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Rejection of Metal Ion (Cu) and Recovery Surfactant in Micellar Enhanced Ultrafiltration

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Abstract:- Excessive use of surfactants in metal waste treatment by the MEUF process resulted a secondary pollution. To overcome the problem, the combination of the acidification method followed by ultrafiltration is an efficient and simple surfactant recovery method. This research studied the effect of pH value on surfactant recovery, metal ion rejection and surfactant micelle formation at low surfactant concentrations. The retentate solution that will be recovered is obtained through the initial MEUF process using Sodium Dodecyl Sulphate (SDS) with an initial concentration of 7 mM less than the Critical Micelle Concentration (CMC), Cu2+ metal ion solution used as the pollutant feed. The recovery process carried out at various pH, namely 3; 2; 1 and 0,5. The separation between metal ions and surfactants increased as the pH value decreased. Optimal surfactant recovery at pH 0,5 with a value of recovery surfactant of 61% and metal ion rejection of 72%. The formation of micelle affects the recovery process by ultrafiltration membranes. At pH 0,5 the surfactant CMC value can decrease up to 69% compared with the pure SDS surfactants CMC value (8,16 mM). The research shows that surfactant micelles formed even under CMC value of pure surfactant by the addition of acid.

***Keywords:-** MEUF; Acidification; Recovery; Surfactant.*

I. INTRODUCTION

The presence of heavy metals in wastewater has been an environmental issue for a long time and poses a serious threat to the health of living things and poses a risk to ecosystems, even at very low concentrations [1]. Concentrations of heavy metal ions that exceed the permissible limits in the food chain, can cause poisoning in humans and other organisms. Direct disposal of heavy metal effluents in sewage systems may inhibit operations in wastewater treatment [2]. The integration of ultrafiltration process surfactant micelles, known as Micellar Enhanced Ultrafiltration (MEUF) exhibited an ability to separate contaminants in liquids, including heavy metal ions [1]. The advantages of MEUF are low energy consumption, high separation efficiency, and simple equipment [3]. The MEUF process proved to be able to remove metal ion waste even at low concentrations by combining the adsorption process of surfactant micelle and ultrafiltration membrane [4].

MEUF technique is performed by adding surfactant in a certain concentration to produce micelles which then bind heavy metal ions to form larger molecules [5]. Due to the high electrical properties of surfactants, when the concentration reaches the Critical Micelle Concentration (CMC), the monomers of the surfactants combine and aggregate to form micelles that entrap the metal ions. The surfactant micelles have a larger diameter than the pores of the ultrafiltration membrane [6]. The micelles cannot pass through the ultrafiltration membrane this mechanism enable the ultrafiltration process to separate micelle that binds metal ions and other organic contaminants [7].

The anionic surfactant, Sodium Dodecyl Sulfate (SDS) is often used in the MEUF method due to its effectiveness in removing heavy metal ions [3]. The use of surfactants with concentrations exceeding the pure surfactant CMC to form micelle can cause surfactants to become secondary pollutants and increase cost, thus reusing surfactants important [8]. Surfactants existence in the water shows negative impacts, such as decreased oxygen transfer and damage to water quality. Surfactants contaminated water is harmful to human health, and therefore several techniques are offered for surfactant recovery such as foam fractionation [9], acidification [10], and alkali-surfactant flooding [11].

The acidification method is the simplest and most efficient method for the recovery of surfactants. This method uses acid to separate heavy metal ions from the surfactant micelles followed by an ultrafiltration process in which ultrafiltration claimed as an effective method for the separation of heavy metal ions which have a relatively large size [12]. Heavy metal ions pass through the membrane and micelles are retained in the feed water [13]. The addition of acid to the solution lowered the pH of the solution. At low pH values, there are abundant H^+ ions all over the surfactant micelles. The separation of surfactant with metal ions occurs because the bond between the metal ions and the micelles of surfactant is replaced by H^+ ions . H^+ ions have an effect on decreasing electrostatic repulsion between surfactant heads and bind to SDS micelles through electrostatic adsorption and replace bonds between metal ions and surfactant [14].

The formation of a micelle can be known from a thermodynamic parameter. Micelle forms at certain value concentration, these values are influenced by other factors including temperature, pressure and ionic strength [15]. Thermodynamic parameters have an important role in the knowledge of micellization processes, such as the standard Gibbs energy of micellization (ΔG^o_m). The tendency of surfactants to form micelles determined based on ΔG^o_m [16]. Negative value of ΔG^o_m indicate that the micellization process is a thermodynamically favorable process. Lower CMC values can be achieved due to the presence of proton ions from H^+. Proton ions decrease the electrostatic repulsion of the charge on the surfactant head by reducing the charge density of the micelles [17].

In the previous research [18] the acidification process was carried out with the concentration of SDS surfactant used of 2 CMC, but the research [4] showed that the presence of metal ions can reduce the CMC value of the surfactant so that it can form micelles at lower concentrations, in addition, research by [19] studied about the effect of pH and the addition of metal ions on the CMC value of SDS surfactant. As a result, the CMC value of the SDS surfactant decrease as the pH decreased. Research on the recovery of surfactant with concentrations below the pure CMC value has never been done.

In this research, recovery of surfactant below pure CMC value and the effect of acid to separate surfactant from Cu^{2+} metal ions was studied. The surfactant used is SDS with a pure CMC value of 8,02 mM. The use of sulfuric acid in addition to separating the bonds between surfactants and metal ions is also reduces the CMC value of pure surfactants. The surfactant recovery process is carried out by the initial MEUF process which is to produce a retentate solution. The retentate solution which still contains surfactant is then used as a recovery feed. The initial surfactant concentration is 7 mM was below the pure CMC surfactant and the value of initial Cu^{2+} is 100 ppm.

II. MATERIALS AND METHOD

A. Material

Sodium Dodecyl Sulfate (>95%) was selected as the anionic surfactant and $CuSO_4.2H_2O$ as the metal ions. H_2SO_4 (95% - 97%) used for adjusting the pH of solution. All of the material prepared on high purity specification, procured from Merck, German. Polyethersulfone membrane (Sterlitech, USA) with MWCO 1 kDa used for ultrafiltration process.

B. CMC surfactant

The CMC value of SDS was measured based on the conductivity of the solution using a conductivity meter from AZ instrument, Taiwan. Measurements were carried out on SDS solution with an increased concentration from 0 mM to 9 mM at pH 0,5 at temperature 25ºC, and atmospheric pressure, from conductivity graph of solution, CMC can be determined and calculate the ΔG^o_m value.

C. Initial MEUF

Initial MEUF process aim to get the retentate solution for surfactant recovery. The feed solution for initial MEUF process was prepared by mixing 7mM SDS with 100 ppm $CuSO_4.2H_2O$. The solution stirred for 1 hour at 200 rpm. The MEUF process was carried out at temperature 25ºC with a pressure 2,5 MPa using Polyethersulfone (PES) membrane. Filtration conducted on a cross-flow system where the retentate solution is recycled into the feed solution until the process complete. Then the MEUF process was carried out until 200 ml of permeate solution was obtained.

D. Acidification and Ultrafiltration

The acidification process conducted by adding sulfuric acid to the retentate solution of initial MEUF to adjust the pH variation 0,5; 1; 2; and 3 of the solution. The solution was then stirred for 1 hour at speed 200 rpm to obtained homogeneous solution and generated surfactant micelle. The ultrafiltration process aims to separate surfactant micelles from metal ions and replaced their bonds with H^+ ions. The ultrafiltration process was carried out at pressure 2,5 MPa. The retentate solution was then analyzed for surfactant content by MBAS method using Shidmazu spectrophotometry. Permeate solution was analyzed for metal ion content by AAS method. The percentage of surfactant recovery and metal ion rejection is calculated by equation (1) and (2) :

$$R_0(\%) = \frac{C_s V_s}{C_i V_i} \times 100\% \quad (1)$$

$$R(\%) = \frac{C_P V_p}{C_f V_i} \times 100\% \quad (2)$$

Where R_0 is surfactant recovery and R is rejection of metal ion. C_s and C_I is surfactant concentration in retentate and feed solution, while V_s and V_i is the retentate volume and intial volume of the feed solution. C_p and C_f is metal ions concentration in the permeate silution and feed solution. V_p is the volume of permeate.

III. RESULT AND DISCUSSION

A. Rejection of Metal Ion (Cu)

The solution to be recovered is the retentate solution from the initial MEUF process. The initial surfactant concentration in the feed solution is 7 mM which is below the CMC value of pure surfactant, with a Cu^{2+} metal concentration of 100 ppm. The initial MEUF process produces a retentate solution which still contains SDS surfactant bounded with Cu^{2+}. Retentate solution from the initial MEUF process became the feed for the acidification and ultrafiltration process to recover surfactant in the retentate solution and separate the Cu^{2+} ions.

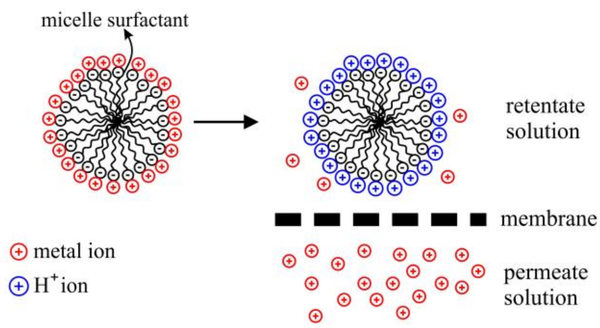

Fig 1. Scheme of metal ion rejection

The effect of the retentate solution pH was studied to determine the role of acid in the acidification process. The retentate solution from the initial MEUF process was added with sulphate acid until it reached a certain pH value. The

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concentration of Cu^{2+} in the initial MEUF retentate solution was still quite high, indicated by the low levels of Cu^{2+} metal ion in the permeate solution (<0,02 mg/L), hence the initial concentration of metal ions in the acidification process was considered to be the same as the initial concentration of initial MEUF process.

The low levels of Cu^{2+} metal ions in the permeate solution of the initial MEUF process also prove that even below the CMC value the SDS surfactant can bind Cu^{2+} metal ions in wastewater treatment with an initial concentration of $CuSO_4$ 100 ppm. The rejection of metal ions increased significantly with a decrease in the pH value. The H^+ ions in the acid replace the bond between the surfactant and the Cu^{2+} metal ions [14].

The result of the ultrafiltration process at various pH variation of 3; 2; 1 and 0,5 indicate that at the lowest pH of 0,5 the metal rejection is quite optimal, which is 72%. This is because when the solution is at a low pH, there are quite a lot of H^+ ions in the acid which can cause metal ions to mix with the surfactant. The metal ions replaced by H^+ ions will then flow through the membrane to the permeate solution [18]. This can be seen in Fig 2 where the metal ion value at pH 3 is lower and continues to increase along with the decrease in pH value, while at pH 2 the metal ion has exceeded 50%. This result is in accordance with research [14] were at a pH of less than 3 metal ions experienced a significant increase, whereas when the pH was above 3 the decrease in metal ions was not very significant.

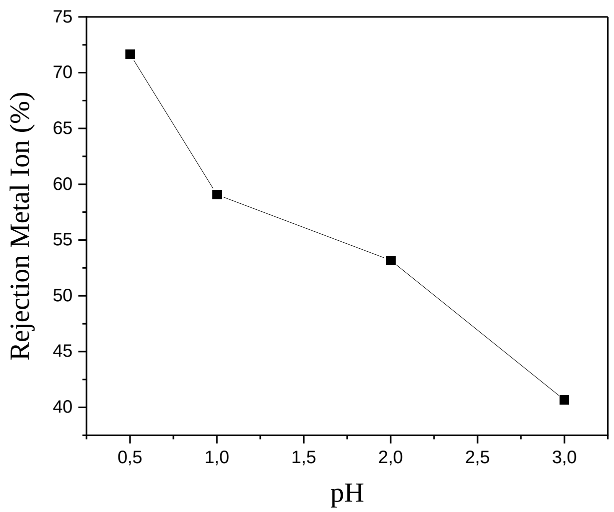

Fig 2. Rejection of metal ion Cd^{2+} with pH variation

B. Recovery Surfactant

At the strong acidity condition, the H^+ ions in the acid replaced the metal ions bonds that bind to the surfactant micelle. The metal ions released from the surfactant micelle pass through the membrane in the ultrafiltration process, but the surfactant micelle which is larger than the pores of the ultrafiltration membrane will still be retained in the retentate solution [20]. Fig 3 shows that even at the same surfactant concentration, the surfactant recovery results are different because of the influence of the acidity of the solution, the role of acid in acidification is not only to replace the bond between metal ions and surfactant micelle but also to stimulate the formation of more surfactant micelle even at low concentration. H^+ ions bind through electrostatic adsorption and bind to the surfactant micelle in the gap between the surfactant heads and cause the stern layer to be compressed so that the repulsion between the surfactant heads will decrease and encourage the formation of more micelles [19].

The surfactant recovery shown in fig 3 decreased by the increasing of pH. Increasing of pH solution causes increasing negative charge of the anionic surfactant, hence the electrostatic repulsion between hydrophilic head group icreases, this leads to restrict of formation a large aggregates [21]. Micelle size effect the ultrafiltration process, where micelle that are larger than the membrane pore will be retained. The highest surfactant recovery of 61% obtained at pH 0.5 although surfactant micelle was easier to form a lower pH due to a decrease in repulsion force, in strong acid conditions the surfactant hydrolysis reaction occurred faster as shown in the following reaction [18]:

$$2C_{12}OSO_3Na + H_2SO_4 \longrightarrow 2CH_{12}OSO_3H + Na_2SO_4$$
$$CH_{12}OSO_3H + H_2O \longrightarrow CH_{12}OH + H_2SO_4$$

Through this reaction, it can be seen that the hydrolysis of SDS surfactant causes the formation of dodecanol which is faster that the reformation micelle of SDS surfactant, in addition to strong acid conditions the membrane pores expand in order that surfactant micelle can easily pass through the membrane to the permeate solution.

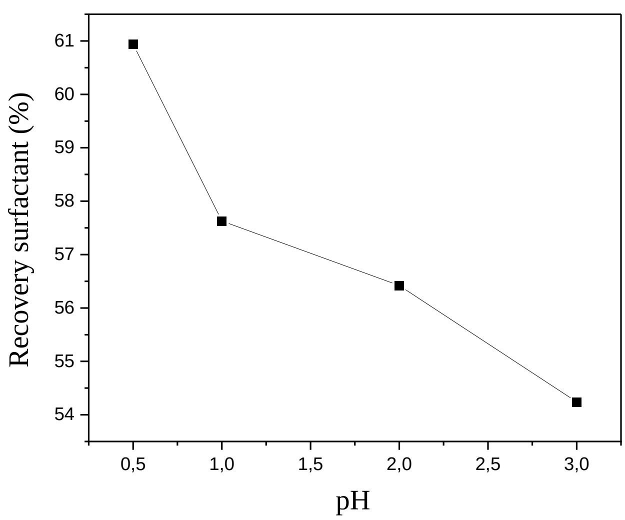

Fig 3. Recovery of surfactant SDS with pH variation

C. Micellization of SDS

The basic principle in the ultrafiltration process is separation based on differences in particle size using a membrane. Surfactants that gather and form larger sizes are called micelle surfactants. In the ultrafiltration process, the formation and size of micelles is important. Micelle surfactant can be formed when the surfactant reaches a certain minimum concentration or is called Critical Micelle Concentration (CMC). CMC needs to be achieved in order for the surfactant to form micelles [22]. In general, the CMC value of surfactants is quite high, but that’s not a certain value and affects by several causes related to a solution. Determining the value of CMC can

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be done by the characteristics of spontaneous changes in the physical properties of a solution such as surface tension or electrical conductivity [23]. In this study, the CMC value was measured by the conductivity of the solution.

The formation of micelles could be known by calculating the value of ΔG^o_m with the following equation :

$$\Delta G^o_m = (2 - \alpha) RT ln X_{cmc} \qquad (3)$$

Thermodynamic parameters can be used to determine the micellization process in surfactants such as ΔG^o_m. The tendency of surfactants to fotm micelles can be determined by ΔG^o_m, where α is the degree of ionization of micelles which can be determined by the equation [24]:

$$\alpha = \frac{S_2}{S_1} \qquad (4)$$

S1 dan S2 are the slopes of premicellar and postmicellar [25].

The CMC value is when the conductivity value starts to stabilize. Fig 4 shows that the CMC value of SDS surfactant in a pH 0,5 is 2,5 mM. pure SDS can decrease by 69% due to the influence of the acid level of the solution. In conditions of strong acid, the CMC value decreases because the H^+ ion in the acid can reduce the repulsion force between the surfactant heads so that the surfactant can more easily form micelles and reduce the CMC value. The decrease in the value of CMC is quite important to be able to reduce the excessive use of surfactants so that it is good for the environment and reduces costs.

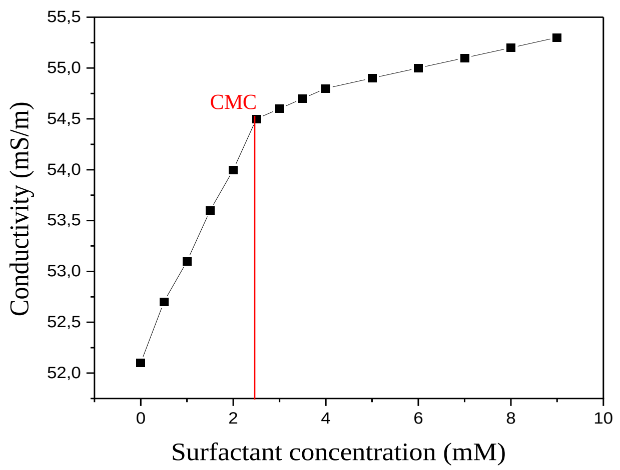

Fig 4. conductivity surfactant solution at pH 0,5

Table 1 shows that the ΔG^o_m value of SDS surfactant in a pH 0.5 solution is more negative namely -59,29 kJ/mol when compared to thevalue at neutral pH solution where the value of ΔG^o_m is -35,24 kJ/mol [25], indicating that surfactant micelle is easier to form spontaneously in a pH 0,5 solution than a pure surfactant [26].

Counterions binding between surfactants with ion H^+ ions in the micellar state contributes to the ΔG^o_m value of SDS surfactant in a pH 0.5. The surfactant CMC value and the ΔG^o_m value of the SDS surfactant obtained can prove that the macroscopic properties of the surfactant, such as the surface free energy of the surfactant ionic groups and electrostatic interactions possible to predict the micellization process of the surfactant which is influenced by the pH of the solution [27].

Table 1. ΔG^o_m and CMC value at pH 0,5 and 7

pH of solution	CMC (mM)	ΔG^o_m (kJ/mol)
7	8,02 [(a)]	-35,24[(a)]
0,5	2,5	-59,29

(a)references from (Shirzad & Sadeghi, 2014)

IV. CONCLUSION

The result showed that the surfactant in the retentate MEUF solution can be recovered even at low concentrations with the addition of sulfuric acid. Optimal conditions for recovery of low concentration surfactants at pH 0,5. At pH 0,5 rejection metal ions can reach 72% and 61% surfactant can be recovered from the retentate solution. The use of acid in the acidification process not only replaces the between metal ions and micelle surfactant but also reduces the CMC value of pure surfactants. The decrease in CMC value is quite significant up to 69% at pH 0,5 when compared to the CMC value at neutral pH solution. The low CMC value and the increasing negative value of ΔG^o_m indicate that surfactant micelle can be easily formed thereby increasing the effectiveness of recovery.

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