Research Paper

Optimization Approach for Solvent Extraction Process of Oily Contaminated Soil with Addition of Biosurfactant

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Objectives : Solvent extraction is a process in which not only enable to reduce oil contaminant from soil residue, but also capable to recover oil from soil matrix of oily contaminated soil which has opportunity to be reutilized. Optimization process has been simulated by previous studies related to type and dosage of solvents, variances of temperature, additional of surfactants, and other related parameters to increase oil removal from oily contaminated soil. This study seeks an approach of optimization for solvent extraction process to oily contaminated solid waste by conducting statistical analysis into laboratory experimentation from perspective of Total Petroleum Hydrocarbon (TPH) removal.

Method : Biosurfactant became single extractors for multistage extraction process and also combined with other solvents which are acetone and toluene. Mixing method that utilized during the study was combination between horizontal shaking at 150 rpm in 15 min duration and centrifugation force at 1,570 g in 10 min duration. Statistical analysis were conducted to seek its multiple regression.

Result : Study describing biosurfactant performance single extractor by using multistage extraction process achieve 77% TPH removal, while combination of biosurfactant and solvent extraction by using toluene and acetone also capable to increase TPH removal 7% higher from original performance of both toluene and acetone at solvent extraction.

Conclusion : Surfactant and solvents combination is promising to improve TPH removal, while statistics analysis that implemented to observed extraction process has possibility to be used for engineering higher efficiency of extraction process.

Keywords : Biosurfactant, Contaminated Soil, Oil Sludge, Soil Washing, Solvent Extraction, TPH

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1. Introduction

Soil remediation attracts a lot of interest due to large volume of contaminated soil produced years behind, yet it keeps continuing to be produced up till now. Its generation would be proportionally related to oil production and the safety and environmental awareness related to oil production. Physical and chemical process may do faster treatment processes that has becoming well known as its major benefit, while biological processes are able to handle bulk of waste in certain period with lower risk to the environment.

As part of physical and chemical process, solvent extraction has been also preferred for its high recovery rate on oil reutilization. Optimization has been studied to gain better performance from the side of recovery, however very few studies report the quality of soil after treatment. Utilization of biosurfactant for solvent extraction has been reported by Zhang et al.¹⁾ that with optimum formulation of biosurfactant, oil recovery of 74.55% was obtained when washing at 20°C and 200 rpm for one hour. Helmy et al.²⁾ in 2014 previously also conduct some studies related to the usage of biosurfactant and reported that usage of biosurfactant from *Burkholderia* sp. were able to enhance the rate of biodegradation efficiency on removing petroleum hydrocarbon up to 65%.

Solvent extraction process essentially is an adsorption-desorption process of oil between the solid and liquid phases.³⁾ Biceroglu⁴⁾ in 1994 has been used intermediate hydrocarbon source to be able to extract oil sludge from refinery storage to become lighter hydrocarbon at several stages of temperature. El Nagggar et al.⁵⁾ studied the usage of some solvents such as naphthalene, kerosene cut, n-heptane, toluene and some other solvents. Zubaidy and Abuelnasr⁶⁾ in 2010 made comparative study related to the effect of some organic solvents such as methyl ethyl keton (MEK) and liquefied petroleum gas condensate (LPGC). The following **Table 1** will describe

summary of solvent extraction studies for oily waste as referred by this study.

Biosurfactant has its unique property of reducing the surface and interfacial tensions using the similar mechanisms as chemical surfactants. During the experiments some solvents has been selected to be implemented at solvent extraction process, the addition of biosurfactant was also observed to understand its contribution for solvent extraction process. This study also conducts statistics analysis to give approach for optimizing process in larger scale. Random sampling method was utilized and multiple regression analysis were conducted for giving closer approach for set of experiments.

2. Material and Method

2.1. Biosurfactant and EP24

As part of characterization process for biosurfactants, Emulsification index (EP24) is determined by performing centrifugation at 13,000 rpm to separate biosurfactant from microorganism cells yielded a biosurfactant cell free.¹⁰⁾ Biosurfactant and crude oil in ratio 1:1 was agitated for 2 min then stabilized for 24 h. Emulsification index (%) determined by measuring the column height of emulsified oil against its total height multiplied by 100.

Selected biosurfactant of the experiments produced by Bioscience and Biotechnology laboratory at Institute Technology of Bandung. Selected isolate of *Burkholderia* sp._PAU02 has capability to reduce surface tension to the point of 47.0 dyne/cm and emulsification index EP24 of 84%. Solvent extraction process and analysis of parameters have been conducted at PPLi laboratory in Cileungsi, Bogor. TPH content was analyzed referring to USEPA 8440 method about total recoverable petroleum hydrocarbons by using infrared spectrophotometry, while metal elements for solid were measured using inductively Coupled Plasma (ICP) analysis

Table 1. Solvent extraction research for oily contaminated solid waste.

Year	Name	Method	Solvent	Oil removal
2005	Gazineu et al. ⁷⁾	Solvent extraction	Turpentine	13-53% oil from original oil sludge mass
2006	Taiwo and Otolurin ⁸⁾	Solvent extraction	Hexane and Xylene	67.50%
2010	Zubaidy and Abouelnasr ⁶⁾	Solvent extraction	Methyl ethyl ketone (MEK) and liquefied petroleum gas condensate (LPGC)	39% for MEK and 32% for LPGC
2010	El Nagggar et al. ⁵⁾	Solvent extraction	Toluene	75.94%
2015	Hu et al. ⁹⁾	Solvent extraction + Freeze thaw	MEK and Ethyl Acetate (EA)	40% for MEK and 60% for EA

base on USEPA 3050 B Method by conducting acid digestion method using HNO_3 and H_2O_2 . Solvent extraction method conducted by running horizontal shaker equal to 150 rpm for 15 min then continued by centrifugation SETA Oil Test Centrifuge at 1,000 rpm (1,570 g) for 10 min duration. Extract of aliquot and solid was separated by using vacuum filtration method using *Whatman series* CAT-1825-047 that has 47 mm of diameter.

2.2. TPH Removal

TPH removal (R_o) from the oily contaminated soil and the oil concentration in the solvent (C_o) were calculated as mentioned in the following Eq. 1 and Eq. 2:

$$R_o = ((\Gamma_0 - \Gamma_{10})) / (\Gamma_0) \quad (1)$$

$$C_o = ((\Gamma_0 - \Gamma_{10})) / (m/V) \quad (2)$$

Where Γ_0 and Γ_{10} are the initial and residue oil contents that measured as Total Petroleum Hydrocarbon (TPH) in the contaminated soil (g/g), respectively, m is the mass of soil (g) and V is the solvent volume (mL).

2.3. Preparation of Sample

The sample was stored in a jar at 25°C . Aliquot of 1,000 grams of contaminated soil were collected in a tray. Sample were dried by using open air for three days to minimize moisture content for further experiments. After drying the solid sample was mixed evenly so to ensure the homogeneity. Homogenous sample would be further observed as the following experimental treatment procedure that listed at **Table 2**.

Table 2. Sequence of experimental procedure.

No	Type	Duration
1	Biosurfactant	15 min shaker for biosurfactant at 150 rpm, 10 min centrifugation at 1,000 rpm. Ratio soil : biosurfactant is 1:1
2	Solvent	15 min shaker for solvent at 150 rpm, 10 min centrifugation at 1,000 rpm
3	Biosurfactant + Solvent	15 min shaker for biosurfactant at 150 rpm, 15 min shaker for solvent at 150 rpm, 10 min centrifugation at 1,000 rpm

Table 3. Raw contaminated soil characteristics.

Parameter	A Jawa	B Sumatera	Unit
pH	8.7	8.3	-
TPH	9.00	17.86	%
Moisture	13.3	11.6	%
Density	1.1	1.2	g/m^3

3. Result and Discussion

This study initiated with examining characteristics of samples that would be treated by using several types of treatments which are mentioned above. Samples then randomly arranged to be treated for selected treatment. Control treatment was conducted using distilled water as blank reference for entire selected treatments and combinations.

3.1. Raw Waste Characteristics

There are two types of waste that has been observed during the study, the following **Table 3** shows the result of waste characteristics of waste type A that has been observed during the study. The average number would be considered as TPH concentration of raw waste.

3.2. Multistage Biosurfactant Extraction

First stage of biosurfactant extraction to waste type A conducted with ratio 1:1 by using the sequence of 15 min shaking then continued with 10 min centrifugation at room temperature as mentioned at **Table 1** was able to provide TPH removal 28.5%. Second stage implemented provided TPH removal up to 56.1%, while third and fourth stage of extraction increase provided result of TPH removal 71.6% and 77.4% respectively.

Observation has been also conducted to oily contaminated soil from contaminated soil from oil drilling base mud contamination which containing average TPH 17.89% named as waste type B in this experiment. Biosurfactant extraction also implemented to the waste type B for four stages of extraction as it has been implemented before to waste type

A which has typical sandy soil. In **Table 3** characteristics of waste type B was also described based on its key parameters.

Waste type B has clay characteristics and having higher TPH content compare waste type A. Raw waste that has 17.86% and obtain result of TPH removal average 14-17% of every stage of biosurfactant extraction. The entire total four stages of extraction process gave 49.53% of TPH removal. The following **Fig. 1** below present complete observation result for four stages of biosurfactant extraction for both type A and type B soil waste.

Analysis of Gas Chromatography-Flame Ionization Detector (GC-FID) also conducted for raw waste type A and every stage of treatment result. A comparison between raw waste hydrocarbon composition prior and after treatment shall give

better understanding for obtaining result. The following **Fig. 2** and **Fig. 3** gave description of raw waste type A and result after bio-surfactant multistage extraction process.

Chromatogram above presented some peaks around C8-C29. Most peaks are available between C20-C25. This is giving verification for source that coming from contamination of crude oil to sandy soil at the shore of an offshore platform located nearby. In the **Fig. 3** provided chromatogram result after 4 stages extraction has been conducted, while by also referring chromatograms comparison at **Fig. S1** until **Fig. S3** the comparison of chromatograms for each of four stages biosurfactant extraction giving confirmation that at the latest stage of extraction, hydrocarbon composition reduced both in concentration and complexities.

Fig. 1. Multistage biosurfactant extraction result.

Fig. 2. Chromatogram of raw waste type A.

Fig. 3. Chromatogram of fourth stage of biosurfactant extraction waste type A.

A comparison for both biosurfactant extraction process has been conducted to have better understanding regarding the performance of biosurfactant during the study. Biosurfactant extraction that involve waste type A which utilized sandy soil, having higher moisture content, and having lower TPH has higher total removal of TPH. Waste type B which has typical clay soil, having moisture content 13.3% and having TPH 17.86% has lower TPH removal rate for every stage of extraction and for total obtained recovery rate.

3.3. Multistage Biosurfactant Extraction Model

Influence of biosurfactant in for TPH removal of oily contaminated soil by using solvent extraction method has been observed at the following set of experiment at **Table S1**. During the experiment there are two types of waste that has been observed. Both type A and type B performed multistage extraction process that involving selected biosurfactant. Comparison between biosurfactant and solid was 1:1 for every stage of solvent extraction process.

Observing the experiments result statistically by utilizing SPSS analysis tool to run multiple regression, the experimental result came to an approach as stated below at the following model stated at Eq. 3:

$$Ro = 49.319 - 1.706 \times r_0 - 1.28 \times St \quad (3)$$

Where, Ro : TPH Removal (%)

r_0 : Initial TPH (%)

St : Extraction stage

Based on model above Initial TPH and extraction stage having contribution 49.78% and 50.22% respectively. Those formulations and values of contribution factor giving

information that degree of TPH removal is proportionally related to the initial TPH concentration of contaminated soil or waste and level of extraction process. Both factors giving lower removal along with higher TPH and higher level of extraction process.

3.4. Combination of Biosurfactant at Solvent Extraction Model

Sample that has been examined at the experiment of combination between biosurfactant and solvents involving toluene and acetone was sample B Sumatera that has TPH 17.86%. In the following **Table S2**, there are 16 batches of treatment that has been conducted to seek the impact of biosurfactant along with other solvent extraction parameters at solvent extraction process.

Based on result that obtained during the experiment by using statistical method using SPSS for multi-regression model. an approach to for removal of TPH is introduced. By using model that stated at Eq. 4 and the selection of independent variables that giving contribution, while the other parameter considered ceteris paribus then make value of result absolute the result in **Table S3** contribution factor of each variable is described.

$$Ro = 71.565 - 27.477b/s - 33.828 \times s/sol + 28.828 \times Sol + 0.298 \times T \quad (4)$$

Where, Ro : TPH Removal (%)

r_0 : Initial TPH (%)

St : Extraction stage

Sot : Solvent type

T : Temperature

Comparing model B with experiments that has been

conducted by Zhang et al.¹⁾ in 2012, this giving confirmation into his experimental graph that showing even solid to solvent varied in to solvent extraction process that using biosurfactant, the variances itself did not giving significant impact. Other parameters such as solvent type and temperature would rather give more impact to TPH removal.

3.5. Regression Analysis Test

There are four assumption that needed to be fulfilled while performing regression analysis. Those are 1) residue scattered normal or normal distribution, 2) residues are homogenous uniform or heteroscedastic, 3) multicollinearity or there is no correlation between independent variables. In the other hand it shall also perform regression 4) model test (R^2), 5) f test ANOVA, and 6) t test. Assumption test conducted for both models and the following are results of those implemented tests.

3.5.1. Normal Distribution Test

Normal distribution test having objective to observed normality of data distribution. Kosmogorov-Smirnov normality test has been utilized and giving the result at **Table S4** for both models. According to output from statistical analysis Asymptotic Significance (2-tailed) of both models have values more than 0.05. Therefore, it can be concluded that data distributed normally.

3.5.2. Homoscedastic Test

Analysis result of homoscedastic test that has been conducted and described at **Table S5** also be able to explain that for model A homoscedasticity occurred at TPH raw variable other than that all parameters showed their non-homoscedasticity.

3.5.3. Multicollinearity Test

Multicollinearity test used to find there is linearity in between independent variables at the regression model. Multicollinearity would be able to be detected by Variance Inflation Factors (VIF). If $VIF < 10$, it indicates there is no multicollinearity occurred, while in the other hand if $VIF > 10$ multicollinearity shall occur. According output of statistical analysis, it has been observed that VIF values for all variable at both models are less than 10. Therefore, assumption that all models have no multicollinearity is fulfilled.

3.5.4. (R^2) Test

R Square value Adjusted on SPSS explained percentage of

compatibility for multi-regression model. In the other word it shall able to show variables independent giving its function to dependent variable. At **Table S7**, described R^2 adjusted values from each model A has 61.5% R square value, while model B has 65.3% R square value.

3.5.5. F Test (ANOVA)

F test has objective to examine influence of independent variable simultaneously that showed at "Sig." Column in ANOVA table. Hypothesis that referred are:

H_0 : All variables not significantly related to dependent variable

H_1 : All variables significantly related to dependent variable
While test Criteria:

- Sig. value > 0.05 H_0 rejected
- Sig. value < 0.05 H_0 accepted

According to values of F test at ANOVA test result table, it is indicated that H_0 accepted.

3.5.6. T Test

T test utilized to examine influence of each independent variables partially to the dependent variable. If Sig. < 0.05 , H_0 rejected. Hypothesis that are referred:

H_0 : Independent variable not significantly influencing TPH removal

H_1 : Independent variable significantly influencing TPH removal

According to statistical analysis that has been conducted both models having independent variable that not significantly influencing TPH removal are extraction stage, temperatures, and solid to solvent ratio.

3.6. TCLP Analysis for Residue of Biosurfactant Extraction

TCLP analysis also conducted to the residual treated contaminated soil to study about its metal leaching properties of residual treatment process for multistage of biosurfactant extraction. Heavy metal key parameters were analyzed to check its contribution on leaching factor for its possibility to be final disposed at controlled landfill. The following **Table 4** provided data that all heavy metal parameters having lower concentration compare to required parameters that regulated by government of Indonesia PP 101 year 2014 so that it can be treated at non-hazardous waste landfill. Further discussion and study shall also be conducted to have more data related to these possibilities.

Table 4. Metal analysis of waste type A residue.

Metal element	Limit value TCLP-A (PP101/2014) Concentration (mg/L)	Limit value TCLP-B (PP101/2014) Concentration (mg/L)	TCLP of Raw waste type A Concentration (mg/L)	TCLP of Residue waste type A Concentration (mg/L)
Sb	6	1	0	0.0203
As	3	0.5	0.131	0
Ba	210	35	0.6145	0.2065
Be	4	0.5	0.0002	0
B	150	25	0.8340	0.3577
Cd	0.9	0.15	0	0.0796
Cr	15	2.5	0	0.0545
Cu	60	10	0.0389	0.0279
Pb	3	0.5	0.315	0
Hg	0.3	0.05	0	0.0091
Mo	21	3.5	0	0.0176
Ni	21	3.5	0.0038	0
Se	3	0.5	0	0.0942
Ag	40	5	0.0094	0.0742
Zn	300	50	0.018	0.0019

4. Conclusion

Application of solvent extraction has been occurred for years, yet the equipment related to the centrifugation process and its supporting equipment for pre-treatment has been available for years. Control of temperatures and mixing condition were also has been applied. Solvent extraction may give better optimum condition for oil recovery, however the optimization of solvent or biosurfactant recycling shall also be considered.

Biosurfactant extraction may give an opportunity to have better TPH removal by using multistage process, however this treatment shall give better alternative to the have natural biodegradative agent for extraction process of oily contaminated soil.

Multistage biosurfactant extraction implementation achieved TPH removal up to 77.44% for contaminated waste that has original TPH 9.00%, while achieve 49.34% of TPH removal for contaminated soil that has 17.89% original TPH.

Based on approached model it all parameters that involved at solvent extraction such as type of soil, moisture has most significant impact for TPH removal. By using the approached model, it shall also perform optimization for TPH removal due to adjustment of parameters referring the model.

Combination of biosurfactant at solvent extraction process is a method that can be implemented as an alternative to remove TPH as pollutant at the contaminated soil and also

an option for recycling to increase longer utilization of oil for any other applicable purposes. Parameters that significantly impacting TPH removal are solvent type and temperature.

Residual result for TPH, Chromatogram, Metal Content, TCLP for metal also indicate solvent extraction process may give opportunity for the residue to be used for other purposes and or having any further bioremediation process.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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