Chemical and Process Engineering Research www.iiste.org
ISSN 2224-7467 (Paper) ISSN 2225-0913 (Online)
Vol.53, 2017

Oil Spill Dispersant Formulation from Diethanolamine (DEA) and Methyl Ester Sulfonate (MES) for Bioremediation Process

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This work was supported by the ["*Insentif Riset Sistem Nasional*" (INSINAS) KEMENRISTEKDIKTI Indonesia] under Grant [no. RT-2016-0570RT-2016].

Abstract
The palm oil industry was developed to produce oleochemical products and derivates, such as surfactant, namely diethanolamide (DEA) and methyl ester sulfonate (MES). The objective of this study is to produce a water based dispersant type from two kinds of surfactants, DEA and MES, then apply it to enhance bioemediation process. Both surfactants were diluted in water to prepare solution of DEA and MES, respectively, then it were determined the critical micelle concentration. The selected solutions were mixed at ratio of DEA and MES solution (9:1 to 1: 9) to obtain the stable emulsion as an oil spill dispersant (OSD). The best characterized OSD formula was tested to enhance bioremediation process for crude oil contaminated soil. The formulation result shows that solution of DEA 1.5% and MES 0.9% are selected at the mixed ratio of 7:3. This OSD product was characterized to density, surface tension, interfacial tension, pH , viscosity and droplet size. The OSD was demonstrated in a microcosm test of crude oil contaminated soil at ratio of crude oil : OSD by (1:1). This result shows that the OSD can enhance the bioremediation process compare to control without OSD.
Keywords: Bioremediation, DEA, MES, OSD, Palm oil derivated, Surfactant

1. Introduction

Palm oil production is vital to the economy of Indonesia. Indonesia is the largest producer and consumer of palm oil in the world, nearly half of the world's supply is produced by Indonesia, therefore, palm oil processing industry in Indonesia is very strategic. To strengthen the palm oil industry in Indonesia, it is necessary to develop downstream products in order to increase the added value of palm oil. Palm oil downstream industry having high added value is oleochemical industry. One of the derivative products is surfactant. Surfactant industry in Indonesia is still limited; however, the surfactant is needed in large quantities for emulsifier materials of personal care products such as shampoo and soap, food products, and cosmetic products. The potential to develop this surfactant is still very large so it is necessary to conduct research on the use of surfactant widely.

A surfactant molecule consists of two structures of polar and non-polar tail groups or the hydrophilic group and hydrophobic of the surfactant molecule determine many of its properties (Gecol 2006). The name of surfactant, due to their physicochemical structure, is where a partition preferentially at the interface between phases with different degrees of polarity and hydrogen bonding such as oil/water and air/liquid interfaces. The presence of surfactant molecules at the interfaces results in a reduction of the interfacial tension of the solution (Franzetti et al. 2010). Surfactant from palm oil derivatives such as APG (alkyl polyglycosides), DEA (diethanolamide) and MES (sodium methyl ester sulfonate) have been formulated for a variety of products, including pesticide, liquid soap, detergent, stimulating oil wells, controlling oil pollution, and bioremediation process of surface water and crude oil contaminated soil (Noredin et al. 2008; Fauziah 2010; Hambali et al. 2008; Elvina et al. 2016; Surya 2015).

The dispersant or OSD (oil spill dispersant) is a mixture of surfactant (surface active agents) and solvent designed to accelerate oil dispersion to form spread droplets and naturally degraded by microbes. In general, the OSD using nonionic and anionic surfactants developed by several investigators are as follows Fiocco and Lewis. 1999; Place et al. 2010; Song et al. 2013. The results of some studies conducted previously showed that with the addition of OSD, it would affect the performance of biodegradation of petroleum and its derivatives by a bacterium. Elvina et al. (2016) stated that the formulation of the OSD of the two types of diethanolamide (DEA) surfactant 3 % in water and a solution of sodium methyl ester sulfonate (SMES) 5 % in the solvent methyl ester, with a ratio of 1:3, could improve the process of biodegradation of petroleum contamination of sea water.

Petroleum waste is classified into the hazardous waste and toxic materials; therefore, it must be treated before discharged to the environment. To reduce petroleum contamination, it can be performed in several ways, namely physical, chemical and biological treatments. The physical and chemical wastewater treatments are relatively short way of handling for managing oil spill waste, but this treatment has the disadvantage that results in other environmental pollution caused by chemicals that are less environmentally friendly. By using biological waste treatment to overcome the problem of hydrocarbon pollution, it is an effective alternative and environmentally friendly.

The crude oil contained light (C_{12}- C_{23}) and heavy (C_{24}-C_{40}) oil fraction of total petroleum hydrocarbon (TPH). The content of hydrocarbons in oil-polluted environment is relatively higher than normal environment. The soil contaminated by crude oil that contained light and heavy fraction. Rosenberg and Ron (1998) describe the bioremediation of petroleum contamination by several methods, such as land farming, biopile, co-composting, biostimulation or bioaugmentation. The oil and gas company who operated in Indonesia, they generally treated the crude oil contaminated soil by land farming or biopile methods and biostimulation of indigenous consortium microrganism with fertilizer (N, P, K). Arifudin et al. (2016) reported that bioremediation of crude-oil contaminated soil by a pilot scale of biopile technique and bioaugmentation by consortium bacteria, the TPH decreased from 4.66% to 1.4% and TPH degradation at 76% for 63days operation. The bioremediated soil was still contained of high molecular weight ($> C_{16}$).

The above description is underlying the research on environmentally friendly OSD formulations to improve the dispersion of petroleum waste. This study aims to develop a product formulation of oil spill dispersant (OSD) consisting of the surfactants of diethanolamide (DEA) and water based methyl ester sulfonate (MES), and apply it to enhance bioremediation process in crude oil contaminated soil.

2. Material and Methods

2.1 Materials

The materials used in this study were surfactants of diethanolamide (DEA) and methyl ester sulfonate (MES) obtained from Surfactant and Bioenergy Research Center (SBRC), Bogor Agricultural University. The crude oil was obtained from Rantau Field, South Sumatera Island, Republic of Indonesia. The latosol soil, sand, and fertilizer (urea and TSP-36) were obtained at Bogor, Indonesia.

2.2 Formulation of OSD

The OSD formulation process was performed in three stages in accordance with the procedure described by Elvina et al. (2016). The first step was to determine the value of the critical micelle concentration (CMC) of the surfactants of diethanolamide (DEA) and sodium methyl ester sulfonate (MES) at several concentrations. For the preparation of water based dispersant, the diethanolamide (DEA) surfactant was diluted with water to make a solution at concentration of 0.5 to 2.5 %, and the MES was at a concentration of 0.1 to 1.0 %. All the solutions were measured the surface tension to determine the CMC values. The concentration of surfactant that has the lowest CMC value would continue to the next step on the OSD formulation. Furthermore, the second step was the formulation by mixing the DEA and MES solutions at the ratio of 9 : 1, 8 : 2, 7 : 3, 6 : 4, 5 : 5, 4 : 6, 3 : 7, 2 : 8, and 1 : 9. The formulation process was carried out, then the stability of the emulsion was visually observed for 7 days. A mixture of surfactant formulation that producing the best stability was selected to further test the surfactant physicochemical properties.

The third step was the analysis of the physico-chemical properties of the selected OSD product. The OSD based on DEA and MES surfactant were analyzed for the interfacial tension, surface tension, viscosity, density, pH and droplet size. The analysis of surface tension was performed by using the Spinning Drop Tensiometer TV brands 500c; the analysis of the density was performed by using density meter Anton Paar DMA 4500M; pH by using pH meter Schott; viscosity using a viscometer Brookfield DV-III Ultra; and the analysis of droplet size by using 100x magnification microscope.

2.3 OSD Test on Crude Oil Contaminated Soil

The OSD application test on crude oil contaminated soil was adopted from Arifudin et al. (2016). The soil contaminated crude oil was mixed from latosol soil (4.2 kg), sand (1.8 kg) and crude oil (360 mL). The latosol soil was selected from fertile, fresh and free from petroleum hydrocarbon or pesticide. The commercial sand from river was washed or leached by tap water to remove the soil. The light crude oil was obtained from the fresh crude oil from wells. The crude oil soil contaminated was transfer to plastic container sized of 40 cm x 20 cm x 12 cm. This crude oil contaminated soil was added with nutrients such as urea and TSP fertilizer adjusted to the amount of oil used by the ratio of C:N:P = 100 : 10 : 1. The crude oil contaminated soil was added by OSD at volume ratio of crude oil to OSD at (1 : 1). This mixed of crude oil contaminated soil were mixed to homogenize and no sterilzed treatment. The treatment of bioremediation test is summarize in Table 1.

Table 1. Composition of soil, sand, crude oil on bioremediation treatment and addition of fertilizer, and OSD

Treatments	Soil (Kg)	Sand (Kg)	Crude Oil (mL)	C:N:P ratio	OSD (mL)
Control	4.2	1.8	360	100:10:1	0
OSD	4.2	1.8	360	100:10:1	360

After mixing, all bioremedition treatments were carried out at room temperature ranged from 22 – 35 ^oC at an average of 26 ^{o}C and manually aerated by mixing, every day for 6 weeks. The samples were taken at initially and 6 weeks. The bioremediated soils were analyzed the moisture content, pH, temperature, and total petroleum hydrocarbon (TPH) by using gravimetric methods (3540C EPA). The TPH biodegradation was calculated from the removal of TPH during bioremediation process for 6 weeks.

2.4 Data Processing

The design experiment used was a simple randomize. The data were analyzed using ANOVA and Duncan Multiple Range Test (DMRT) processed by SPSS 20.

3. Result and Discussion

3.1 Eco-Friendly Surfactant

The formulation of OSD (oil spill dispersant) was carried out using the non-ionic surfactant of DEA and ionic-surfactant of MES. The DEA and MES surfactants were produced from palm oil that was renewable and biodegradable (Hambali et al. 2002; Hambali et al. 2008). The sodium fatty acid methyl ester sulfonate, MES powder is commercially promoted as a new type of Eco-Friendly surfactants (Change Newborui Fine Chemical Factory Co.id (http: //newborui.en. alibaba. com/). This surfactant is made from renewable natural resources, with better compatibility to environment, fast 100% biodegradation, low toxicity and low irritation to skin. The MES's characteristics are high effect surfactant produced by natural plant and animal oil and fat; excellent emulsification, wetting, softening, anti-hard water; good solubility, biodegradable ability; and can reduce irritation to skin. It is a new type of anionic surfactant with excellent performances having good wetting, detergency, emulsifying, thickening, softening, calcium soap dispersibility and resistance to hard water, high frothing ability, good salient chelating capacity of Ca and Mg ions, and it can soften hard water.

3.2 Determination of CMC Value

The fundamental property of surfactant is the ability to form micelles which is responsible for the excellent detergency and dispersing properties of these compounds. The concentration above, of which the formation of micelles is thermodynamically favored, is called Critical Micelle Concentration (CMC) (Haigh 1996). The number of molecules required to form a micelle generally varies between 50 and 100; this is defined as the aggregation number. As a general rule, the greater the hydrophobicity of the molecules in the aqueous solution, the greater the aggregation number is the energy required to increase the surface area of liquid in a unit area (Rosen 1989). The CMC is commonly used to measure the efficiency of a surface active agent. The CMC becomes the point where the value of the surfactant association structure forms surfactant (Rosen 1989). The CMC of surfactants in aqueous solution can vary depending on several factors, such as molecule structure, temperature, presence of electrolytes and organic compounds in solution. The association of surfactant expected in this product is water-in-oil micro emulsion. The CMC is also known as the saturation point of the surfactant that can work to bind water and oil. At the value of CMC, surface tension remains constant even if the surfactant concentration increased. The higher concentration of surfactant used after passing the CMC value, therefore, the more inefficient it is. This is because the use of surfactant doses greater than the value of CMC can cause the reverse emulsion (re-emulsification).

The measurement of surface tension of surfactant DEA were performed between 1.0 % to 2.5 % (Figure 1a). From the measurement of the surface tension of DEA surfactant, it can be seen that the higher concentration of surfactant was indicated to the lower surface tension. The water used as a solvent surfactant had a surface tension value of 67.80 dyne cm^{-1}. Water had a greater surface tension between liquids mostly because the cohesive force is greater than hydrogen bonding (Charlena 2010). The surface tension of DEA of 1.0 % and 1.5 % decreased from 27.94 to 25.49 dyne.cm^{-1}, while DEA of 2.0 % and 2.5% increased from 26.37 to 27.06 dyne.cm^{-1}. This result shows that the CMC for DEA surfactant at a concentration of 1.5 %. Previously reported (Franzeti et al. 2010) that at the concentrations above the CMC, additional quantities of surfactant in solution will promote the formation of more micelles. The formation of micelles leads to a significant increase in the apparent solubility of hydrophobic organic compounds, even above their water solubility limit, as these compounds can be separated into the central core of a micelle.

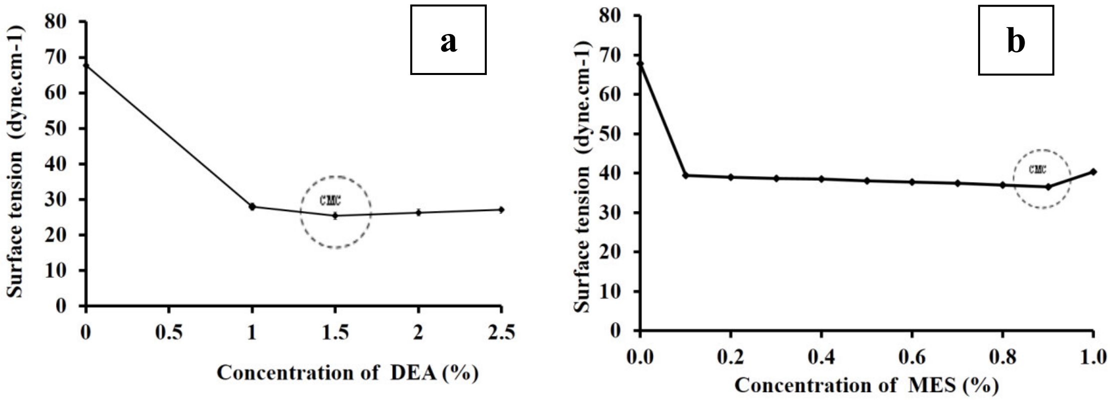

Figure 1. Selection of DEA (a) and MES (b) concentrations at the lowest surface tension as critical michelle concentration (CMC) .

The surface tension of various surfactant concentrations of MES is shown in Figure 1b. The value of surface tension of MES at the concentration of 0.1 % to 0.9 % decreased from 39.50 to 36.60 dyne cm^{-1}, and at the concentration of 1.0 % increased to 40.44 $dyne.cm^{-1}$. This indicates that the value of CMC for MES surfactant was at the concentration of 0.9 %. This concentration was chosen that it will be used as a dose at the formulation of dispersant. The surfactant characteristics of DEA and MES are presented in Table 2. The density of both DEA (1.5%) and MES (0.9%) surfactants were the same as 0.995 $g.cm^{-3}$. The viscosity of DEA (1.5%) is higher than MES (0.9%). This indicated that the molecule of DEA was stronger than MES to hold water. The pH of MES was neutral at 7.15, that caused by the process neutralization by sodium hidroxide.

Table 2. Characteristics of DEA and MES solutions

Characteristics	Unit	Surfactant solution	
		DEA 1.5%	MES 0.9%
Density (30^{o}C)	$g.cm^{-3}$	0.995	0.995
Viscosity	cP	1.32	1.06
pH	-	9.84	7.15
Surface tension at CMC value	$dyne.cm^{-1}$	25.49	36.60

3.3 Dispersant Formulation

The formulation of dispersant was made by mixing DEA (1.5%) and MES (0.9%) and then the emulsion stability was observed visually. From the mixed solution, it was observed the clarity appearance and emulsion stability. The emulsion stability test of the dispersant product was performed by scoring 1-5 from unstable to very stable (Table 3). The higher value of the score, the better emulsion stability was obtained. Based on the stability of the emulsion, the dispersant product was selected for the next stage which has a value of 4-5. The test results show that a stable emulsion system at DEA (1.5%) and MES (0.9%) were equal to 9:1, 8:2, 7:3, 6:4 and 5:5 (Table 3).

Table 3. Emulsion stability of OSD formula

Ratio of DEA 1.5% : MES 0.9%	Clarity appearance	Stability emulsion	Emulsion stability score
9:1	Very Clear	Very stable	**5**
8:2	Very Clear	Very stable	**5**
7:3	Very Clear	Very stable	**5**
6:4	Clear	Stable	4
5:5	Clear	Stable	4
4:6	Not clear	Fairly stable	3
3:7	Not clear	Fairly Unstable	2
2:8	Two phase	Unstable	1
1:9	Two phase	Unstable	1

3.4 Surface Tension

Surface tension is a thermodynamic property and can be measured under constant temperature and pressure, and its value represents the amount of minimum work required per unit area to create a greater surface area. In measuring surface tension, one is measuring the free energy per unit area of the surface between liquid and the air (erg cm^{-2} or J m^{-2}). Surface tension is also quantified as the force acting normal to the interface per unit length of the surface at equilibrium ($dyne.cm^{-1}$ or $mN.m^{-1}$). The surface tension of water at 25 ^{o}C is 72.0

dyne.cm^{-1}. The surface tension of water at 20^{o}C (72.8 dyne.cm^{-1}) is higher than the surface tension of chloroform (27.14 dyne.cm^{-1}) (Glecol 20016).

According to Schramm (2000), the decrease in surface tension occurs because of the force of cohesion and adhesion on the surface. The adhesion force which occurs on the surface can make the molecules on the surface will pull the molecules below the surface. The low density shows the low value in particles that the force necessary when breaking out the surface is low (Young and Cerniglia 2004). Using surface tension ANOVA, the five formulations of OSD with DEA (1.5%) and MES (0.9%) ratio amounted to 9:1 and 5:5 were not significantly different (Figure 2a). Similarly, the OSD products of 8:2 and 6:4 had some values that were not significantly different. While the OSD product of 7:3 had a surface tension value of the lowest among other OSD products as 23.57 dyne.cm^{-1}. The formula of DEA (1.5%) and MES (0.9%) ratio of 7:3 was considered to be a good formulation.

The surface tension is considered to have quite important effect to OSD performance to enhance biodegradation process of oil compared to other physical and chemical properties. Surface tension is the energy required to increase the surface area of liquid in a unit area. Therefore, the lower the value, the better the surface tension is the energy required to increase the surface area of liquid in a unit area (Rosen 1989). Surfactant can increase the solubility of the oil in the liquid phase through the dispersion process, so that the surface of the oil degraded by bacteria can grow (Heriyantoro 2005). The role of surfactant in the bioremediation process is to increase the bioavailability of oil compounds that have a high solid content so that it can be dissolved in the media. According to surface tension, as very important point in bioremediation, later, the surface tension score was determined by 40% for weight scoring (Table 4).

3.5 Interfacial Tension

The value of interfacial tension (IFT) generated by the surfactant increased along with the increase in the MES in formulated OSD. This test was performed to determine the performance of the surfactant in decreasing the interfacial tension of oil in water. IFT value was determined for weight scoring of 20% in the valuation of OSD (Table 4). The ANOVA results showed that interfacial tension generated by ratio of DEA and MES at 5:5 was the highest and it was significantly different from other formula (Figure 2b).

3.6 Viscosity

The viscosity of surfactants expresses its resistance to shearing flows, where adjacent layers move parallel to each other with different speeds. The high viscosity values affect the formation of more perfect micelles in the surfactant solution (Elfiyani et al. 2013). The viscosity of a fluid is the fluid properties affected by the size of molecules and intermolecular forces. Viscosity parameter has a relationship with the stability of emulsion. The magnitude of viscosity can increase to emulsion stability because it can inhibit the process of merging of the micelles or coalescence. Table 2 shows that the viscosity of DEA 1.5% (1.32 cP) is higher than MES 0.9% (1.06 cP). When they are mixed, the viscosity will be decreased in the ratio of DEA (Figure 2c). The ANOVA results showed that the parameter of viscosity was significantly different. The formula at the ratio of DEA and MES by 9:1 was the highest and it was significantly different from the ratio 7:3 to 5:5 (Figure 2c). The density was determined for weight scoring of 10% in the valuation of OSD (Table 4). In general, the density associated with fluid viscosities which are denser will have a higher viscosity. This is demonstrated by the data from OSD product density that is directly proportional to viscosity.

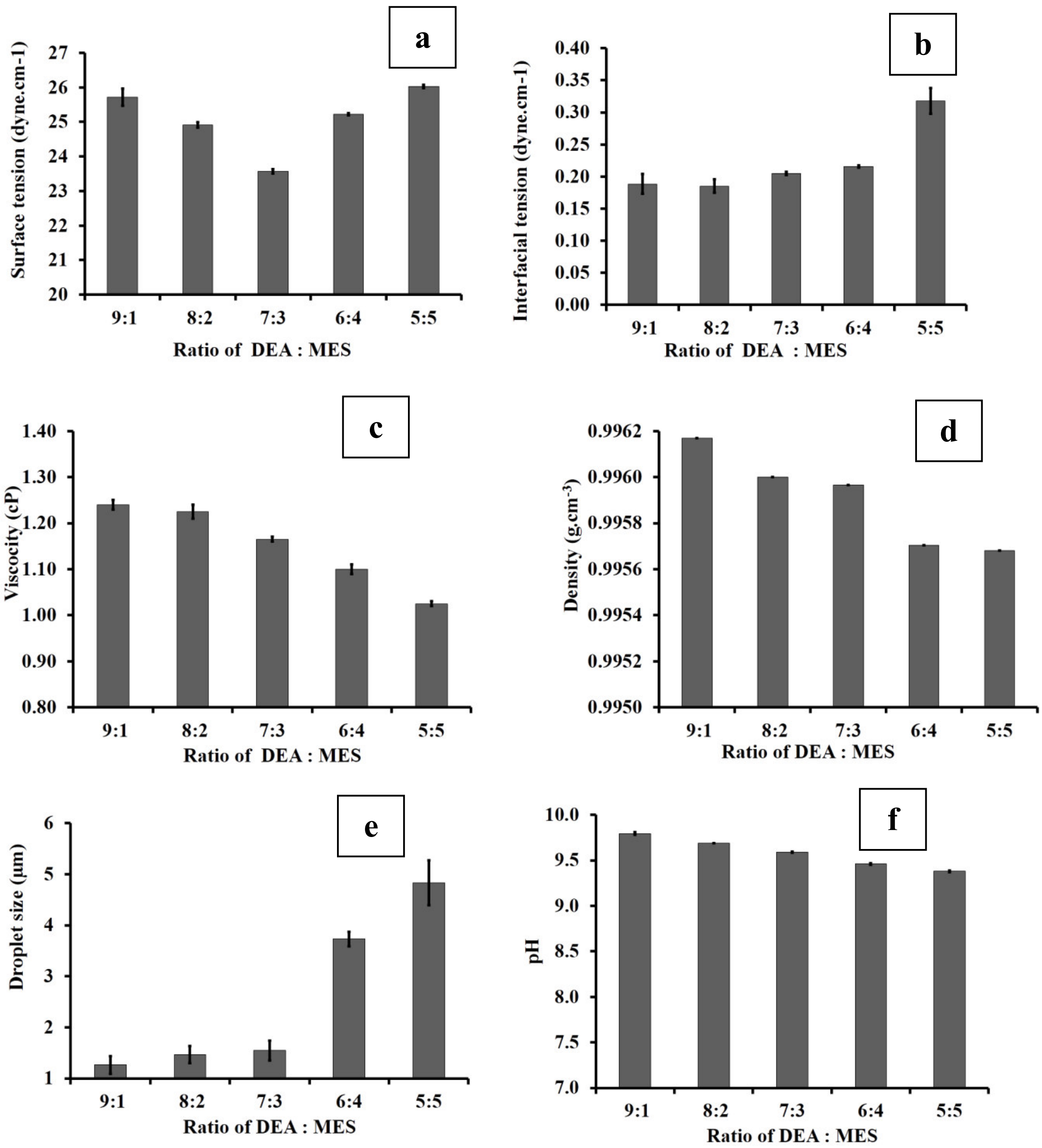

Figure 2. Evaluation of DEA and MES ratio for OSD formulation; a. Surface tension, b. Interfacial tension, c. Viscosity, d. Density, e. Droplet size, and f. pH.

3.7 Density

The volumetric mass density, or density of substance is the mass per unit of volume of a liquid or solution. Therefore, any liquid or solution has a different density. The results of the analysis of the density of OSD solution with a ratio of two different surfactants can change the resulting density values (Figure 2c). The density of DEA 1.5% and MES 0.9% at room temperature (22 - 32 °C) are about 0.995 g.cm^{-3} (Table 2), and the mixed of them varies from 0.9950 – 0.9960 g cm^{-3} (Table 3) and this value is near to the density of water by 1.000 g.cm^{-3} (20°C) as their solvent. The ANOVA results showed that the parameter of density was significantly different. The formula at the ratio of DEA and MES at 9:1 was the highest and it was significantly different from ratio 7:3 to 5:5 (Figure 2d). The density was determined for weight scoring of 10% in the valuation of OSD (Table 4).

3.8 Droplet Size

The droplet size in an emulsion system is very influential factor in emulsion stability (Raymondo et al. 2005).

The smaller droplet size of the emulsion will form a more stable emulsion (Fingas et al. 2008). The results showed that the increasing ratio of MES surfactant was followed by increasing droplet size (Figure 2e). From the Anova calculation, the droplet size was significantly different. Based on the OSD formula, the ratios of 9:1 to 7:3 were not significantly different, and they were different with the ratios of 6:4 and 5:4. The droplet size parameter was weighed by 10 % in determining it (Table 4).

3.9 pH

The pH values of the formulations are higher than 7 or alkaline (Figure 2f). The result showed that the pH decreased with the addition of MES, because there was a stoichiometric balance between the two kinds of surfactant ions in the mixture. The greater concentration of MES indicated the lower pH. The optimum condition for the bioremediation process was usually between 6-9. The ideal pH value for use in environments was 6-9 or near neutral. Even though the pH of OSD was high, the amount of OSD will be added to soil contaminated at low portion. In generally, soil has a good buffering capacity, then the pH parameters of OSD was weighed with the score of 10 % (Table 4).

Table 4. Results of OSD valuation based on the weighting and score on OSD parameters

Ratio of DEA (1.5%) : MES (0.9%)	Parameter and weight score						
	Surface tension	Interfacial tension	Viscosity	Density	Droplet size	pH	Total score
	40%	20%	10%	10%	10%	10%	100%
9:1	1	2	1	2	2	1	2.20
8:2	2	2	1	2	2	1	2.60
7:3	2	2	2	1	2	2	**2.70**
6:4	2	2	2	1	1	2	2.20
5:5	1	1	2	1	1	2	1.60

The physico-chemical properties of formulated OSD and the DMRT (Duncan Multiple Range Test) with significant level 5% as presented in Figure 2. Based on these values and the importance of parameter on bioremediation process, the scoring method is based on high and low ratings (scores 1 and 2). Table 4 shows the calculation of weight scoring of all parameters of OSD. The highest of total score of 2.70 was the OSD at DEA (1.5%) and MES (0.9%) ratio of 7:3. The characteristic of OSD (7:3) is the surface tension by 23.57 dyne cm^{-1}, interfacial tension by 0.20 dyne cm^{-1}, viscosity 1.17cP, density 0.9960 g cm^{-3}, the mean of droplet size 1.55 µm, and pH 9.59 (Figure 2). The best formulated dispersant is used to test on bioremediation process.

Elvina et al. (2016) previously reported that the best OSD formulation from two types of surfactants, diethanolamide (DEA) 3% in water and a solution of sodium methyl ester sulfonate (SMEs) 5% in the solvent methyl ester, at the ratio of 1:3. The physicochemical properties of this OSD product are surface tension 25.59 dyne.cm^{-1}, density 0.90 g.cm^{-3}, viscosity 131 cP, and pH 9.1. In comparing with this result, the formulated OSD product is water base dispersant, and the concentration of DEA and MES are lower than the previous OSD product (Elvina et al. 2016). This formulated OSD will be easier to handle and cheaper than that produced OSD by Elvina et al. (2016) or other petroleum based surfactants.

Both DEA and MES surfactants are produced from palm oil, they have biodegradable and environmentally friendly properties. This is due to the raw material of the second surfactant derived from palm oil. In addition, the surfactant also has good dispersing properties, caused by both surfactants that have hydrophilic and hydrophobic groups. The hydrophilic group will bind water molecules, while the hydrophobic moieties will bind molecules that can bind the oil in the emulsion system.

This experiments use nonionic surfactants of DEA and MES, these types of surfactant has no charge when dissolved in aqueous media. The surfactant contains polyethylene oxide chain as a hydrophilic group so it is easily dissolved in water (Tardos 2005). The nonionic surfactant is known to stimulate biodegradation of polyaromatic hydrocarbons through increased bioavailability (Zeng and Obbard 2001). Nonionic surfactant is commonly used in hydrocarbon biodegradation studies, because it is less toxic to bacteria and does not cause changes in pH that may interfere with the process of biodegradation (Volkering et al. 1995). At this time, many modern dispersant or OSD use the solvents with low toxicity such as glycols, glycol esters, and hydrocarbons non-aromatic. The dispersant products of DEA and MES surfactants have lower viscosity due to the use of water as a solvent. In addition, the water is naturally non-toxic, environmentally friendly, and easy to obtain. The formulated dispersant is grouped to the third generation.

Currently the dispersants have been developed to the third generation (Su 1992). The main components of the first generation dispersant are anionic surfactants and solvents of aromatic hydrocarbon compounds. The first generation dispersant has been missing from the market because it is made from aromatic hydrocarbon which gives a toxic effect on the environment. The second generation dispersant is more environmentally friendly because it does not use aromatic hydrocarbon compounds. Dispersant is referred to as "conventional dispersants" because it can be used in the ocean directly without having dissolved before used. Finally, the third generation dispersant is called " concentrate dispersant ", this generation needs to dissolve dispersants before used. This third generation dispersant is divided into two types namely water-based solvents and hydrocarbons based. The third generation (UK type 2) with application methods of the concentrated dispersant using water based, and the dose (dispersant /oil) at 5-15% (IMO/UNEP 2011). A summary of the generation dispersants is reported and described in guidelines for the use of dispersant (IMO/UNEP 2011).

3. 10 OSD applied to Bioremediation Test

The application of OSD was tried to enhance bioremediation of soil contaminated by crude oil. The latosol soil, sand, and crude oil were mixed then treated with and without OSD addtion (Tabel 1). The physical and chemical characteristics of the soil was reported by Arifuddin *et al.* (2016). The physical characteristics of latosol soil were porosity 58.7%, soil density 1.01 $g.mL^{-1}$, fast drainage porous 14%, slow drainage porous 6.4%, water avalaibility 26.6%, and moisture content 54.8. The chemical characteristics were C 0.54%, N 0.06%, C/N ratio at 9, and P_2O_5 7 ppm. The soil texture composition was clay 85%, ash 12% and sand 3%. The soil was air dried, sieved (2 mm sieve), storage before mixing and without sterilization. To increase the porosity, this soil was added with sand. The indigenus microbes were stimulated by addition of fertilizer (NPK) to to set the ratio of C:N:P = 100:10:1 that supported the growth of bacteria.

The bioremediation test was carried out at ambient temperature for 6 weeks. The room temperature were observed daily at an average of 26.3°C. The bioremediation soil was manually mixed to give aeration every day. The moistured soil was maintained at least 20% by sterilized aquadest addition. The moisture content of control treatment changed from 20.0% to 18.8%, while soil with OSD changed from 22.5 % to 21.7% (Figure 3). The soil pH was maintained at neutral by addition of H_2SO_4 solution. The pH of control change from 8.28 to 7.50, while OSD treatment change from 8.33 to 6.84.

The initial of bacterial population of control and OSD treatment are at log 6.98 CFU/g and 6.66 CFU/g, respectively. The indigenous bacterial were grown actively to biodegrade crude oil. After 6 weeks operation, the bacterial population of control and OSD treatments increased to log 8.12 CFU/g and 8.90 CFU/g, respectively. This growth of indigenous bacterial were stimulated by addition of fertilizer and OSD.

The performance of bioremediation process were observed at initially and after 6 weeks operation that presented in Figure 3. For control , the bioremediation process performs as biostimulation, in which the TPH decreased from 5.08% to 3.39%, and the TPH-degradation is 33.27 %. For OSD treatment at the ratio of dispersant to oil (DOR) at (1:1), the TPH decreases from 5.49% to 2.82%, and the TPH-degradation is 48.70%. The application of OSD shows that bioremediation process increases about 1.46 times faster than control. This shows that the performance of indigenous microbes in the crude oil contaminated soil can degrade the oil faster with the addition of OSD. The dispersant or surfactant that has been discussed above can reduce the surface tension, interfacial tension, and droplet size, so that the oil is much more easily degraded by microbes.

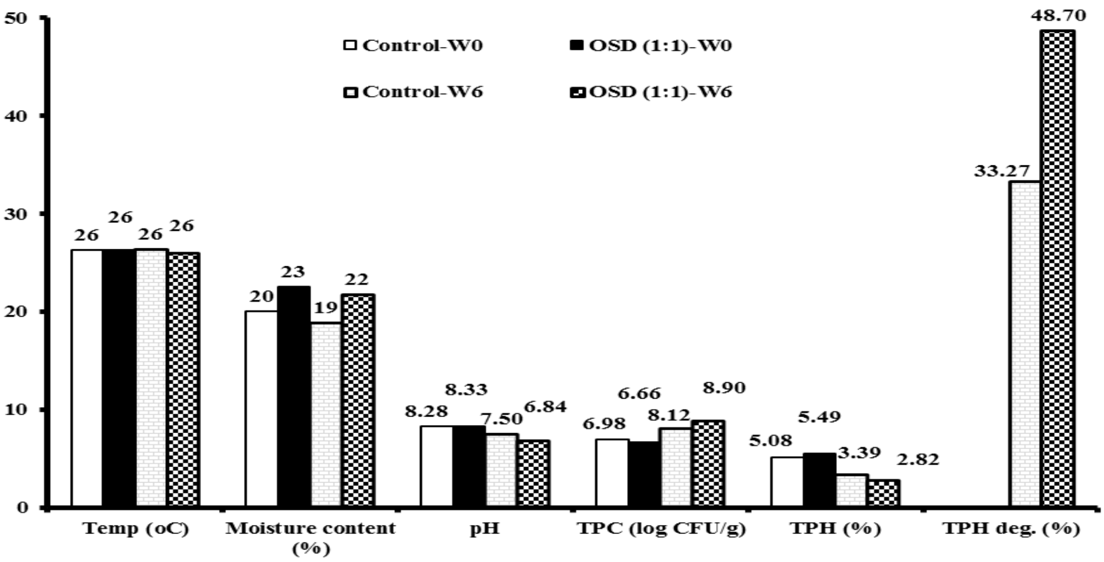

Figure 3. The changes of bioremediation parameters of crude oil contaminated soil without OSD (control) and using OSD (1:1) for 6 weeks operation.

3.11 Future Application of OSD

Biodegradation of hydrophobic organic compounds in polluted soil is a process involving interactions among soil particles, pollutants, water, and micro-organisms. Surface-active agents or surfactants are compounds that may affect these interactions, and the use of these compounds may be a means of overcoming the problem of limited bioavailability of hydrophobic organic pollutants in biological soil remediation. The effects of surfactants on the physiology of micro-organisms range from inhibition of growth due to surfactant toxicity to stimulation of growth caused by the use of surfactants as a co-substrate (Volkering et al. 1995). The formulated OSD from DEA and MES is supposed to stimulate indigenous microbe and enhance to TPH biodegradation process. The addition of OSD on bioremedition can enhance the TPH degradation (Figure 3). The addition of surfactant can significantly increase the bioavailability of the contaminated soil (Tiehm *et al.* 2001). Volkering et al. (1997) stated that the most important effect of surfactants on the interactions among soil and pollutant is the stimulation of mass transport of the pollutant from the soil to the aqueous phase. This can be caused by three different mechanisms: emulsification of liquid pollutant, micellar solubilisation, and facilitated transport.

According to Swisher (1987), the physiological and psychochemical effects of surfactant play an important role in the microbial life process, because it can form a complex compound with the cell membrane proteins around the cell membrane. The membrane protein plays a very important role in the transport of the material passing through the cell wall (Suardana *et al.*2002). From the interaction of surfactants with these microbes, surfactants further form a surfactant proteins complex that can improve the material transport mechanism. The effect of reduction in surface tension of hydrocarbons (oil contaminant or polluted) into the micro-emulsion surfactant occupational will help the work for microbial enzymes to degrade substrate, to be more easily utilized for the purpose of metabolism. Therefore, surfactant may increase the occurrence of biodegradation substrate, such as hydrocarbon compounds by microbes in the bioremediation process (Tiehm et al. 2001). Surfactant play a role in decreasing the surface tension of the oil so that it can expand oil surface contact with the water through the formation of micro-emulsions. Therefore, microbes are easier to degrade hydrocarbons. While increasing oil and water contact surface, it will facilitate the entry of the supply of oxygen and nutrients needed by microbes to enhance biodegradation process of oil or petroleum waste. As reported previously by Hardiyantoro (2005), the addition of Tween 80 surfactant affects the performance of petroleum degrading bacteria. The performance of biodegradation process depends on hydrocarbon composition of crude oil and environmental factors (Atlas 1981).

The research on the use of surfactants and dispersant to stimulate the process of biodegradation of petroleum has been conducted with various types of surfactants and various operating conditions (Table 5). The OSD formulation from diethanolamide (DEA) 3% in water and sodium methyl ester sulfonate (MES) 5% in methyl ester solvent, at the ratio of 1:3, that it can disperse the waste oil in sea water (Elvina et al. 2016*).* The dispersant of a mixture of nonionic surfactants as sorbitol derived and biosurfactant using ethylene glycol butyl ether solvent are used for the application on oil pollution in sea water (Song et al.2013). The surfactant of Rheodol TSW-120V is used to enhance biodegradation of petroleum hydrocarbons in the slurry bioreactor (Syafrizal et al. 2010). The Tween 80 surfactant can assist the bioremediation of oil-polluted soil (Cueva et al. 2016).

Table 5. Application of various surfactant and dispersant on bioremediation

Surfactant materials	Solvent	Application on bioremediation	References
DEA, MES	Water	Crude oil contaminated soil	This research
DEA, MES	Water, methyl esther	Oil spill in sea water	Elvina et al. (2016)
DEA	Water	Crude oil contaminated soil	Surya (2015)
DEA	Water	(Solid soap)	Hambali et al. (2002)
MES	Gasoline, kerosene, diesel oil	(Oil well stimulation)	Hambali et al .(2008)
APG	Water	Pesticide	Noerdin (2008)
Tween 80	Water	Oil-polluted soil	Cueva et al. (2016)
Rheodol TSW-120V	Water	Petroleum hydrocarbons in the slurry bioreactor	Syafrizal et al. (2010)
Sorbitan monolaurate, sodium lauryl sulfate. ethoxylated sorbitan trioleate, and isopopyl amide dodecyl benzene sulfonate	Ethylene glycol monobutyl ether. dipropylene Glycol monomethyl ether. de-aromatized kerosene, isoparaffinic	Oil spill in sea water	Fiocco and Lewis (1999)
Tween 80, span 80. bis (2-ethylexyl) sulfo-succinate	Water based	Oil spill in sea water	Place et al.(2010)
Polysorbate 85, and sorbet-40 tetraoleate	Ethylene glycol butyl ether	Oil spill in sea water	Song et al.(2013)

The application of surfactants from palm oil is not only as control of oil pollution on land or at sea (Elvina et al. 2016; Surya 2015). Surfactants such as APG can be applied to pesticide formulation (Noerdin 2008), DEA for bar soap and detergent (Hambali *et al.* 2002), or MES as stimulating oil wells Hambali et al.(2008) (Table 5).

Based on the CMC, DEA and MES surfactants were selected at the concentration of 1.5% and 0.9%, respectively. Both surfactants were diluted by water, as water based surfactant of third generation of type 2. The best formulated dispersant (Table 3) was mixed of DEA 1.5% and MES 0.9% at ratio of 7:3. By calculation surfactant used was totally 1.32 % of concentrated surfactant. Then, this formulated surfactant was applied to bioremediation test at ratio to oil 1:1, therefore the ratio of dispersant to oil is 1.32%. This value is lower than reported by IMO/UNEP (2011) at ranged of 5 – 15% ratio of dispersant/oil. This formulated dispersant will be implemented and developed on bioremediation of soil contaminated by several methods from laboratory to a pilot scale, before being applied in the field scale. The ratio of OSD : oil tested is 1:1, so it is necessary to further study the optimum ratio to enhance the process of bioremediation on oil

4. Conclussion

The surfactant of DEA and MES were produced from Palm Oil product by certain chemicals engineering process. Both surfactants were diluted by water, as water based surfactant of third generation of type 2. Based on the critical michele concentration of DEA and MES solutions in water based were observed at 1.5% and 0.9%, respectively. The mixed of DEA 1.5% and MES 0.9% solutions showed the variation of emulsifing performance and the result obtained at ratio of 7:3. The characterstics of a new OSD product were the surface tension at 23.57 dyne cm^{-1}, interfacial tension at 0.20 dyne cm^{-1}, viscosity at 1.17cP, density at 0.9960 g cm^{-3}, the mean of droplet size at 1.55 μm, and pH at 9.59.

This is a new formulated OSD product was demonstrated in a microcosm test of crude oil contaminated soil at ratio of crude oil : OSD by (1:1). This result shows that the OSD can enhance the bioremediation process about 1.46 times compare to control without OSD. This formulated dispersant could be implemented and developed on bioremediation of soil contaminated by several methods from laboratory to a pilot scale, before being applied in the field scale.

Acknowledgements

The authors wish to acknowledge the insightful comments and suggestions from the anonymous reviewers and editors for improving the content of this manuscript. This work was supported by the "Insentif Riset Sistem Nasional" (INSINAS) KEMENRISTEKDIKTI of Indonesia, under Grant no. RT-2016-0570RT-2016.

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