Development of nanofluid detergent based on methyl ester sulfonates surfactant from waste cooking oil and titanium dioxide nanoparticles

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Abstract. In this study, nanofluid detergent was synthesized from methyl ester sulfonate (MES) surfactant and titanium dioxide nanoparticles while MES surfactant was synthesized from waste cooking oil (WCO), a low-cost material. The purpose of this study was to obtain an eco-friendly nanofluid detergent with optimum stability and performance. In the synthesis of MES surfactant, WCO has been purified first then followed by trans-esterification and sulfonation process. Concentrations of MES surfactant and CMC (carboxymethyl cellulose) were varied for detergent synthesis, while TiO2 concentration was kept at 0.1%. Performance test of detergent was studied by stain removal and stain degradation test. Optimum quality of MES surfactant was obtained at pH 7 with disalt content of 4.47%. The results showed at MES surfactant concentration of 1.5%, detergent had the best stability about 99% and after the addition of CMC 4%, no sedimentation occurred within two weeks. MES concentration of 1.5% has the best performance for stain removal and after the addition of CMC 4%, detergent performance increased about 14%. While stain degradation test showed that detergent performance can be improved by TiO2 photocatalytic reaction, which respectively increased about 11% and after the addition of CMC increased 5%.

Keywords: detergent performance, nanofluid detergent, MES, TiO2 nanoparticles, WCO

1. Introduction
In detergent products, surfactant is the main ingredient in formulation which is used as cleaning agent [1]. Recently detergent industries have been competitive over the eco-friendly, cost-effectiveness and the detergent performance. These led to development of detergent with the use of eco-friendly surfactant such as methyl ester sulfonate (MES). The low cost of MES production and its eco-friendly properties have been taking the detergent industry’s interest [2]. MES is an oleo-chemical based anionic surfactant, can be easily synthesized using bio-oil feedstock and can be used for detergent application [3]. The advantages of MES are higher detergency at lower doses, stable in hard water, good biodegradability, harmless oral toxicity (2.2-3.8 g/kg weight), low toxicity on animal (low toxicity range) and good skin compatibility [3-5]. In MES production, the most commonly used as raw material is vegetable oil. MES from waste cooking oil (WCO) can be considered as an alternative method for waste oil utilization. These oils are not re-useable for consumption due to the presence of toxic components and most of WCO is being disposed to environment causing pollution. The cost of WCO is cheaper than vegetable oils, therefore can reduce the production cost of MES [3, 6-8]. In MES product, there are two active matters: RCH(CO2Me)SO3Na (MES) and RCH(CO2Na)SO3Na (disalt). Disalt can reduce the surface
activity and solubility of MES in hard water [3]. It is important to avoid extreme pH when the neutralization process, therefore can prevent the formation of disalt due to MES hydrolysis [9].

In this study, detergent was synthesized in the form of nanofluid based on MES surfactant and TiO₂ nanoparticles. Surfactant and TiO₂ will disperse each other in detergent. The surface of TiO₂ will adsorb hydrophobic tail of surfactant so particles have the same charge (negatively charged), there will be repulsion forces to prevent agglomeration [10]. The use of surfactant to improve TiO₂ stability in nanofluid have been reported previously, but most of these works are the use of nanofluid as working fluid such as cooling fluid for heat exchanger [11-13]. On the other hand, TiO₂ in detergent is expected to degrade pollutants, if laundry wastewater discharged into environmental waters.

A major concern for detergent in the form of nanofluid is stability, to improve detergent stability, carboxymethyl cellulose (CMC) was added. CMC can bind water, therefore increases the viscosity of detergent [14]. CMC has been commonly used in liquid detergent as anti-redeposition agent to prevent dirt being redeposited. The addition of excess CMC into detergent can decrease detergent performance. In large quantities, CMC will cause surfactant molecules trapped and difficult to move [15]. So in this study, variation of MES surfactant and CMC concentrations were done to obtain the optimum detergent performance.

In the present study, MES surfactant was synthesized from WCO then disalts content in MES product was analysed at various pH neutralization to get optimum quality of MES. After that, detergent was synthesized from MES surfactant and TiO₂ nanoparticles. Concentration of MES surfactant was varied to obtain optimum stability and detergent performance, then followed by the addition of CMC as detergent stabilizer. Concentration of CMC was varied as well to get the optimum stability and detergent performance. This study is expected to give solution for the environmental problems due to the use of non eco-friendly detergents.

2. Experimental Section

2.1. Materials

WCO was obtained from food stalls in Kukusan, Depok, West Java, Indonesia which have been purified first in our laboratory with an acid value of 0.69 mg KOH/g oil, free fatty acid (FFA) content of 0.96% and moisture content 0.58% [8], methanol (Merck, P.A), sodium bisulfite (Smartlab, P.A), sodium hydroxide (Merck, P.A), TiO₂ P25 (Evonic Industries, average particle size of 21 nm), CMC (carboxymethyl cellulose), methylene blue (Merck, P.A), bromocresol green (Merck, P.A), hyamine 1622 (Merck, 0.004 mol/l), chloroform (Merck, P.A), sulfuric acid (Mallinckrodt, P.A) and aquadest (Wilosco).

2.2. Synthesis of Methyl Ester Sulfonate from WCO

MES was synthesized through trans-esterification and sulfonation processes. The trans-esterification process was carried out with mole ratio of WCO and methanol of 1:9 with catalyst KOH 1% (wt. % of oil) at temperature reaction 60°C for 1 h and stirred at constant speed. The methyl ester was analysed by a Gas Chromatography-Mass Spectrometer (GC-MS) with 5975C mass selective detector and capillary column (HP Innowax, 30 mx0.25 mm (I.D) x 0.25 μm). Second step, sulfonation was carried out at temperature 100°C for 4.5 h with mole ratio of methyl ester and NaHSO₃ of 1:1.5. The mixture was centrifuged at 1500 rpm for 30 min to separate residual NaHSO₃. Then, followed by purification with methanol 40% (v/v MESA) at 50°C for 1.5 h, evaporate the excess of methanol on hot plate (50-60°C). After evaporation, neutralization was performed with NaOH solution 20% at 55°C for 30 min [8, 16].

The disalts content of MES was determined by two-phase titration method using two coloured indicators i.e. methylene blue for sulfonate group detection and bromocresol green for sulfonate and carboxylate groups [17-19]. The disalts were determined by subtracting the value of hyamine bromocresol green titration with the value of hyamine methylene blue titration.
2.3. Synthesis of Detergent
MES surfactant-TiO$_2$ nanoparticle detergent was prepared by mixing MES surfactant into aquadest while stirring until homogeneous, then the addition of TiO$_2$ to the mixture (TiO$_2$ concentration was kept at 0.1%) and stirred for 30 minutes. Ultra-sonication was performed in sonicator bath for 30 minutes. The sonication process uses to break the aggregates of TiO$_2$ particles which are still formed in the detergent. These cause TiO$_2$ to be more dispersed and its particle size will be under 100 nm. In synthesis detergent with the addition of CMC, synthesis detergent between MES surfactant-TiO$_2$ was done as well with the same steps. Simultaneously, CMC solution was prepared by mixing CMC with water and stirring at temperature 70-80°C for 30 minutes. Then added the detergent mixture (MES surfactant-TiO$_2$) into CMC solution slowly and stirred for 30 minutes at 70-80°C.

2.4. Stability and Detergent Performance Test
In detergent MES-TiO$_2$, stability was analysed by spectrophotometer UV-Vis (Thermo Scientific Genesys 10S). The stability of TiO$_2$ was observed by measuring sedimentation rate of TiO$_2$ in detergent. The sedimentation rate was determined by the absorbance of detergent at wavelength 420 nm (white sulfate wavelength of BaSO$_4$). If sedimentation rate of TiO$_2$ after 3 hours is below 5%, then it can be considered as stable detergent [20]. While for detergent with addition of CMC, stability was observed visually for two weeks. When there are no separation occurred for two weeks of storage then it is considered stable. For detergent performance was performed based on stain removal, stain degradation and surface tension test.

In stain removal and stain degradation test, the test was performed on fabrics stained with methylene blue (used as dirt model) under ordinary washing conditions using photo-based washing machine reactor. Reactor equipped with a light source for stain degradation test. Washing was done for 30 min with the speed of agitation 52 rpm, then methylene blue residue on the fabrics were extracted with 0.4% surfactant solution. Methylene blue concentration in the solvent (0.4% surfactant solution) was measured by spectrophotometer UV-Vis ($\lambda$=652 nm). The results are expressed as detergency which is the ability of detergent to clean.

Surface tension was measured by surface tensiometat (Model 21 Cole-Parmer) equipped with a platinum-iridium ring. The measurement of solutions at different concentrations was performed by the du Nouy method (ASTM D-1331) at 25°C and detected three times until the surface tension remained constant.

3. Results and Discussion

3.1. MES Surfactant from WCO
MES surfactant has been synthesized from WCO with trans-esterification and sulfonation process. Methyl ester was prepared by trans-esterification process with yield about 96%. The methyl ester was analysed by GC-MS. The result showed that the highest percentage of component present in methyl ester is methyl oleate (43.25%). Then methyl ester was sulfonated with NaHSO$_3$. Disalt content at various pH neutralization shows in Fig. 1. The highest disalt content of 7.54% obtained at pH 8 and the lowest of 2.22% at pH 5 (see Fig. 1). Disalt in MES product must be lower than 5% due to negative impacts on its application [3, 21]. Based on our previous study, effect of pH neutralization on surface tension of MES showed that the lowest surface tension is 32.4 mN/m (dyne/cm) at pH 7 [8], so the optimum neutralization pH was obtained at pH 7 with disalt content of 4.47%.

The hydrophilic lipophilic balance (HLB) value of surfactant can be determined by equation of Griffin and Davies-Rideal based on constants of each groups. MES surfactant consists of alkyl, ester and sodium sulfonate groups. The constant value for alkyl group is 0.475; ester is 2.4 and sodium sulfonate (-SO$_3$Na) is 11 [22]. Based on our previous study, MES surfactant from WCO contain mostly atom of C19 (from methyl oleate) [8]. HLB value of MES is 12.33 (HLB=7+11+2.4-17x0.475) which shows that this value has fulfilled the HLB range for detergent applications (3-15) [22].
3.2. Effect of MES Surfactant Concentration on Detergent Stability

Liquid detergent based on MES surfactant and TiO$_2$ nanoparticles is produced in the form of nanofluid, so stability test is required to maintain the stability of nanofluidic system. Absorbance of TiO$_2$ was measured at time of 0 h and after 3 h. The value of absorbance reduction after 3 h indicates the stability of TiO$_2$ nanoparticles in detergent. The result of stability test at various concentrations of MES surfactant shows in Fig. 2.

![Figure 1. The disalt content (wt.%) at neutralization pH of MES surfactant.](image1.png)

![Figure 2. Detergent stability at variation of MES surfactant concentration (for 3 h).](image2.png)

Detergent stability is smaller than 90% at MES concentration below 1.1% and tends to be stable at concentration above 1.1% about 99% (see Fig. 2). This is due to the interaction between TiO$_2$ and surfactant which have hydrophilic and hydrophobic group. The interaction between surfactant and TiO$_2$ nanoparticles can prevent the sedimentation of TiO$_2$ because surfactant will decrease aggregate growth [23]. TiO$_2$ will be dispersed well in the solution because hydrophobic group of surfactant will bind/adsorb to hydrophobic group of TiO$_2$ nanoparticles, while hydrophilic group of surfactant will bind to water [24].

3.3. Effect of MES Surfactant Concentration on Detergent Performance

In addition to the stability test, effect of MES surfactant concentration on detergent performance consist of stain removal and stain degradation were analysed. Stain degradation test was done with the help of mercury lamps. TiO$_2$ nanoparticles have the degradation ability when TiO$_2$ gets photon induction (exposure to the light) [25, 26]. The results of stain removal and stain degradation test are shown in Fig. 3. Detergent performance of stain removal increase as the MES surfactant concentration increase. The highest performance of stain removal 70.82% at MES concentration 1.5%. Few studies reported that detergency of MES surfactant was about 60-80% when tested to remove stains such as pigment, oil, mineral, sebum, soot and protein [2, 17, 27].

![Figure 3. Detergent performance in stain removal and degradation.](image3.png)

![Figure 4. Laundry wastewater of MES surfactant 1.5% at (A) stain removal and (B) stain degradation test.](image4.png)
On the other hand, detergent performance in stain degradation test was 82.18% at MES concentration 1.5%. The result showed that the stain has been degraded by TiO$_2$ thus improving performance of detergent. Laundry waste water of MES concentration 1.5% shows in Fig. 4. The stain degradation test, colour of laundry waste water was white compared to stain removal test, the colour was blue. These showed that methylene blue was used as dirt model has been degraded by TiO$_2$ in laundry waste water. The presence of mercury lamp in stain degradation test causes the excitation of electrons in TiO$_2$ (photon induction). TiO$_2$ produced OH• radicals which are able to degrade the stain. The ability of TiO$_2$ to degrade methylene blue into CO$_2$, H$_2$O and inorganic molecules have been widely reported [12, 28-31]. Furthermore, it has been reported that TiO$_2$ also can degrade organic impurities such as bacteria, virus and fungi [25, 32-37]. Therefore, TiO$_2$ can improve detergent performance which can act as an antibacterial agent. The ability of TiO$_2$ to degrade methylene blue does not occur in the stain removal test because TiO$_2$ does not get the light source. TiO$_2$ is inactive and causes the laundry waste water to remain blue (there is no stain degradation process).

3.4. Effect of CMC Concentration on Detergent Stability
The addition of CMC in detergent serves as detergent stabilizer additive [14]. Based on effect of MES concentration obtained at MES concentration 1.5% with TiO$_2$ 0.1% having the best stability and performance, then it was used as constant composition. The CMC concentration was varied. Stability test with the addition of CMC was performed qualitatively (visual) with observation for 14 days (two weeks). The results at 0 hour are shown in Fig. 5. However, the effect of CMC concentration on detergent stability at 0 hour has not been seen because there are no two layers formed (homogeneous phase).

The results at two weeks showed that the addition of CMC with concentration of 4-5% still formed a stable detergent system (see Fig. 5). While at the CMC concentration of 1-3% formed two layers on detergent clearly visible (mark in black lines). It showed that the higher CMC concentration can improve detergent stability because detergents are becoming thicker. On the other hand, in previous study reported that the higher CMC concentration will decrease the detergent performance. This is the opposite of detergent stability, so the effect of CMC on detergent performance was analysed as well.

![Figure 5](image.png)

**Figure 5.** Effect of CMC concentration on detergent stability at 1% (A), 2% (B), 3% (C), 4% (D) and 5% (E).

3.5. Effect of CMC Concentration on Detergent Performance
Commonly liquid detergents use CMC as a thickener to prevent the separation between ingredients in detergent into two phases and also serves as an anti-redeposition agent [38]. Detergent performance test consist of stain removal and stain degradation were analysed. The results are shown in Fig. 6, in stain removal test at CMC concentration 0-1% and 3-4% detergent performance tends to be constant about
71% and 85% respectively. Then the performance decreased at CMC 5% to 80%. In stain degradation as well, detergent performance tends to be constant at CMC 0-1% and 3-4% about 82% and 90% respectively then decreased at CMC 5% to 86%. On the other hand, it can be seen that detergent performance in stain removal test higher compared to stain degradation. These showed that stain had been degraded by TiO$_2$, the decrease at CMC concentration 5% can be caused by the CMC covering surface of TiO$_2$, therefore the degradation process did not go well.

Figure 6. Detergent performance in stain removal and degradation.

Meanwhile the decrease of detergent performance in stain removal test causes of thickening effect due to the interaction between water with CMC in detergent. Thick liquid will cause the surfactant molecules trap and making it difficult to move. Thickening effect due to the addition of CMC is caused by interaction of water with CMC because CMC is polymer having hydrophilic groups OH to absorb water [15, 39]. While detergent performance can improve causes of the function of CMC as anti-redeposition. CMC will be adsorbed on the surface of fabric causing the surface of fabric to be negatively charged. CMC effectively work on cotton fabric [38, 40]. Laundry wastewater at CMC concentration 4% showed in Fig. 7. The colour of laundry wastewater in stain degradation test was white compared to the stain removal which was blue. These showed that stain had been degraded in laundry wastewater by TiO$_2$.

Figure 7. Laundry wastewater of CMC 4% at (A) stain removal and (B) stain degradation test.

3.6. Effect of TiO$_2$ in Detergent

The main purpose of adding TiO$_2$ was to help dispersion of surfactants in detergent. The addition of hydrophobic compounds such as TiO$_2$ will help surfactant to form a micelle therefore the cmc (critical micelle concentration) point will be achieved faster without adding surfactant in excess amount. The cmc is the concentration when a set of surfactant molecules form a micelle. Surfactant will have surface-active properties (surface activity) if the concentration has reached cmc point [41, 42]. Effect of TiO$_2$ on detergent performance shows in Fig. 8. The results showed that with the addition of TiO$_2$ at MES concentration 1.5% can improve detergent performance in stain removal test about 6% and at this concentration is the highest detergent performance. The detergent performance of MES surfactant was lower than after TiO$_2$ nanoparticles added. It can be caused by concentration of MES surfactant used has not reached the cmc point. When TiO$_2$ nanoparticles were added the concentration increases and started to reach the cmc point.

On the other hand, when the cmc point has been reached, the decrease of surface tension is becoming larger as well. Effect of TiO$_2$ on surface tension reduction shows in Fig. 9. Surface tension of water initially was 80.5 dyne/cm decreases with the addition of surfactant and TiO$_2$ nanoparticles. The result showed that MES concentration 1.5% has the lowest surface tension of 32.8 dyne/cm. It was smaller than the surface tension of MES surfactant alone was 35.9 dyne/cm. TiO$_2$ can reduce surface tension to 56.8 dyne/cm. This is because TiO$_2$ can interfere the cohesion forces between water molecules, and the adhesion forces between molecules of water and air. While surfactant can reduce surface tension due to hydrophobic and hydrophilic groups [10].
4. Conclusion
MES surfactant from WCO at pH 7 has fulfilled the limit requirement of disalt content in MES product which must be lower than 5%. Liquid detergent in the form of nanofluid has been successfully synthesized with the best stability and detergent performance obtained in the optimum composition of detergent at 0.1% TiO$_2$, 0.5% MES surfactant and 4% CMC. TiO$_2$ nanoparticles in detergent showed that it can improve detergent performance such as stability, stain removal, stain degradation and the surface tension. Other than that TiO$_2$ in detergent can be used as an anti-bacterial agent due to the ability of TiO$_2$ which can degrade bacteria and also the addition of TiO$_2$ can reduce the amount of surfactant was used in detergent.

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