Faculty of Resource Science and Technology

MOTOR OIL STAIN REMOVAL BY NONIONIC SURFACTANT BRIJ 35 ON COTTON FABRIC AND ITS EFFECT ON BIODEGRADATION BY PSEUDOMONAS AERUGINOSA

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List of symbols/abbreviations

NH_4Cl	Ammonium Chloride
CMC	Critical Micelle Concentration
Na_2HPO_4	Disodium Phosphate
FT-IR	Fourier Transform Infrared Spectroscopy
MSM	Mineral salts medium
KH_2PO_4	Monopotassium Phosphate
$MgSO_4$	Magnesium Sulfate
KCl	Pottasium Chloride
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide

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Abstract

Used motor oil dumped in water sources is one of the factors that cause water pollution in our environment. Therefore, this study aimed to increase the solubility of motor oil by using nonionic surfactant, Brij 35 and the biodegradability of used motor oil by *Pseudomonas aeruginosa*. The fresh motor oil was used in this experiment as comparison with used motor oil. The results showed that the best concentration of Brij 35 to remove used of motor oil is at concentration of 0.00008 M and mixing speed at 250 rpm with percentage efficiency 6.79% compared to 3.83% at 150 rpm mixing speed. The removal of used motor oil was supported by the FTIR analysis data. In the biodegradability test, there were emulsions formed thus, indicated that the used motor oil was successfully degraded.

Key words: Non-ionic surfactants, Used motor oil, Biodegradability

Abstrak

Minyak motor terpakai dibuang dalam sumber air ialah salah satu faktor yang mengakibatkan pencemaran air di persekitan kita. Lantarannya, kajian ini bertujuan meningkatkan kelarutan minyak enjin dengan menggunakan surfaktan Brij 35 dan penguraian minyak motor terpakai oleh Pseudomonas aeruginosa. Minyak motor baru telah digunakan di eksperimen ini sebagai perbandingan dengan minyak terpakai. Hasil kajian menunjukkan kepekatan dan kelajuan putaran yang terbaik untuk menyingkirkan minyak oleh Brij 35 adalah pada 0.00008 M dan 250 rpm dengan peratusan 6.79% berbanding dengan 3.83% di 150 rpm. Penyingkiran minyak motor terpakai disokong oleh data analisis FTIR. Manakala, dalam ujian penguraian, terdapat emulsi yang terbentuk menunjukkan minyak enjin yang digunakan telah berjaya terurai.

Kata kunci: *Surfaktan, Minyak motor terpakai, penguraian*

1.0 INTRODUCTION

1.1 Background study

Surfactants are the main ingredient in detergents used to remove dirt on fabric. Current laundry products and procedures exhibit deficiencies to clean oil stain particularly hydrocarbon stains, from fabric especially used motor oil stain found on clothes. Used motor oil consists of metal-containing compounds and carbon particles (Chi & Obendorf, 1999). Thus, this study will identify the effect of concentration and mixing speed as parameters of in removing oil stain on fabric using non-ionic surfactant Polyoxyethylene 23-lauryl ether (Brij-35). Non-ionic surfactant depends on the CMC of the surfactants relative to the cloud point for solubilization to occur (Myers, 2006). Surfactants addition is purposely to reduce the surface tension by changing the surfactant's concentrations (Zacarias-Salinas *et al.*, 2013). There are two way to remove contaminants present in the water system which are solubilization of compounds due to the reduction of surface tension (bellow the surfactant's critical micelle concentration (CMC) and the adsorption of hydrophobic compounds due to the presence of the surfactant, at concentrations higher than surfactant's CMC value (Zacarias-Salinas *et al.*, 2013).

In this study, solubilization was evaluated as a mechanism to remove oil stain on fabric. The surfactant helps to release the hydrocarbons adsorbed to fabric and increase the aqueous concentrations of hydrophobic compounds to increase the rates of mass transfer by solubilization or emulsification. This method is considered as a clean technology since the surfactant used is biodegradable. Recent studies reported that the presence of the microorganism can enhance the biodegradation of used motor oil along with surfactant.

In this study, the effect of Brij-35 on the removal of fresh motor oil on fabrics and the biodegradation on fresh motor oil by *Pseudomonas aeruginosa* will also be studied. Motor oil that discarded to the environment is a major health concerns because they exhibit toxic, mutagenic, and carcinogenic effects (Fallon, 1998). Thus, *Pseudomonas aeruginosa* will be used as the degrader's organism to degrade the hydrocarbons removal by surfactant. Polyaromatic hydrocarbon (PAH) is one major classes of hydrocarbon that hard to be removed in our environment.

1.2 Problem Statement

Anionic surfactant is commonly used in the detergent but anionic is not easily degraded thus causing the pollution to the environment. In addition, there are some issue arise regarding the non-biodegradable surfactant that lead to the toxicity to the marine life. Thus, this study introduced non-ionic surfactant Brij-35 because this type of surfactant can easily degrade as it consists of straight chain carbon. The used motor oil will cause toxic to marine life as the runoff waste water from the laundry will release into water bodies. Biodegradable test using *Pseudomonas aeruginosa* was evaluated to study the biodegradation of used motor oil when treated with nonionic surfactant, Brij 35. The efficiency of Brij 35 needs to be achieved by studying its mixing speed and concentration to remove the used motor oil.

1.3 Objectives

The objectives of this study are:

i. To identify the best concentration and mixing speed of Brij 35 to remove the used motor oil stain on fabric.

ii. To identify the efficiency of Brij 35 solubilize used motor oil by using n-Hexane extraction method.

iii. To study the biodegradation of used motor oil by *Pseudomonas aeruginosa* with addition of Brij-35.

2.0 LITERATURE REVIEW

2.1 Surfactants

Surfactant is the contraction from the term surface-active agent. Surfactant is a substance that can greatly reduce the surface tension of water when used at very low concentration (Rosen, 2012). According to Singh (2012), surfactants are amphiphilic molecules consisting of a non-polar, hydrophobic part which is their "tail" and a polar, hydrophilic part which is their "head". General surfactant monomer is shown in Figure 2.1. The hydrophobic tail is usually a branched or linear long-chain hydrocarbon residue with a chain length in the range of 8-18 carbon atoms (Singh, 2012). Dependent on the nature of the hydrophilic part the surfactants are classified as anionic, cationic, non-ionic and zwitterionic. Anionic surfactants have negative charged group such as carboxyl ($RCOO^-M^+$), sulfonate ($RSO_3^-M^+$), sulafte ($ROSO_3^-M^+$) or phosphate ($ROPO_3^-M^+$). Cationic surfactants carry positive charge at the hydrophile head group and widely used for typical applications such as softeners and antistatics. Nonionic surfactants have no charge and normally have polar group such as polyexythylenes that contribute to the water solubility of the surfactant. Zwitterionic surfactants have both negative and positive charges at the hydrophile head groups under specified conditions (Myers, 2006). When a surfactant is dissolved in an aqueous environment, the hydrophobic tail interacts weakly with water molecules via van der Waals forces. Research by Singh (2012) reported that the hydrophobic part used van der waal forces to interact with water molecules while, hydrophilic part of the surfactant interact with the water molecule by using dipole-dipole or ion-dipole forces. These strong forces make the surfactant to be water soluble. Surfactants are therefore forced to the interfaces of the system, where the hydrophobic tails get oriented in a way to keep minimum contact with water (Singh, 2012).

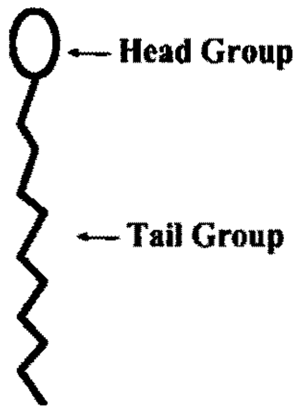

Figure 2.1: General Structure of the Surfactant Monomer (Mckay, 2010)

2.1.1 Nonionic Surfactant

Nonionic surfactants are the interest in this study because they are widely used in household, industrial, institutional cleaning and wool scouring (Karsa, 1999). Nonionic surfactants are good oil solubilizer compared to charged surfactants because they can adsorb onto surfaces with either the hydrophilic or the hydrophobic that oriented towards the surface (Rosen & Kunjappu, 2012). This can best describe as the *hydrophobic effect*. When the non-polar groups approach each other until they are in contact, there will be a decrease in the total number of water molecules in contact with the non-polar groups. The formation of the hydrophobic bond in this way is thus equivalent to the partial removal of hydrocarbon from an aqueous environment (Aulton, 2007). The growing use of non-ionic surfactants is related to their good detergent performance, which is not affected by water hardness, and, in most cases, are low toxicity (Szumała & Szeląg, 2012).

2.1.1.1 Polyoxyethylene (23) lauryl ether (Brij-35)

Polyoxyethylene (23) lauryl ether is a non-ionic surfactant which also known as Brij-35. The molecular formula is $(C_2H_4O)_{23}$–$C_{12}H_{25}OH$, with molecular weight 1199.56 g/mol and has critical micelle concentration in the range of 0.00074mol/L- 0.00091mol/L. Brij-35 exist in pellets form and soluble with water (Elsayed & Prasher, 2013). Figure 2.2 shows the chemical structure of Brij 35.

Figure 2.2: Chemical Structure of Brij 35 (Skold, 2008)

2.2 Critical Micelle Concentration (CMC)

Critical micelle concentration (CMC) is the key parameter for surfactant. It defined as the concentration of surfactant in which micelles form spontaneously. Micellization is an important property that affected the detergent efficiency especially in anionic and non-ionic surfactant (Kalali *et al.*, 2011). A micelle is a formation of number of molecules of the surfactant when they aggregate.

2.3 Solubilization

Solubilization is a preparation of a thermodynamically stable isotropic solution of a substance normally insoluble or very slightly soluble in a given solvent with the help of surfactant (Kr, 2012). Thus, it helps to make the hydrophobic compound which mostly insoluble in a solvent becomes soluble (Singh, 2012). Solubilization occurs by the presence of micelles and will not take place below the CMC. Research by Singh (2012) also supports that the solubility is slightly higher below the CMC of the surfactant than in the pure insoluble solvent. According to Singh (2012) the solubility increases in a linear fashion by adding more surfactants that are just above their CMC. According to Singh (2012) this is because the insoluble substance can be accommodating by the micelles formed. Thus, the micelle that formed in surfactant helps to treat the oil before the exposure to the environment by increasing the solubility of hydrophobic material (Edwards *et al.*, 1991).

2.4 Mechanism of Emulsion

Emulsion form from at least two immiscible liquid phases in a thermodynamically unstable system. Emulsifier is an agent that needed to disperse two immiscible liquids. Rosen & Kunjappu (2012) studied that emulsifying agent is usually a surface active agent. The liquid droplets (the disperse phase) are dispersed in a liquid medium (the continuous phase). Mechanism of emulsion needs components of oil, water, surfactant and energy in order to occur. Surfactants role is to lower the interfacial tension simultaneously causes a reduction in droplet size of the emulsion. The concentration of the surfactant that determines the reduction in surface tension affects the amount of the surfactant that needed to reduce the size of the droplets of the emulsion (Tadros, 2003).

2.5 Biodegradation of hydrocarbon

Biodegradation is a process that reduces toxicity and the migration potential of hydrocarbons. Hydrocarbon is the source for the degrading organism to obtain energy source and a carbon source. For petroleum hydrocarbons, the biodegradation is complicated because it depends on the nature and on the amount of the hydrocarbons present. There are four classes of petroleum hydrocarbon which are saturates, aromatics, asphaltenes (phenols, fatty acids, ketones, esters, and porphyrins), and resins (pyridines, quinolines, carbazoles, sulfoxides, and amides). One vital factor that limits biodegradation of oil pollutants in the environment is their limited availability to microorganisms. The susceptibility of hydrocarbons to microbial degradation and can be generally ranked as follows: linear alkanes, branched alkanes, small aromatics cyclic alkanes. Not all compounds can be degraded, such as the high molecular weight polycyclic aromatic hydrocarbons (PAHs) and may not be degraded at all (Das & Chandran, 2011).

2.6 Removal of oil by surfactant

Fallon (1998) had studied the the feasibility of using aerobic microbial degradation to treat and reduce volume of hydrocarbon wastes from a railroad maintenance facility. In this study, the performance of native and introduced bacterial species was compared, the role of bio-surfactant in the biodegradation was investigated and the dewatering properties of the waste were evaluated. It was recommended that the waste oil be diluted prior to biodegradation to reduce potential toxic effects to the biomass and reduce the oxygen demand. The result shows that when a native bacterial species was introduced for biodegradation the process accelerated. In this study, the data suggested that microorganisms degraded simple compounds first, and then produced biosurfactants.

Ying (2006) studied about the effects of surfactants and their degradation products in the environment. The behaviour of anionic, cationic and non-ionic surfactants were studied in this study. The results show that aquatic chronic toxicity occurred at concentration greater than 0.1 mg/L but are not acutely toxic to organisms at environmental concentrations.

Zacarias-Salinas *et al.* (2013) studied that surfactant enhanced soil washing process. The surfactant type and its concentration were studied for the removal of the automotive waste oil by solubilization. Fifteen different surfactants were used to identify the one with the highest TPH removal. Surfactants included five anionics, two zwitterionic, five nonionics and three natural gums. The addition of the surfactant in the soil washing increase the removal of TPH range from 38% to 68%, compared with water with only 0% of TPH removal. The TPH removals employing the different surfactants were in the range from 38% to 68%, in comparison to the soil washing with water (10% of TPH removal).

Ahmad *et al.* (2005) studied that the effect of mixing speeds on the adsorption of residual oil on synthetic rubber latex powder. The increase in stirring speed results in a reduction in surface film resistance, thereby allowing residual oil to reach the particle surface more easily. Surface film resistance slowed the rate of adsorption. The rate of oil adsorption increased with an increase in mixing speed.

According to Baziar *et al.* (2013) speed has an important role in soil washing to remove the total petroleum hydrocarbon (TPH). The patterns show that TPH concentration decreasing with increasing agitation speed to 250 rpm. The most removal yields obtained at 250 rpm for Tween 80 and Brij 35. The strong collision between soil particles and increasing agitation speed helps the stripping of the adsorbed or crusted contaminants. Besides, concentration of surfactant above CMC is the main reason for decreasing the TPH solubility. Interfacial behavior of surfactants plays an important role in these observations. For concentration lower than the CMC, the surfactants appear as soluble macromolecules in the medium and cannot interact with contaminants. At higher CMC, the interactions with hydrophobic particles and mineral particles increased.

Peng *et al.*, (2011) has studied that the removal of polyaromatic hydrocarbon (PAH) was enhanced by using surfactant with optimum parameters such as the effect of stirring speed, washing time, surfactant concentration and liquid/solid ratio. The study shows that increasing stirring speed to 250 rpm increases removal ratio of PAH but at 300 rpm the removal ratio of PAH started to drop. The removal ratio of PAH keep increasing with increasing concentration but there is an inflection point for effectiveness called as CMC where the micelles starts to aggregate.

3.0 EXPERIMENTAL

3.1 Materials

Nonionic surfactant Brij-35 (waxy-solid form) was obtained from Acros Organics. Pottasium Chloride (KCl) (powder form) with molecular weight 74.55 g/mol was obtained from Merck Millipore and was used as solvent. Cotton was purchased at the nearby shop. Used motor oil was obtained from local garage at Samarahan area. MSM and glucose was obtained from the Virology Laboratory, UNIMAS, Sarawak. *Pseudomonas aeruginosa* was provided by the Virology Laboratory, UNIMAS, Sarawak.

3.2 Methods

3.2.1 Preparation of Brij-35 solution

2.0×10^{-4} M of Brij-35 solution was prepared by adding 0.06 g of Brij 35 to a volumetric flask and diluted to 250 mL with deionized water. Then, the flask was shaken well for the surfactant to dissolve completely in water. Then, the mixture was rested for a while for the foam to be disappeared (Kalali *et al.*, 2011). This Brij 35 was prepared to be the stock solution for making dilutions to determine the CMC.

3.2.2 Preparation of KCl solution

0.1 M of Pottasium Chloride (KCl) solution was prepared by adding 7.45 g of KCl to a volumetric flask and diluted to 1000mL with deionized water. The flask was shaken well for the KCl powder to be completely dissolved in the water.

3.2.3 Determination of surfactant critical micelle concentration (CMC)

Dilutions were made by diluting the previous stock solution of Brij-35 with KCl solution into eight concentrations which were 0.00004M, 0.00005M, and 0.00006M, 0.00007M, 0.00008M, 0.00009M, 0.0001M and 0.00011M. The CMC was determined by the conductivity method by using YF-3700A Multimeter to perform the conductivity measurements at eight different concentrations. For every conductivity measurement, the electrode was cleaned by rinsing with deionized water before tested the conductimetric value. Then, 25mL of each of the concentrations was stirred for 30 s, and then left for 1 min before reading the minimum and maximum conductivity value. All conductivity measurements were done at least three times. The CMC value was determined by plotting conductance versus concentrations of surfactant. A break in the specific conductivity versus surfactant concentration curve signals the onset of the micellization process (Nese & Sarac, 2013).

3.2.4 Parameters

The parameters that have been tested in this experiment were the surfactant concentrations and the mixing speed.

3.2.4.1 Equilibrium Solubilization

The equilibrium solubility of fresh motor oil was determined by using conical flask of 50 mL. The surfactant concentrations ranging from below CMC, at CMC and above CMC were prepared in room temperature. Each conical flask were filled with 5 mL of used motor oil and then with 5mL of surfactant solutions at different concentrations which were 0.00004 mol/L, 0.00005 mol/L, 0.00006 mol/L, 0.00007 mol/L, 0.00008 mol/L, 0.00009 mol/L, 0.0001 mol/L, and 0.0011 mol/L. The conical flasks were placed on a rotary shaker for 24 hours at 150 rpm to reach equilibrium in room temperature. After that, centrifugation was done to complete the