SURFACTANT UTILIZATION IN OIL SLUDGE BIODE GRADATION USING SLURRY BIOREACTOR

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ABSTRACT

Oil sludge from petroleum industry effluent is classified as hazardous waste and required special treatment before discharge to the environment. Biodegradation using bacterial activities is a general treatment for oil sludge processing. However, the bacterial ability in oil sludge biodegradation is blocked by non-aqueous phase liquid of oil sludge. Two possible ways of enhancing the bioavailability of oil sludge are surfactants application and slurry bioreactors system. The objective of this study is to obtain the surfactant which can increase oil sludge biodegradation using simple slurry bioreactor. The surfactant selection obtained Emulsogen LP (58% effectiveness) which was examined based on HLB value, nonionic character, and surfactant effectiveness. Emulsogen LP is readily biodegradable which reached 93% biodegradability in 15 days. The biodegradation test showed that Emulsogen LP addition on its Critical Micelle Concentration (10 mg/L) enhanced oil sludge biodegradation in 3 bacterial cultures of Pseudomonas aeruginosa, Bacillus subtilis, and Actinobacter baumanni after 48 hours. By surfactant addition, oil sludge biodegradation reached 37-49% whereas without surfactant addition it only reached 28-33%. The highest oil sludge biodegradation was obtained in P. aeruginosa cultures with Emulsogen LP addition (49%). The surfactant addition had no effect on microbial growth. Moreover, P. aeruginosa population was increased by surfactant addition.

Key words: Nonionic surfactant, oil sludge, biodegradation, bioavailability, slurry bioreactor.

I. INTRODUCTION

Oil sludge from petroleum industry effluent is classified as hazardous waste. The hydrocarbon contents in oil sludge such as benzene, toluene, ethyl benzene, xylene, and heavy metals are potentially carcinogenic. Oil sludge is composed of oil, water, solids, and their characteristics, make them highly recalcitrant and very difficult to reutilize [1]. Therefore, it required special treatment before discharge to the environment. Biodegradation using bacterial activities is a general treatment for oil sludge processing. However, the bacterial ability in oil sludge biodegradation blocked by non-aqueous phase liquid of oil sludge. Thus, bioavailability might be the limiting factor controlling the biodegradation of such compounds. Two possible way of enhancing the bioavailability in hydrophobic organic compounds are surfactants application and slurry bioreactors system. Surfactants reduce surface and interfacial tensions by accumulating at the interface of immiscible fluids, thus enlarge the surface areas of insoluble compounds which lead to increased mobility, bioavailability and subsequent biodegradation [2]. The slurry bioreactor method is able to increase hydrocarbon biodegradation rate due to the contacts between liquid medium, oil sludge, and bacteria take place simultaneously in one reactor chamber [3]. The research from Machin-Ramirez et al. demonstrated that the use of microbial consortium together with slurry bioreactor enhanced biodegradation of weathered oil sludge [4] whereas Soriano and Pereira revealed that the toxicity of oil sludge decreased after biological treatment in bioreactor[1].

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The objective of this study is to obtain the surfactant which can increase oil sludge biodegradation using simple slurry bioreactor.

II. RESEARCH METHODS

A. *Oil sludge properties*

The oil sludge and production water in this study were obtained from PPT Migas Cepu Refinery in Central Java. The physical and chemistry properties of oil sludge are described in Table 1.

B. *Surfactant selection*

The selection of surfactant determined by surfactant screening and surfactant effectiveness. The surfactant screening is base on the hydrophilic-lipophilic balance (HLB) value >10 and nonionic character. The surfactants that are most successful in the washing of oil-contaminated soils usually have an HLB higher than 10. Nonionic surfactants are usually used in hydrocarbon biodegradation researches because in general they are less active against bacteria than ionic surfactants. Furthermore, nonionic surfactants are uneasily ionized in the water, thus avoid pH change which can disturb biodegradation process [5,6]. Nonionic surfactant stimulated polycyclic aromatic hydrocarbon biodegradation through increase bioavailability [7].

Surfactant effectiveness test for screening surfactants was conducted by using Swirling Flask Dispersant Effectiveness Test (SFDET). The selected surfactant from effectiveness test was examined by biodegradability test using OECD 306 method during 15 days. Sodium benzoate was used as reference material in this test. The percentage of biodegradability based on its Dissolved Oxygen (DO). The calculation of biodegradability used the following formula:

$$\%\ \text{Biodegradability}_{t\,day} = \frac{(\text{DO Sample}_{(0)} - \text{DO Sample}_{(t)}) - (\text{DO Blank}_{(0)} - \text{DO Blanko}_{(t)})}{\text{Demand}} \times 100\%$$

The concentration of selected surfactant was based on its Critical Micelle Concentration (CMC) value which was determined by

Table 1
Physical and chemical properties of oil sludge

Physical	Color	:	Black
	Moisture	:	40%
	Texture	:	Solid, oily
	Contain	:	Sand, sludge, organic
Chemical	pH	:	6.9
	Water content	:	21.46%
	TPH	:	34.69%

Table 2
Surfactant screening

No	Surfactant	Chemistry Name	Ionic	HLB
1	Emulsogen LP	*Secondary alcohol ethoxylate 5*	Nonionic	10,6
2	Genaphol X 060	*Isotridesil PEG ether ethoxylate*	Nonionic	11
3	Emulsogen PN extra	*Alkyl PEG ether*	Nonionic	11
4	Softanol 70	*Secondary alcohol ethoxylate 7*	Nonionic	12,4
5	Genaphol OX 080	*Ethoxylate 8 C12/15 Polyglicol ether*	Nonionic	13
6	Tergitol NP 9	*Nonil phenol ethoxylate 9*	Nonionic	13
7	Tergitol NP 13	*Nonil phenol ethoxylate 13*	Nonionic	14,2
8	Tween 20	*Oleic acid*	Nonionic	15
9	Tween 80	*Lauric acid*	Nonionic	16,7

Source: Tri Tunggal Multichemical 2007

Surface tension (SFT) in concentration range 0 - 10.000 mg/L using Processor Tensiometer Kruss.

C. *Bacterial culture preparation*

Three bacterial cultures of *Pseudomonas aeruginosa*, *Bacillus subtilis*, and *Actinobacter baumanni* from Biotechnology Lemigas Culture Collection (BLCC) were used in this study. The cultures were activated in Nutrient Broth (NB) medium and adapted sequentially in 100 mL N/P 5:1 medium with 0.1% yeast extract and 0.1% crude oil addition. The incubation was examined during 48 hours at room temperature with 100 rpm using shaker incubator. After three sequential adaptations, the bacterial growth curve of each culture was measured using Total Plate Count (TPC). 10% v/v bacterial culture contains 10^6 cell/mL from the last sequential adaptation was applied for biodegradation test using aseptic technique. Total colonies of each bacterial culture determined before and after biodegradation process.

D. *Oil sludge biodegradation test*

The slurry bioreactors used were Erlenmeyer flasks which were added with 6% (w/v) oil sludge, selected surfactant which concentration is based on CMC, 100 mL sterile production water with N/P source 5:1, 0.1% yeast extract, and 10% (v/v) of single bacterial culture. The flasks were placed in shaker incubator at room temperature and 100 rpm for 48 hours. Total petroleum hydrocarbon (TPH) was estimated gravimetrically before and after biodegradation test.

III. RESULT AND DISCUSSION

A. *Surfactant Selection*

The first surfactants screening obtained 9 surfactants described in Table 2. The HLB value of surfactants is >10 which means oil-in-water emulsifier.

The effectiveness test obtained Emulsogen LP as selected surfactant with highest result in effectiveness (Table 3). The highest result of Emulsogen LP showed that the raise of HLB value had not increased in the surfactant effectiveness. McClement restated that the maximum stability of emulsions for oil-in-water emulsion is obtained using surfactant with HLB number of around 10 to 12. Moreover, the functional properties of a surfactant molecule are altered significantly by changes in temperature or solution condition [8]. Thus the temperature variation can be applied in surfactant screening to obtain more considerable result.

Table 3
Result of Surfactant effectiveness test

No.	Surfactant	Effectiveness (%)
1.	Emulsogen LP	58
2.	Genaphol OX 080	41,3
3.	Emulsogen PN extra	36
4.	Softanol 70	32
5.	Genophol X 060	29,3
6.	Tergitol NP 13	26
7.	Tergitol NP 9	25,3
8.	Tween 80	19,3
9.	Tween 20	9,3

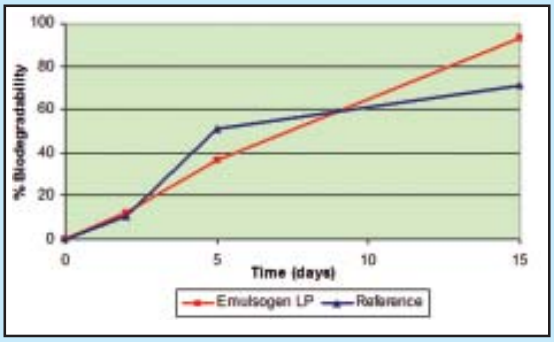

Figure 1
Surfactant Biodegradability

B. *Biodegradability test and concentration determination of selected surfactant*

The biodegradability test showed that Emulsogen LP is classified as Readily Biodegradable due to the result is >60% biodegradability after 15 days incubation (Figure 1). In fact, Emulsogen reached 93% biodegradability while reference material only 71%. The presence of a degradable surfactant may enhance the uptake rate of hydrocarbons [5].

Concentration determination of Emulsogen LP showed that the CMC value of Emulsogen LP is 10 mg/L (Figure 2). This is used as surfactant concentration. In CMC, surfactant favoring micelle forma-

tion leads to increased dispersion of a compound in solution above its water solubility limit [9] thus enhancing hydrocarbon solubility [10].

B. ***Bacterial Growth Curve***

The bacterial growth curves of *Pseudomonas aeruginosa*, *Bacillus subtilis*, and *Actinetobacter baumanni* were described in Figure 3. The highest initial population and short lag phase of *P. aeruginosa* showed the great adaptation capability and made this species preferred to use in biodegradation process.

E. *Hydrocarbon Biodegradation in Slurry Bioreactor*

It was clearly appeared that Emulsogen LP as surfactant addition on its Critical Micelle Concentration (10 mg/L) enhanced oil sludge biodegradation in 3 bacterial cultures of *P. aeruginosa*, *B. subtilis*, and *A. baumanni* after 48 hours. By surfactant addition, oil sludge biodegradation reached 37-49% whereas control (without surfactant addition) only reached 28-33% (Figure 4). The highest oil sludge biodegradation was obtained in *P. aeruginosa* cultures with Emulsogen LP addition (49%). Probably Emulsogen LP was used by *P. aeruginosa* as nutrient resource or the structure and functional properties of this surfactant increased *P. aeruginosa* population (Table 4).

The result of hydrocarbon biodegradation from oil sludge which did not reach above 50% could be caused by short time of degradation process (48 hours). The complexity and stability structure of oil sludge require sufficient time to degrade all hydro-

Table 4
Bacterial population before and after biodegradation process

Culture	Before biodegradation (cell/mL)	After biodegradation (cell/mL)	
		control (without surfactant addition)	with Emulsogen LP addition
P. aeruginosa	12×10^6	10×10^7	11×10^7
B. subtilis	8×10^6	2×10^7	2×10^7
A. baumanni	2×10^6	4×10^7	4×10^7

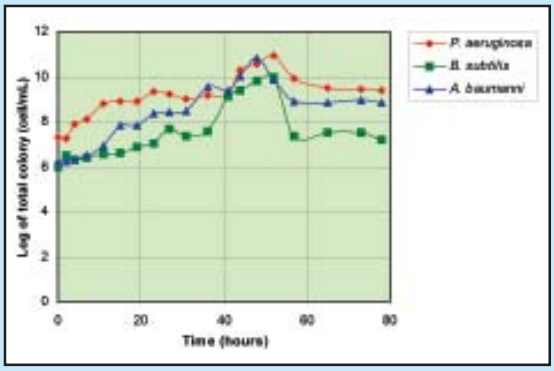

Figure 3
Growth curves of three bacterial cultures

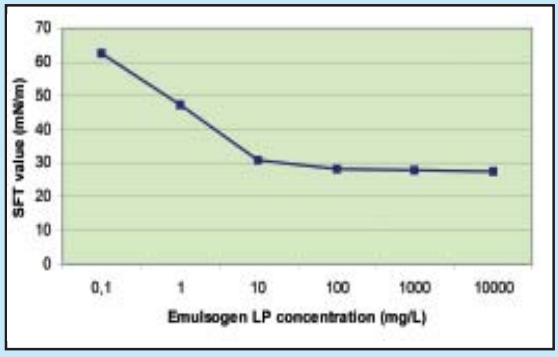

Figure 2
Critical Micelle Concentration (CMC) determination of Emulsogen LP

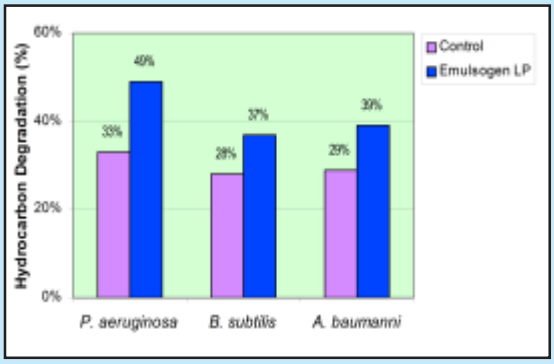

Figure 4
Oil sludge hydrocarbon degradation in slurry bioreactor

carbon components. Available aeration and agitation in slurry system should be examined to create optimum process condition. Rahman [2] denoted that quantity of the hydrocarbon degraded depend on environmental condition, chemical structure of the pollutant compound, type and amount of oil present.

The bacterial populations in all treatments increased during biodegradation process (Tabel 4). The similar population after biodegradation process between control and treatment showed that surfactant addition increased biodegradation but did not increase microbial growth. Moreover, Emulsogen LP is suitable for *P. aeruginosa* growth because of its increased population by surfactant addition.

V. CONCLUSION

Emulsogen LP addition in its CMC (10 mg/L) enhances oil sludge biodegradation. The surfactant addition had no negative impact in microbial growth. Improvement in design of slurry bioreactor such as availablity of aeration, proper agitation, and favorable condition of biodegradation process should be investigated to enhance hydrocarbon biodegradation.

REFERENCES

1. Soriano, AU and N Pereira Jr. 2002. Oily sludge biotreatment. In: IPEC & CESE (Eds.). 9th Annual International Petroleum Environmental Conference. Albuquerque, New Mexico.
2. Rahman, KSM. G Street, R Lord, G Kane, TJ Rahman, R Marchant, and IM Banat. 2006. Bioremediation of petroleum sludge using bacterial consortium with Biosurfactant. In: SN Singh & RD Tripathi (eds). Environmental Bioremediation Technologies. Springer Publication. p: 391-408
3. Mohan, SV. M Ramakrishna, S Shailaja, and PN Sarma. 2007. Influence of Soil-Water Ratio on the Performance of Slurry Phase Bioreactor Treating Herbicide Contaminated Soil. Bioresource Technology 98: 2584-2589.
4. Machin-Ramirez, C. AI Okoh, D. Morales, K. Mayolo-Deloisa, R. Quintero, MR. trejo-Hernandez. 2008. Slurry-phase biodegradation of weathered oily sludge waste. J. Chemosphere 70 (2008): 737-744.
5. Volkering, F. AM Breure, and WH Rulkens. 1998. Microbiological aspects of surfactant use for biological soil remediation. J. Biodegradation 8: 401-417.
6. Volkering, F. et.al., 1995. Influence of nonionic surfactants on bioavailability and biodegradation of polycyclic aromatic hydrocarbon. Applied and Environmental Microbiology. vol. 61 (5): 1699-1705.
7. Zheng, Z. and JP Obbard. 2001. Effect of nonionic surfactant on biodegradation of polycyclic aromatic hydrocarbon (PAHs) in soil by Phanerochaete chrysosporum. J.Chem. Technol. Biotechnol. 76: 423-429
8. McClement, DJ. 1999. Food emulsion: principles, practice, and techniques. 2nd ed. CRC Press. Boca Raton. 104, 108 pp.
9. Cristofi, N. and IB Ivshina. 2002. A review: Microbial surfactants and their use in field studies of soil remediation. J. Appl. Microbiology. 93: 915-929.
10. Aronstein, BN. YM Calvillo, and M Alexander. 1991. Effect of surfactants at low concentrations on the desorption and biodegradation of sorbed aromatic compounds in soil. *Environ. Sci. Technol.* vol. 25 (10): 1728-1731.˘