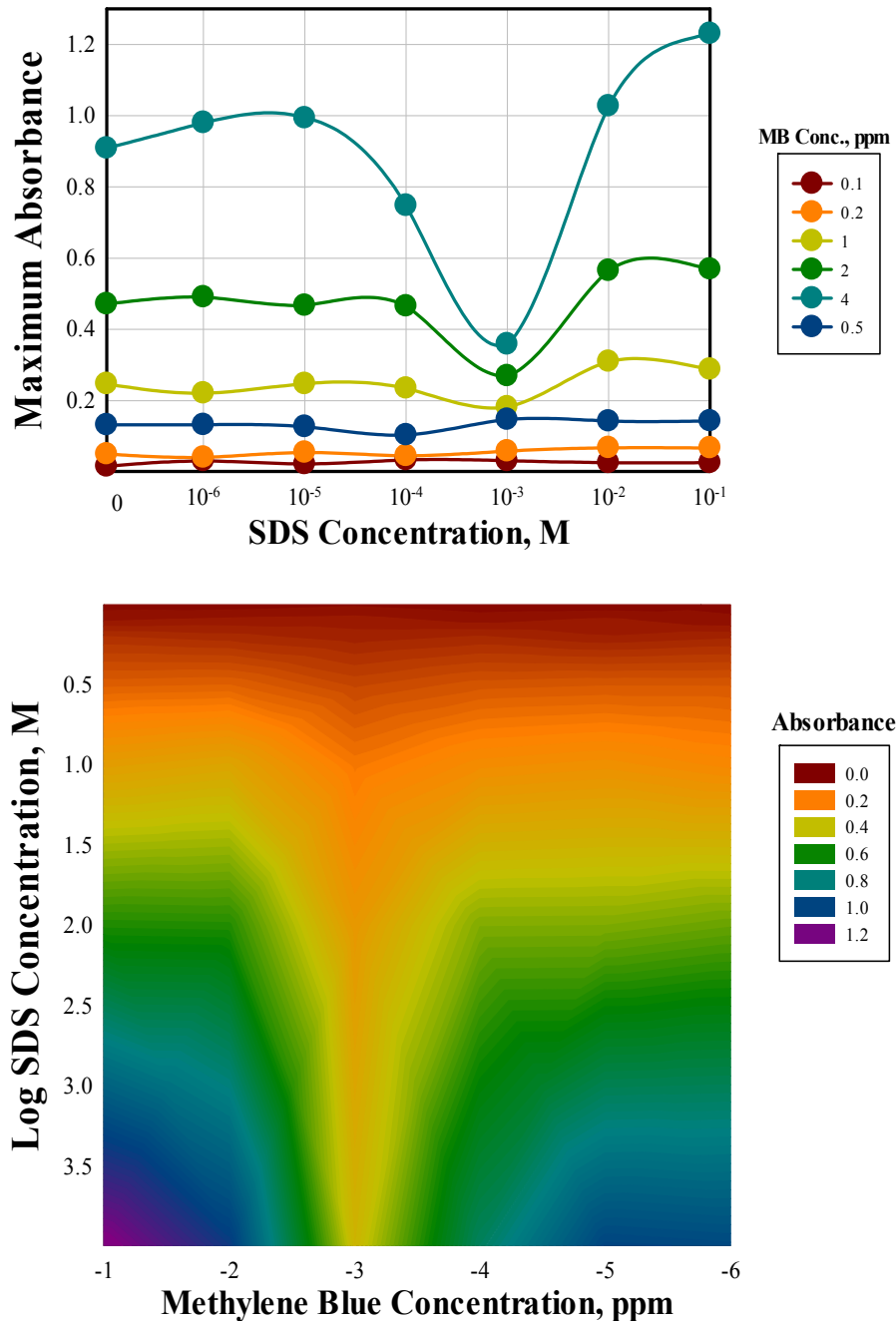

Figure 4.6. UV-Absorbance of MB in the presence of SDS.

However, in the case of TX-100 (Figure 4.7) no effect of surfactant on MB absorbance was observed for all the concentrations tested. That is the concentrations of MB during the ultrafiltration studies in the presence of no charge nonionic surfactant,

TX-100 could be determined safely using UV-Absorbance spectrometer. The results of these experiments were also used to have some ideas about the interactions among surfactant molecules, filter paper and MB molecules.
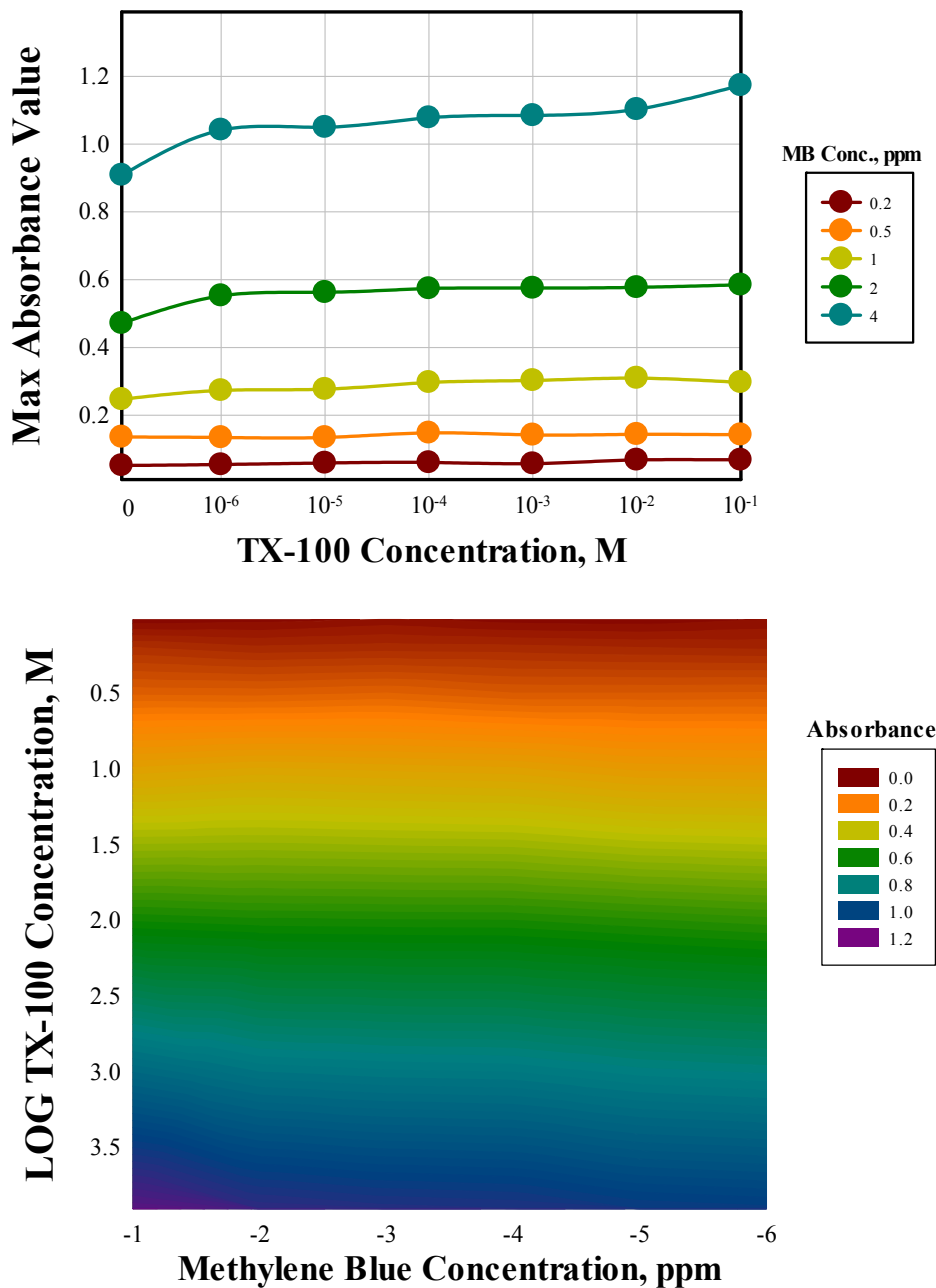
Figure 4.7. UV-Absorbance of MB in the presence of TX-100.

Similar to TX-100, the effect of positively charged a cationic surfactant, CTAB, on the absorbance of MB molecules were also insignificant. As it is seen from the Figure 4.8 that there is almost no change in the absorbance of MB in the presence of

CTAB. That is UV-absorbance method could be safely used to determine the solution concentrations of MB in the presence of CTAB.

Figure 4.8. UV-Absorbance of MB in the presence of CTAB.

4.4. Ultrafiltration of MB

4.4.1. Removal of MB in the presence of SDS, TX-100 and CTAB

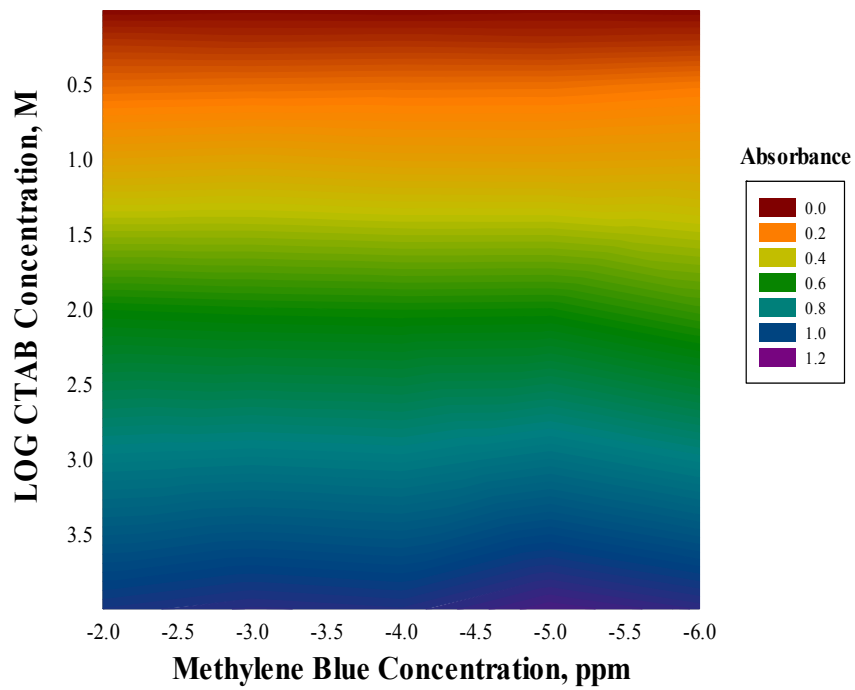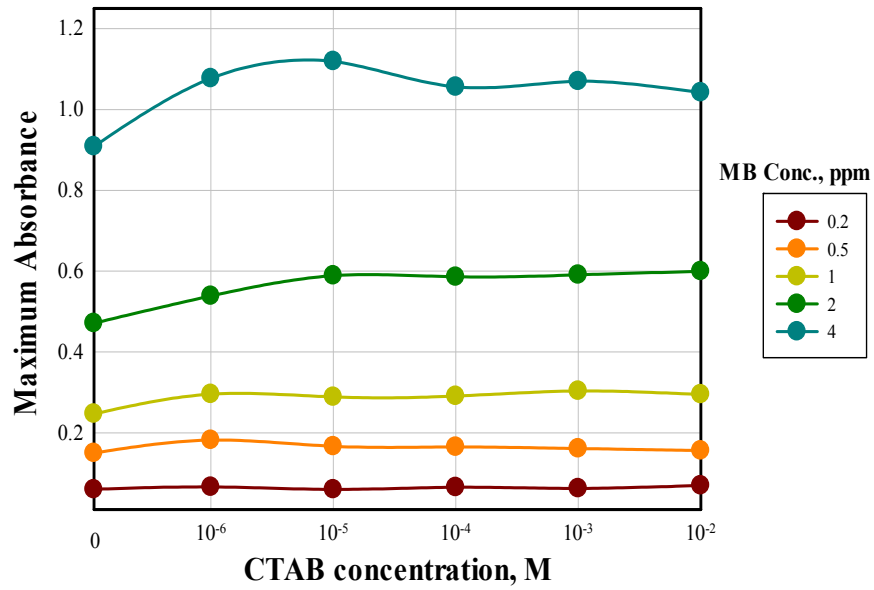In this part of the study, ultrafiltration experiments were performed to remove MB from aqueous solutions in the absence and presence of surfactant molecules or micelles. Therefore ultrafiltration experiments were conducted as a function of surfactant concentrations and the results are presented in Figure 4.9, Figure 4.10, Figure 4.11 and Figure 4.12. It was observed that the presence of surfactant molecules affect the removal of MB depending on their concentration significantly for all the surfactants used. It was expected MB molecules pass through filter in the absence of surfactant because filter pore (450 nm) is much larger than the size of the MB molecules (see Chapter 3 Section 3.1). However, Figure 4.9 shows about 80 percent removal percent. The reason for this most probably, the filter has predominantly negative charge while the dye have positive charge. Hence, there is electrostatic interaction.
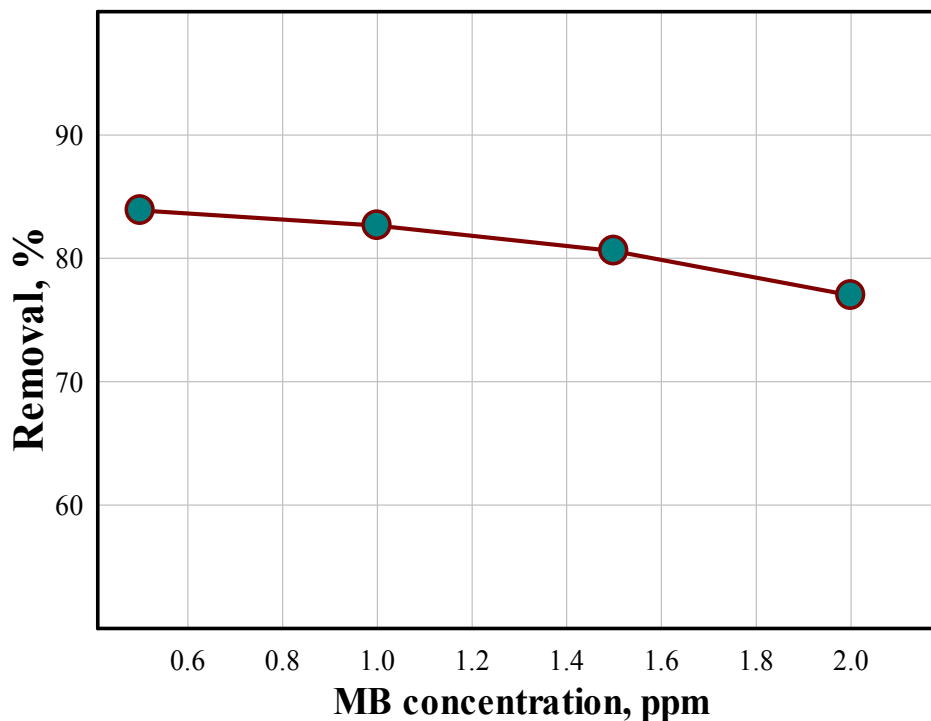

Figure 4.9. MB removal by ultrafiltration in the absence of surfactants.

In the presence of SDS (Figure 4.10), at low concentrations, the MB-SDS interaction could be through the both electrostatic and hydrophobic attraction due to positive charge of MB and negative charge of SDS. This may create larger and loose MB-SDS structures to stay on filter surface. This will cause an increase in the MB removal efficiency at lower concentrations (at 10^{-5}, 10^{-4} and 10^{-3} M) where there are enough surfactant molecules for each MB. However, the removal efficiency decreases at high concentration (10^{-2} M) where the number of surfactant molecules increase to form micelles most probably due to compact and small structured micelles that also includes MB molecules. Moreover, there is no significant change in removal percent according to pore size of the filter.
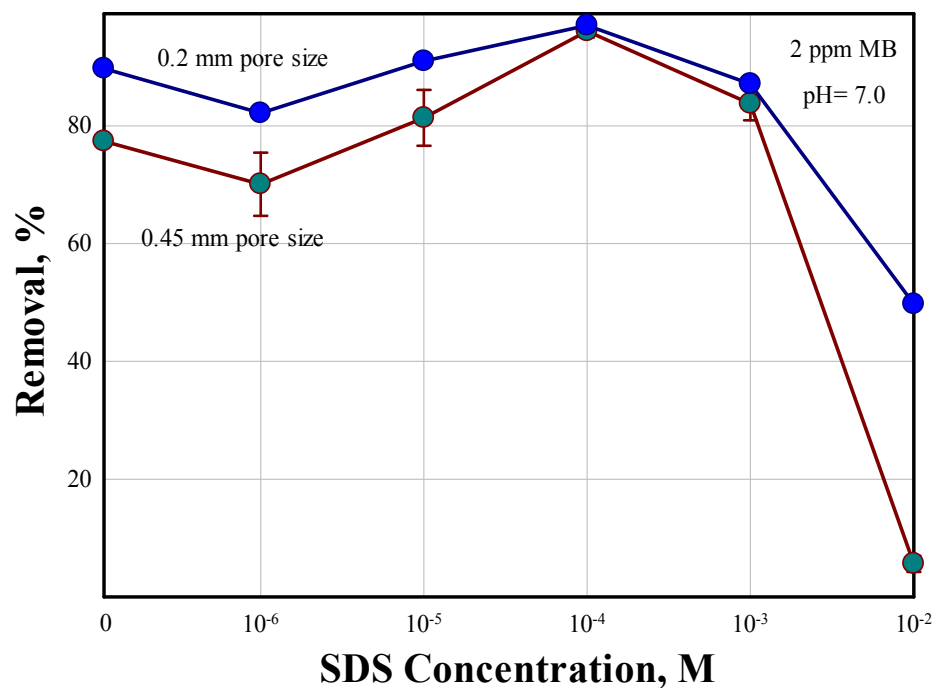
Figure 4.10. MB removal by ultrafiltration in the presence of anionic surfactant, SDS.

This effect was negative except for SDS at low concentrations (10^{-5}, 10^{-4} and 10^{-3} M). That is all the other surfactants and concentrations decrease or prevent MB removal from water. In the case of CTAB, removal efficiency decreases sharply as seen from Figure 4.11. That means MB and surfactants or filter surface and surfactants interacts and the capture is impossible. In the presence of TX-100, initially removal efficiency does not change up to CMC that means there is not much interaction between the filter paper, surfactant and MB. After CMC, presence of the surfactant micelles

43

affects the system. What is probably happening in this condition is that MB molecules are in the structure of micelles like surfactant molecules but they do not change the size of micelles. Therefore size distribution experiments showed no changes. But ultrafiltration experiments show a decrease in the removal efficiency. This suggests micelles that are smaller in size and can pass through the pore of filter paper hence, MB molecules cannot attach to the filter surface. All in all, at low surfactant concentrations, the relation of MB seems to be through single surfactant molecules. Therefore the presence of hydrophilic and negatively charged filter surface (used in this study) became the important variable of this work.

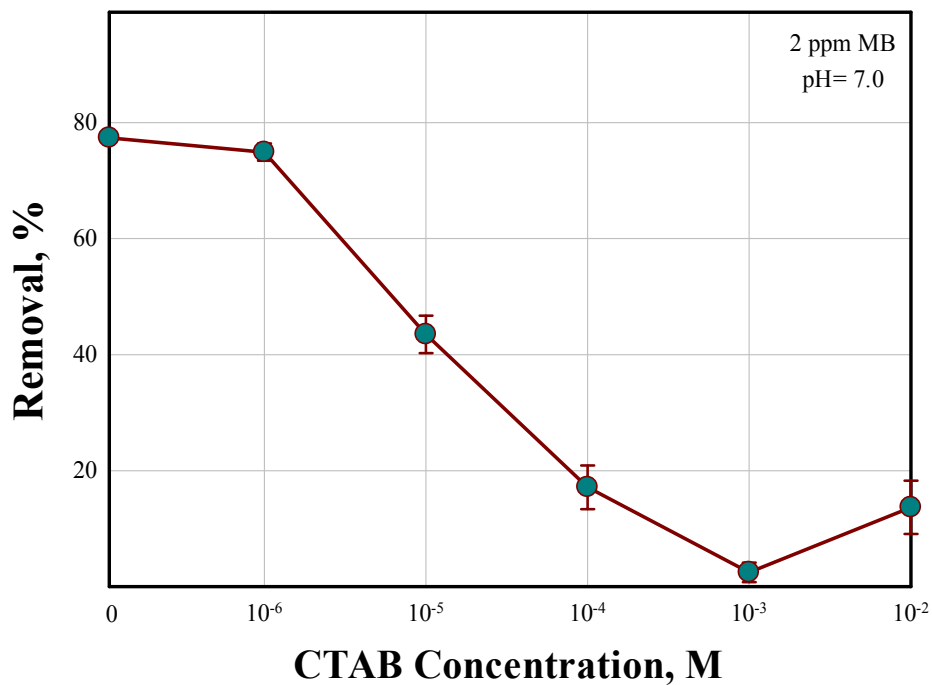Figure 4.11. MB removal by ultrafiltration in the presence of cationic surfactant, CTAB.
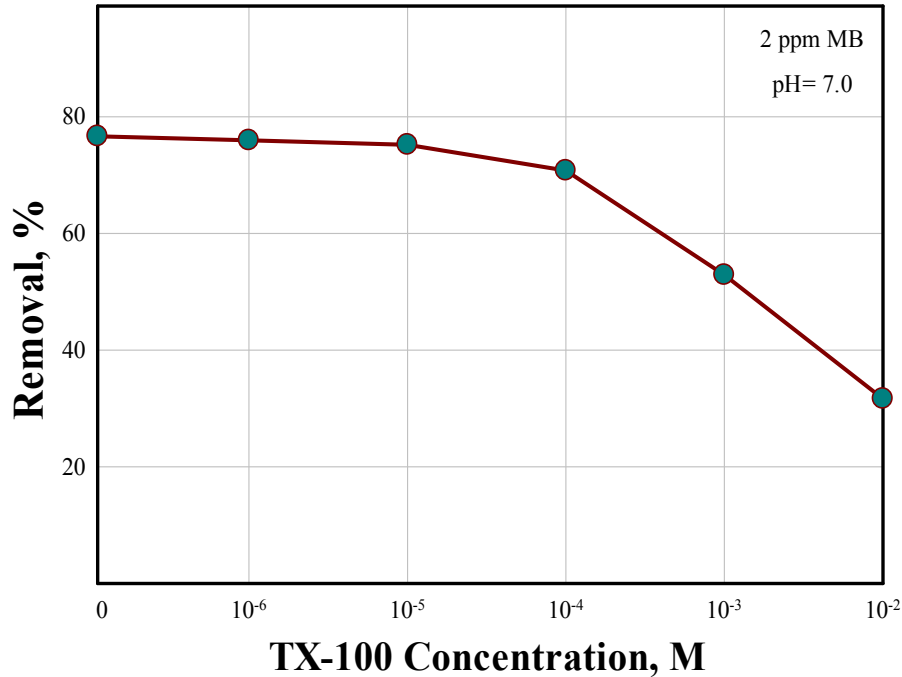
Figure 4.12. MB removal by ultrafiltration in the presence of nonionic surfactant, TX-100.

A schematic representation of possible interactions suggested among filter surface, surfactant and MB molecules are given in Figure 4.13 a, b, c and d. In the case of no surfactants, MB molecules adsorb at filter surface through electrostatic attraction due to the opposite charges of MB and filter paper surface. In the case of CTAB, the MB-CTAB interaction is most probably through hydrophobic attraction and these pairs attach to the filter surface due to positive charge on both side of the molecules and the surface of filter becomes hydrophobic (see the contact angle measurements, Figure 4.16). These interactions decrease MB removal as a function of concentration. Similarly, in the case of TX-100, MB/TX-100 interaction is again most probably through hydrophobic attraction and these pairs attach to the filter surface due to positive charge on MB side.

However, no change in the size measurements of micelles in the presence of MB molecules (Figure 4.14) shows that MB contribute to the structure of surfactant micelles but they are not enclosed in the core of micelles and they do not increase size of micelles as believed in the past studies. That is, at concentrations above CMC, the efficiency of MB removal is low due to the formation of surfactant-micelles that are smaller in size compare to the pore size of filter.
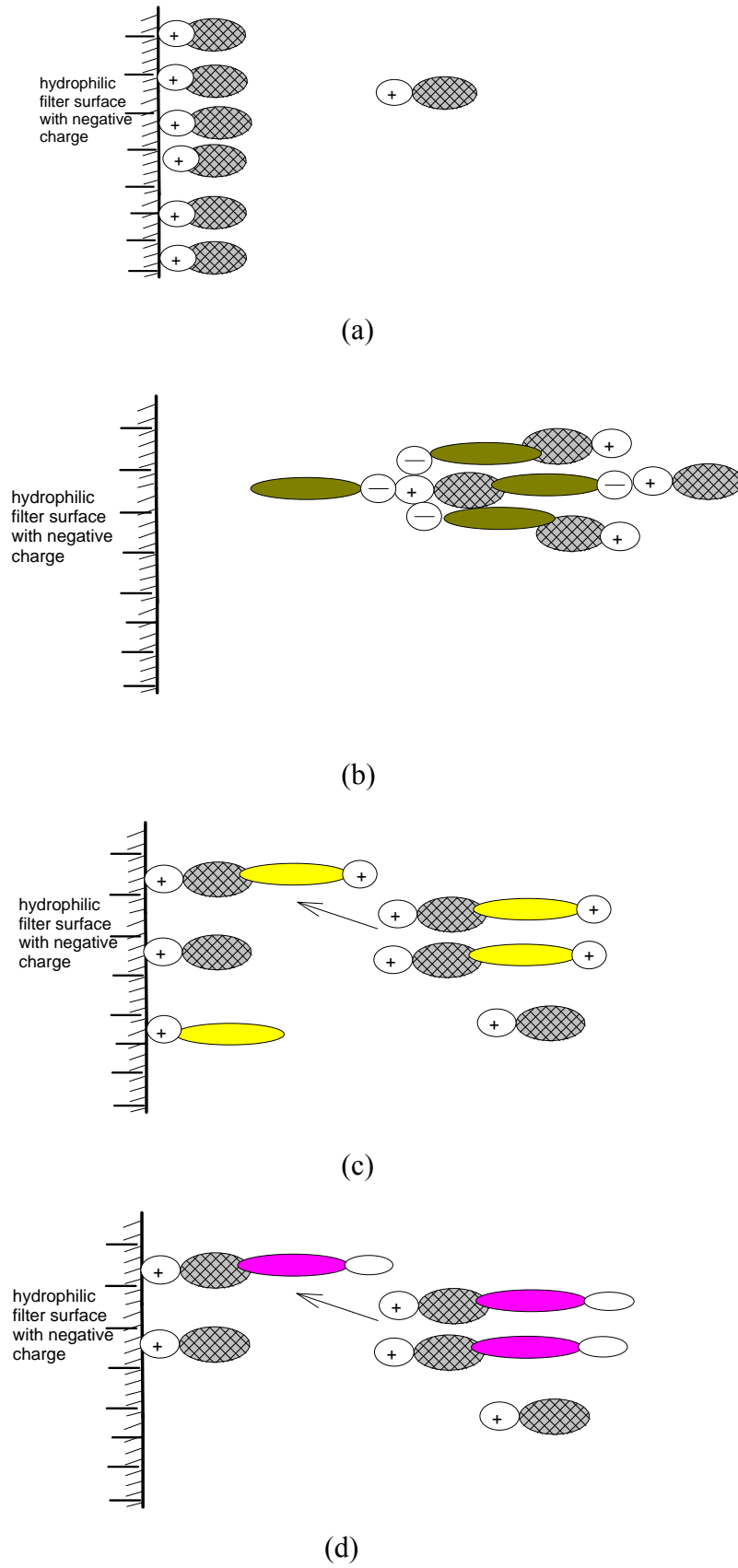
Figure 4.13. A schematic representation of possible interactions among filter surface, MB molecules (a) and surfactants, SDS (b), CTAB (c), TX-100 (d).
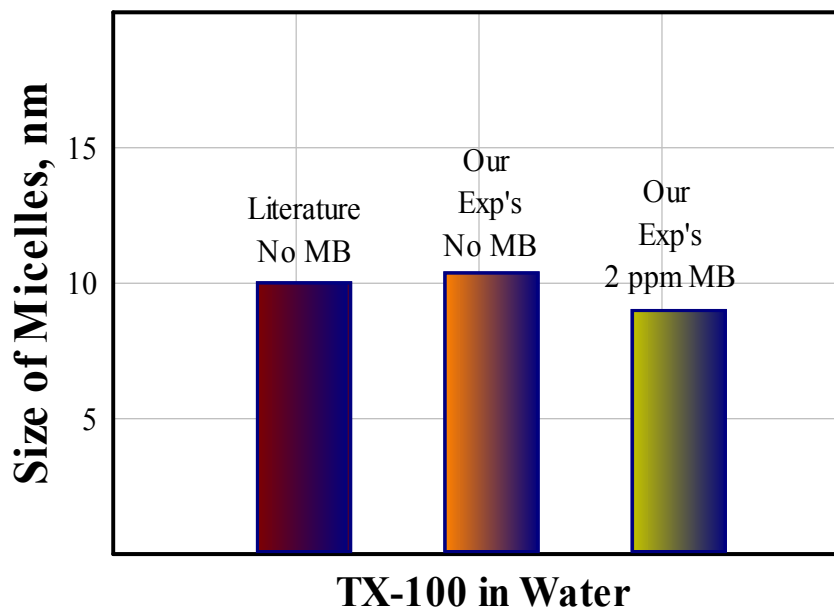
Figure 4.14. Size of TX-100 micelles in the absence and presence of 2 ppm MB in solution together with theoretical micelle size (Malvern Zetasizer).

4.4.2. Removal of MB in the Presence of SDS, and CTAB with Saturated Filter Paper

Similar tests were also conducted with surfactant saturated filter papers for ionic surfactants, SDS and CTAB, and the results are presented in Figure 4.15. As it is seen there is not much difference in the case of SDS due to any interaction of negatively charged SDS with the same charged filter surface in the absence of MB. In the case of CTAB, however, coverage of surface is expected and this seems to somehow increase MB removal. To prove the adsorption of surfactants on filter surface, contact angle studies using sessile drop method were also conducted after saturation of filter in surfactant solutions and the results are presented in Figure 4.16. As it is seen from the figures that both MB and the MB-surfactant pairs adsorb at filter surface and make it more hydrophobic. In the absence of MB, however, adsorption of SDS is less compared to the SDS-MB pair adsorption due to negative charges of both filter surface and SDS.

Figure 4.15. Ultrafiltration with surfactant saturated filter papers.
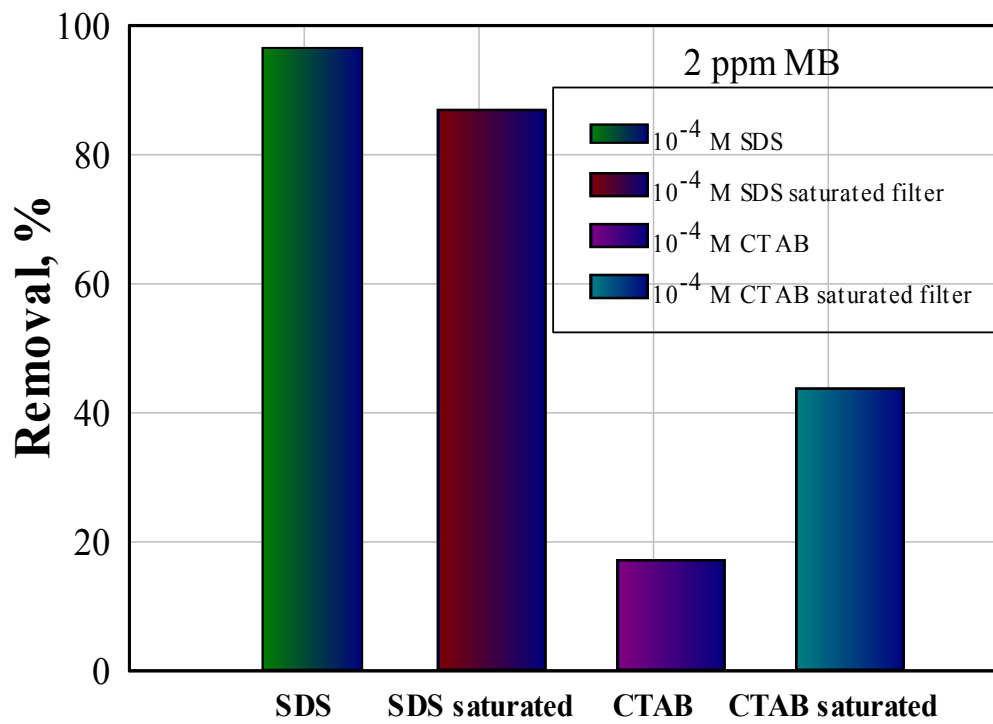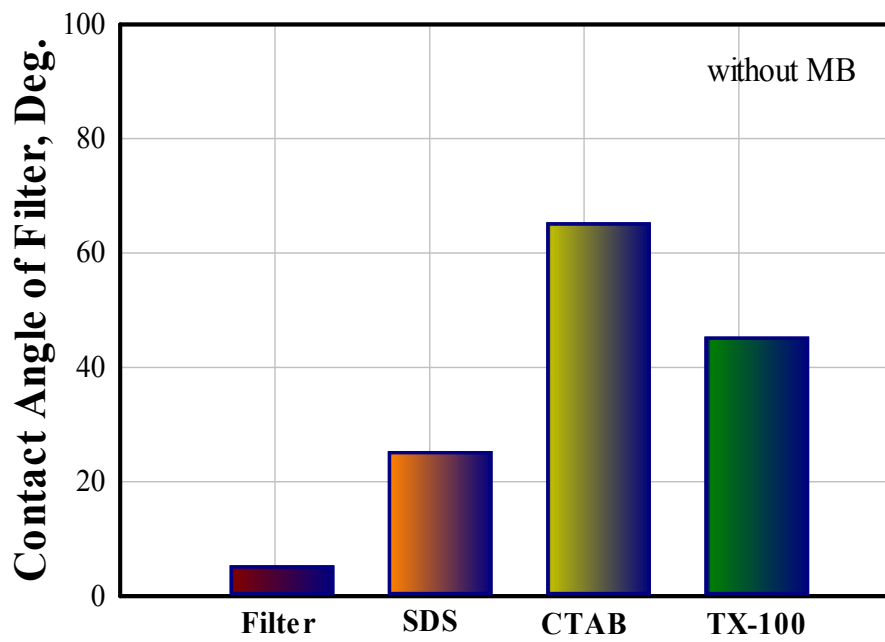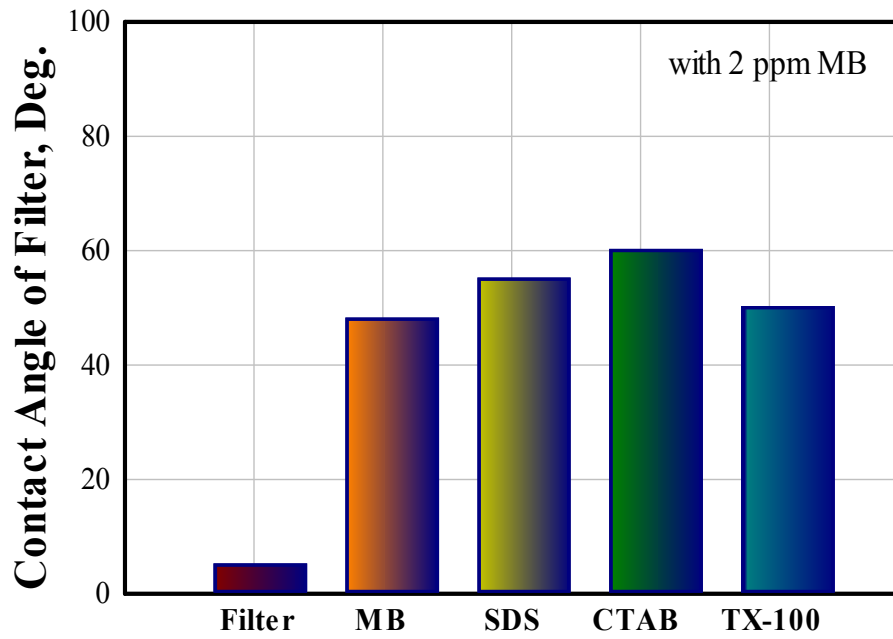
Figure 4.16. Contact angle measurements of filter surface after saturation with MB and surfactant solutions (all surfactants were used at 10^{-5} M concentration).

4.5. Discussion

The experiments conducted in this study can be summarized as follows a) surface tension measurements as a function of surfactant concentration in the absence and presence of MB, b) ultrafiltration experiments with different surfactant and MB concentrations, c) charge and size measurements of MB-surfactant pairs at different concentrations. Based on the results of these studies, in general, one can conclude that surfactants decrease the efficiency of MB removal. In the absence of surfactants, however, the removal efficiency is high due to the attachment of MB on the negatively charged cellulose nitrate filter. In the case of anionic surfactant, SDS, the ultrafiltration efficiency increases at low concentrations. This is most probably due to the fact that at low concentrations, electrostatic and hydrophobic interactions create large-loose MB-SDS aggregates which cannot pass the filter paper. In the case of cationic surfactant at low concentrations with similar charge, however, the MB-CTAB interactions are most probably through hydrophobic attraction only and this interaction creates MB-cationic surfactant pairs that can attach to the filter surface due to the positive charge on these structures. These interactions cause a decrease in MB removal as a function of concentration. Similarly the MB-TX-100 interactions are also most probably through hydrophobic attraction only and this interaction creates MB-nonionic surfactant pairs that can attach to the filter surface due to the positive charge on these structures. These interactions also cause a decrease in MB removal as a function of concentration.

At surfactant concentrations above CMC, the efficiency of MB removal is low most probably due to the formation of surfactant-micelles that are smaller in size compare to the pore size of filter. MB molecules were suggested to be in the structure of micelles not in the core of micelles (as believed in literature) based on the size distribution experiments conducted in this study.

In summary, this study has shown conclusively that presence of surfactants affected the behavior of a model LMWC in ultrafilration significantly. The observed effect could be positive or negative depending on the type and the concentration of the surfactant employed. Hence, before utilizing such advanced removal technologies as ultrafiltration or MEUF, systematic characterization studies such as done in this thesis must be carried out to determine the potential success and the window of operation of these techniques.

CHAPTER 5

CONCLUSIONS

Low Molecular Weight Contaminants (LMWCs) with molecular weights less than 800 Dalton cannot be satisfactorily removed using classical treatment techniques such as chemical coagulation, biological treatments and adsorption. Therefore, they pose a serious environmental concern and more complicated removal techniques such as ultrafiltration and micellar enhanced ultra filtration have been developed to improve removal efficiency.

However, LMWCs are invariably co-exists with surface active agents in contaminated waters. Therefore, an understanding of how these contaminants interact with various surface active agents is an important factor in successfully applying these more recent removal techniques.

In this study, a widely used LMWC, methylene blue, was chosen as the model contaminant. Anionic (sodium dodecyl sulfate, SDS), cationic (hexadecyltrimethyl-ammonium bromide, CTAB) and non-ionic (ethoxylatedoctylphenol, TX-100) surfactants were used as model surface active agents to investigate their interactions with methylene blue. The MB-surfactant systems were characterized through surface tension, size and charge and contact angle measurements in order to elucidate the forms of surfactant and MB-surfactant molecules in aqueous solutions as a function of concentration. These studies also provided information on the critical concentrations where micelles form in absence and presence of MB.

The simulated contaminated waters (MB-surfactant solutions) were also subjected to ultrafiltration tests to correlate the findings of the characterization studies with filtration efficiencies. Ultraviolet-Visible spectroscopy (UV) was used to determine the MB concentrations in these studies.

Based on the results of this study, the following specific conclusions could be made:

- MB-surfactant pairs form either through electrostatic of hydrophobic attraction depending on the surfactant type.

- In general, surfactants decrease the efficiency of MB removal. In the absence of surfactants, the removal efficiency is high.

- In the presence of SDS, the ultrafiltration efficiency of MB removal increases at low concentrations. The large-loose MB-SDS aggregates which cannot pass the filter paper form.

- In the presence of CTAB, the ultrafiltration efficiency of MB removal decreases as a function of surfactant concentration. The MB-cationic surfactant pairs which can attach to the filter surface form.

- In the presence of TX-100, the ultrafiltration efficiency of MB removal also decreases as a function of surfactant concentration. The MB-nonionic surfactant pairs which can attach to the filter surface form.

- At concentrations above CMC, the efficiency of MB removal is low for all the surfactants. Surfactant-micelles that are smaller in size compare to the pore size of filter form.

- Size distribution experiments show that MB molecules are in the structure of micelles not in the core of micelles and do not change the size of micelles.

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