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An overview of Micellar – Enhanced Ultrafiltration in Wastewater Treatment Process

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Abstract. Micellar-enhanced ultrafiltration (MEUF) process is one of the promising technologies in separating the low molecular weight of substance from the wastewater. The MEUF process involved the combination use of surfactant and ultrafiltration membrane. The selection of surfactant is very important which depends on the nature of contaminants (i.e organic, inorganic). Critical micelle concentration of surfactant plays an important role in selection of surfactant concentration for MEUF process. Many researchers have reported that MEUF and nanofiltration process has the same removal capacity of contaminants from wastewater but the uniqueness of MEUF is it requires less energy due to low operating pressure.

Keywords: micellar-enhanced ultrafiltration, surfactant, micelles.

1. Introduction

Micellar-enhanced ultrafiltration (MEUF) is known as a powerful separation process developed recently to remove various contaminants such as heavy metals (i.e lead, cadmium, zinc), toxic organic materials (i.e phenol, di-butyl phosphate (DBP), tri-butyl phosphate (TBP), trihalomethane (THMs)) and lower molecular weight of contaminants including Reactive Black 5 and Orange 16, Eosin dye, Direct Blue 71 and Methylene Blue from wastewater [1-10].

MEUF is a modified separation of ultrafiltration (UF) process [1]. It is known as a process which combines high selectivity of reverse osmosis and high flux of ultrafiltration [11]. This process involved a combination of surfactant and UF process for the separation of ions and small organic molecules which can only be separated using nanofiltration (NF) or reverse osmosis (RO) [12].

The advantages of MEUF are relatively low energy requirement and low pressure driven. The required pressure needed to drive MEUF range from 97 to 587 kPa only. Anisotropic membranes ranging in nominal pore size from about 10 to 100 Å (1000 to 50,000 MWCO) can be used to reject surfactant aggregates called micelles [13]. Furthermore, the performance on the solute rejection for MEUF of solute with low molecular weight (MW) is quite similar to reverse osmosis (RO) and nanofiltration (NF). Therefore, MEUF may be an alternative to overcome the inherent limitations of the RO process [1].

2. MEUF Mechanism

Micellar-enhanced Ultrafiltration (MEUF) is one of the viable alternative techniques as it has proved its ability in removing contaminants from wastewater. Surfactant is the main ingredient of MEUF process and the general structure of surfactant is shown in Figure 1 (a). The MEUF phenomenon is illustrates Figure 1 (b). In MEUF, surfactant is added into the aqueous stream containing contaminants or solute (e.g metal ion, organic materials, low molecular weight solute) above its critical micelle concentration (CMC) [4]. When the surfactant concentration exceeding the CMC value, the surfactant monomers will assemble [8, 14] and aggregate to form large amphiphilic transparent micelles [5] having hydrodynamic diameter significantly

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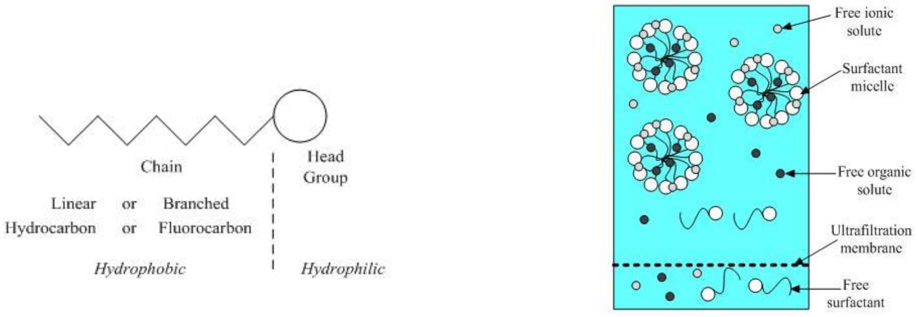
larger than the pore diameter of ultrafiltration membrane [2, 7, 8, 15]. The contaminants or solute will entrap in micelles if they tend to strongly attracted by micelle surface and will solubilize in the micelle interior [10]. Micelles containing solubilized contaminants with larger diameter than membrane pore size will be rejected by the membrane during ultrafiltration process leaving only water, unsolubilized contaminants and surfactant monomers in permeate stream [7, 10].



(a) (b)

Fig. 1: (a) General structure of surfactant (b) MEUF phenomenon

The principle of MEUF process introduces the importance of surfactant's critical micelle concentration (CMC) for the selection of suitable surfactant concentration for MEUF process. Critical micelle concentration (CMC) is defined as the concentration of surfactants which micelles starts to form spontaneously and it is one of the most important physical parameters of surfactants [16]. The addition of surfactant into the water system will results in the decrement of water surface tension. As the concentration of surfactants increases, the surface will be covered by the surfactant hence the surface free energy (surface tension) will be reduced. Subsequently, the surfactants will start to aggregate, thus the contact area of hydrophobic parts of the surfactant with water will be reduced. As a result, the system free energy will also decrease. Once the surfactant concentration reach CMC, the air-water interface is assumed to remain saturated with the surfactant so that the surface tension becomes minimum at this state [17]. The hydrophobic ends of the molecules in micellar aggregates tend to stick together while the hydrophilic ends protect the resulting micelles from external influences through repulsive forces. The aggregation number of micelles is depends on the type of surfactant. The non-ionic surfactants normally constitute clusters of 1000 or more molecules [18], 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 [7, 18].

Figure 2 shows the schematic representation of a spherical micelle. Generally micelle can be divided into two sections; the core of micelle which is composed of hydrophobic hydrocarbon chains and the surface of micelle which is composed of hydrophilic head groups and water of hydration. The solubilization of solute into micelles occurs at four sites in micelle: at the micelle–water interface, between the hydrophilic head groups, in the palisade layer of the micelle and in the inner hydrophobic core of micelle. The palisade layer of micelles is located between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups that comprise the outer core of the micelle interior [6]. However, the solubization of solute into surfactant micelles is depends on how the material binds with the surfactant micelles. The binding mechanism of solute is based on the type of solute whether organic, inorganic or metal ions. In MEUF, metal cations and inorganic pollutants forms a bond with the head of the ionic micelles surface which is oppositely charged via electrostatic interaction [2, 5, 7, 15] but this is not applicable for MEUF of organic materials. In MEUF of organic contaminants, dissolved organic solutes will be solubilized within the palisade layer or the core of micelles (tail of the micelles) via Van der Waals force [2, 5, 7]. The extent of solubilization do relies on the characteristics of surfactant and the structure of the solute [8]. Luo et. al [5] proved that the removal of phenol using cetylpyridinium chloride (CPC) are higher as compared to octadecyl trimethyl ammonium bromide (OTAB) due to the rule of similarity and interiscibility since the CPC and phenol all possess an aromatic ring.

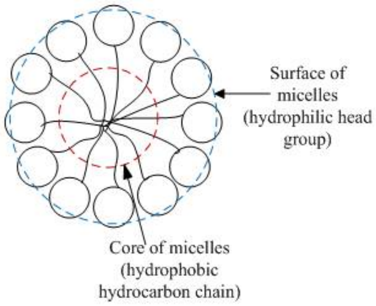


Fig. 2: Schematic representation of a spherical micelle

Selection of surfactant is very important to ensure the efficiency of MEUF process. The chemical classification of surfactant is based on the nature of the hydrophilic head, with the sub groups based on the nature of hydrophobic tail. Basically, the surfactant can be classified into four; anionic, cationic, nonionic and amphoteric surfactant [19]. However most of the researchers show their interest on the potential of cationic, anionic and nonionic surfactant in wastewater treatment via MEUF process. Based on the literature study, the MEUF of wastewater commonly can be classified into four categories; (i) MEUF using cationic surfactant, (ii) MEUF using anionic surfactant, (iii) MEUF using nonionic surfactant, and (iv) MEUF using mixed surfactant.

2.1. MEUF using Cationic surfactant

The hydrophilic head of cationic surfactants bears a positive charge which makes it possible to attract the anionic contaminants such as anionic dyes [9, 19]. Instead of acknowledging the use of cationic surfactants in fabric softeners, corrosion inhibitors and antimicrobial agents [20], this surfactant has shown its potential in wastewater treatment via MEUF. Cetylpyridinium chloride (CPC) is identified as one of the potential surfactant that can be used to remove anionic contaminants from wastewater. Purkait et. al [1] shows that 74% removal of eosin dye was achieved using CPC as surfactant. Ahmad et. al [9, 21] had done studied on MEUF of reactive dyes (Reactive Black 5 and Reactive Orange 16) using CPC as surfactant and achieved higher removal of dyes (99%).

The potential of CPC also has been tested on removal of organic materials from wastewater via MEUF. Luo et. al [5] obtained that the removal of phenol using CPC is higher (93.8%) as compared to the other cationic surfactant; hexadecyltrimethylammonium bromide (CTAB) (85.9%) and octadecyl trimethyl ammonium bromide (OTAB) (92.4%) due to the similarity and interiscibility since the CPC and phenol all possess an aromatic ring. These researchers also reported that for the surfactant with the same hydrophilic group (CTAB and OTAB), the hydrophobic chain length (hydrophobic tail) does influence the solubilization of phenol into micelles (palisade layer or core of micelles). The increment of hydrophobic alkyl chain of surfactant results in the decrement in CMC of surfactant, hence enhance the solubilization of phenol into micelles. This is proved when the removal of OTAB is higher as compared to CTAB. Zaghbani et. al [11] studied on the effect of hydrophobic alkyl chain using n-Alkyltrimethylammonium bromide surfactants; dodecyltrimethylammonium bromide (C_{12}TAB), tetradecyltrimethylammonium bromide (C_{14}TAB), cetyltrimethylammonium bromide (C_{16}TAB) and octadecyltrimethylammonium bromide (C_{18}TAB) on Eriochrome Blue Black R (EBBR) dye. From the study, they found that the dye retentions increased as the hydrophobic alkyl chain increased (C_{12}TAB (34.6%) < C_{14}TAB (51.1%) < C_{16}TAB (99.6%) < C_{18}TAB (99.9%)) due to hydrophobic interaction which contributes to the increment in solubilization of dyes by micelle.

2.2. MEUF using Anionic surfactant

Unlike the cationic surfactant, the hydrophilic head of anionic surfactant owns a negative charge [19] where it has potential to interact with contaminants bears cationic charge such as metal ion [22]. Anionic surfactants are widely use in production of detergent powders since it is known to be more effective than other surfactant in soil removal, especially for natural fabrics [20]. The study on the potential of anionic surfactant in removal of inorganic and organic materials from wastewater by MEUF process has confirmed that higher percentage of solute removal was achieved [4, 23]. The use of sodium dodecyl sulfate (SDS) as anionic surfactant in removal of heavy metal ion from wastewater has been widely explored by researchers. Yenphan et. al [2] and Samper et. al [22] proved 90% to 100% removal of ion Pb^{2+} was achieved using SDS.

Instead of Pb^{2+}, Samper et. al [22] also had done studied on removal of other metal ion; Cd^{2+}, Cu^{2+},Ni^{2+}, Zn^{2+} using SDS and linear alkylbenzene sulfonate (LAS) as surfactant via MEUF. They verified that metal retention higher than 90% was obtained except for Ni^{2+} for both SDS and LAS surfactant. Misra et. al [7] also showed that SDS has proved its capability in simultaneous removal of uranyls ion (UO_2^{++}) as well as dissolved organic materials; di-butyl phosphate (DBP) and tri-butyl phosphate (TBP) from aqueous solutions. Their results indicated the removal of TBP and DBP is more than 90% while removal of UO_2^{++} is more than 80%. They found that there is no significant effect observed on the rejection of DBP in the presence of UO_2^{++} and TBP.

2.3. MEUF using Nonionic surfactant

Nonionic surfactants consist of hydrophilic head with no charge [19]. These surfactants are effective in removal of oily soil. Most nonionic are more tolerant to water hardness, effective at low concentration since they have good cold water solubility and low CMC value [20]. However, the use of nonionic surfactants alone via MEUF is suitable only for removal of organic contaminants.

As mention earlier, the ionic (cationic or anionic) components have the tendency to create bond with the head of the ionic micelles surface which is oppositely charged via electrostatic interaction. Theoretically, less removal of ionic contaminants via MEUF can be expected using nonionics as surfactant. Yenphan et. al [2] studied on removal of Pb^{2+} ion using Triton X-100 (TX-100) and nonylphenyl ether (NP12) as nonionic surfactants and found that the Pb^{2+} ions removal were low, about 9% to 18% for TX- 100 and 30% to 37% for NP12. They believed the removal of ions was due to the complex formation between the Pb^{2+} ions and ethylene oxide (EO) groups of TX-100 and NP12. To proof the nonionic surfactants is quite suitable for removing organic contaminants using nonionic surfactant via MEUF, Chung et. al [8] had performed their study on removal of toxic organic trihalomethane (chloroform) using polyethylene glycol alkylether as nonionic surfactant via MEUF and observed more than 80% of chloroform was removed from the wastewater.

2.4. MEUF using mixed surfactant

MEUF using mixed surfactant involve the mixture of ionic surfactant (cationic or anionic) with nonionic surfactant to produce better separation of contaminants via MEUF. Currently, more researchers are interested to explore the potential of MEUF using mixed surfactant systems especially when the process deals with the use of anionic surfactant. Unlike nonionic surfactants, anionic surfactants are sensitive to hard water [20] and have high CMC value [2]. Since the CMC of anionic surfactants is known to be high, the MEUF process requires large amount of anionic surfactant used for the separation resulted in excessive concentration polarization, fouling and high concentration of surfactants in permeate; which makes the process uneconomical [2, 15]. Theoretically, additional of nonionic surfactant into anionic surfactants lowering the CMC of anionic surfactant where the nonionic surfactant will reduce the repulsive force between the anionic charge hence resulting in a decrement of anionic surfactant's CMC value [2, 15].

MEUF using mixed surfactant has shown its potential in Cd^{2+} ion [15] and Pb^{2+} ion [2] removal. Huang et. al [15] showed that the CMC of SDS was decreased as the mole ratio of nonionic/anionic surfactant used in MEUF of mixed surfactant increases. Yenphan et. al [2] found almost 99% rejection of Pb^{2+} ion via MEUF was achieved either using SDS only, mixed surfactant SDS/TX-100 or SDS/NP12. However, the rejection of SDS using mixed surfactant (80%) is higher as compared to MEUF using SDS alone (60%).

3. Conclusion

As a conclusion, MEUF was proved to be one of the alternative methods that promising higher rejection of contaminants from wastewater. The knowledge of surfactant selection and MEUF process system is very important to enhance the effectiveness of this process in removing contaminants from wastewater.

4. Acknowledgements

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