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Kinetics Modeling of Straw Bioremediation as Nutrition in Processing Liquid Waste of Oil and Gas

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Abstract : Processing performance of hazardous wastes in Indonesia, mainly produced in mining, energy and mineral industries, is well below target. One suitable technique for processing such waste is bioremediation which utilize microorganism activities. Waste rice straw is one potential substrate which carries and supports the bioremediation microorganisms. Lignin in the straw provides nutrients for bacteria and fungi which enable the production of enzymes to degrade pollutants in the waste. Lignin can also increase interfacial surface tension between hydrophobic and hydrophilic fractions in the waste mixture to facilitate their separation. The objective of this study is to model the kinetic of bioremediation which represent the relation between bioremediation period and reduction rate of Total Petroleum Hydrocarbon (TPH). The model utilized characterization results of retentate from waste filtration in terms of water content and pH. The bioremediation process involved mixing of waste rice straw and processed liquid waste from a petroleum refinery plant at 1:20 (m/v) ratio for varied duration of 10, 15, 20, 25, and 30 days. Results showed that the formation rate of water (measured as moisture content in retentate) which indicate the reduction rate of TPH follows 1.2 order of reaction at rate constant of 0.594 day⁻¹. Prediction of Michaelis-Menten model was also performed. The pH of retentate was 8, and organoleptic test observed the turning of color from turbid yellow into dark brown as well as the disappearance of petroleum oil smell, which demonstrated that the processed waste is safe for the environment.

Key words: bioremediation, rice straw, nutrient, petroleum refinery waste, total petroleum hydrocarbon (TPH).

Introduction

Environment pollution caused by wastes, particularly industrial ones, increases every year. The largest portion of hazardous industrial wastes is produced in mining, energy and mineral industries, which accumulation in 2015-2019 is predicted to be 755,6 million tons. Within 2015-2017, less than 40% of such waste was appropriately handled[1].

Based on Minister of Environment Decree No. 128 Year 2003 about biological processing of dangerous waste, one of processing techniques for petroleum refinery waste is bioremediation. Bioremediation utilizes the biocatalytic advantage of microorganisms fed with certain nutrient.

Liquid waste used in this study was processed waste taken from a petroleum refinery plant prior to its disposal to the sea. The waste sample was deep black, with typical oil smell. Rice straw containing lignin of 12 to 16 % was added as the substrate in bioremediation process. Lignin is a natural co-polymer found in cell walls of woody plants including rice straw. It is formed by three kinds of monomers: (1) p-coumaryl alcohol (p-hydroxyphenyl unit), (2) coniferyl alcohol (guaiaacyl unit), and (3) sinapyl alcohol (syringyl unit) [2]. Lignin can degrade bacteria found in liquid waste as well as function as surfactant to reduce interfacial surface tension between the hydrophobic and hydrophilic fractions of the waste mixture.

Experimental

Equipment and Material

Equipment used in this study were centrifuge, oven, filter paper, glass breaker, hot plate, digital scale, glass bottle, measuring cup, drop pipette, and pH meter. Materials used were rice straw of IR variety and liquid waste from petroleum refinery plant.

Methods

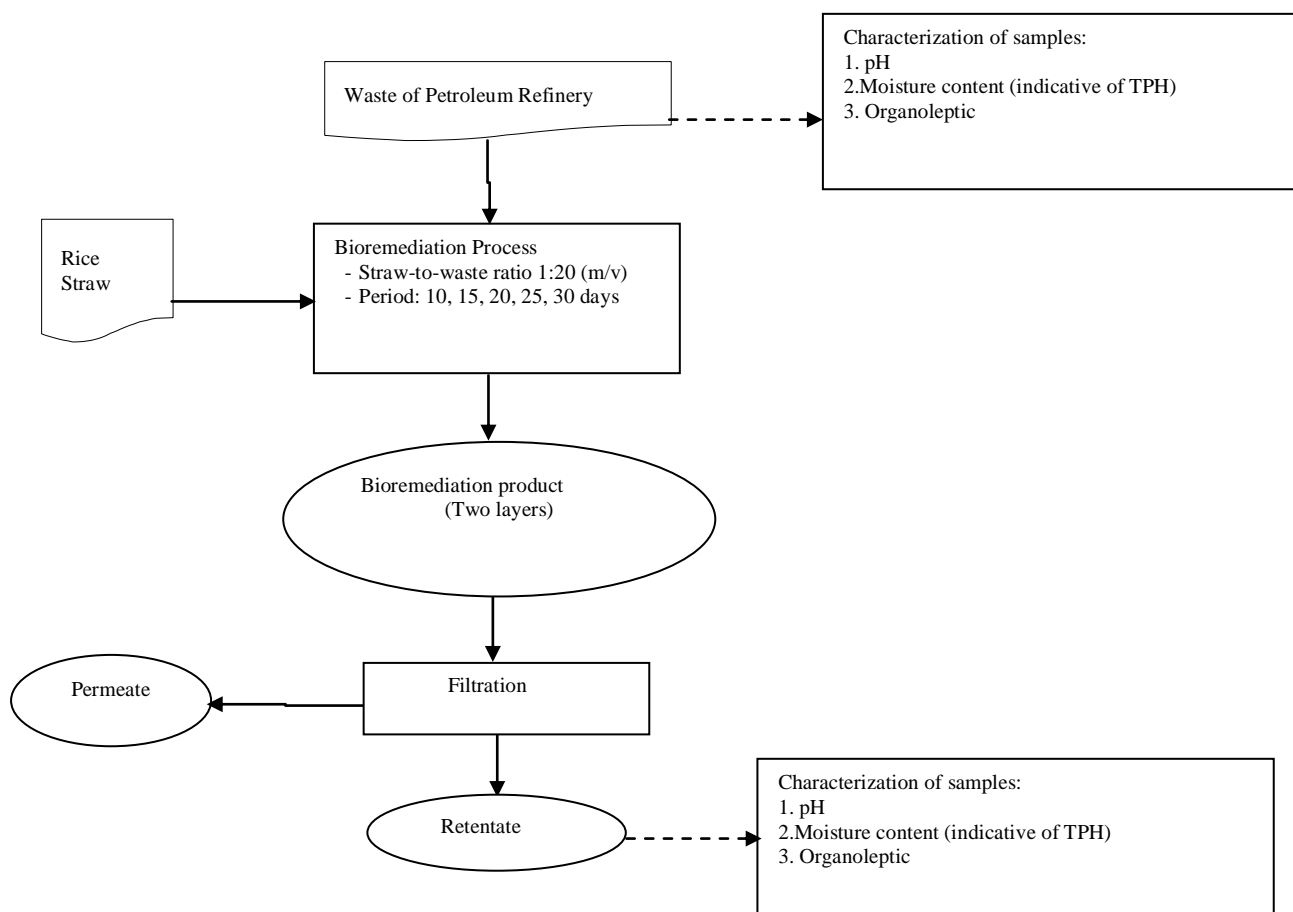


Figure 1. Experimental procedures of bioremediation study

First of all, waste sample was characterized for its pH and moisture content which indicate bacterial activity in the reduction of hydrocarbon content. Rice straw (5 g) was then cut into small pieces and added into the liquid waste samples (100 ml) in beaker glasses at 1:20 (m/v) ratio. Durations of bioremediation process were varied for 10, 15, 20, 25, and 30 days. During the process, a hydrophobic layer emerged separately from the hydrophilic layer. Afterwards, the hydrophobic layer can be separated from the hydrophilic one through filtration. The retentate on filter papers was then subjected to moisture content and pH measurements (procedures are explained elsewhere [3]), as well as organoleptic analysis to measure retentate qualities that were odor and color. These data were then processed to generate a kinetic model which relate between bioremediation period and reduction of TPH content.

Results and Discussion

Organoleptic test

Results of bioremediation process for 10 days, 15 days, 20 days, 25 days, and 30 days were subjected to organoleptic test to indicate the content of samples, as presented in Table 1.

Table 1. Result of organoleptic test

Period (Day)	Odor	Color
0	Petroleum Oil	Turbid yellow
10	Rotten straw	Dark brown
15	Rotten straw	Dark brown
20	Rotten straw	Dark brown
25	Rotten straw	Dark brown
30	Rotten straw	Dark brown

Based on results in Table 1, it is indicated that the remaining oil in the waste sample was degraded by the bioremediation process into fermentation products indicated by the rotten straw odor and dark brown color as the typical petroleum oil smell and turbid yellow color disappeared. This colour changing phenomenon is indicative of microbial activities within the samples in degrading the hydrocarbon compounds.

pH test

Control of pH and moisture is required for biological remediation of the environment [4]. The pH values of samples after bioremediation process in 10 days, 15 days, 20 days, 25 days and 30 days are shown in Figure 2.

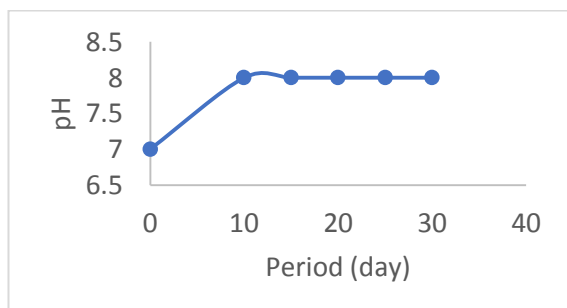


Figure 2. Relationship between bioremediation period and pH of retentate

Based on measurement results in Figure 2, it can be seen that bioremediation process apparently increased pH value of samples from 7 to 8. Microbial activities in lignin-containing rice straw substrate might produce alkaline compounds which raised the alkalinity of retentate. These pH values are within the ideal range for microorganism growth that 6-9 with optimum range at 7-8 [5].

Moisture content (indicative of hydrocarbon content)

Microbial enzymes are biocatalyst for degradation reaction of hydrocarbon compounds into water, carbon dioxide, and energy for living and growth of the microbes. Therefore, the reduction of hydrocarbon content due to degradation in the waste samples can be indicated by the increasing moisture content of substrate.

Figure 3 shows that prior to bioremediation process, the retentate samples contained 30.61% moisture. Within 10 days, the moisture content increased into 57.89%. The increase indicates that there were microbial activities during bioremediation process which produced water. The moisture content decreased in day-15 to the amount of 42.86% and quite stable up to day-20 at 42.50%. This result may reflect the stabilization of microbes at this stage. Afterwards, the moisture content increased to 50.82%, potentially due to domination of microbes in the oil fraction of samples. Then the moisture content decreased on day-30 to 21.10%. These range of moisture contents is in accordance with a previous study at 20.25 – 65.3% [6].

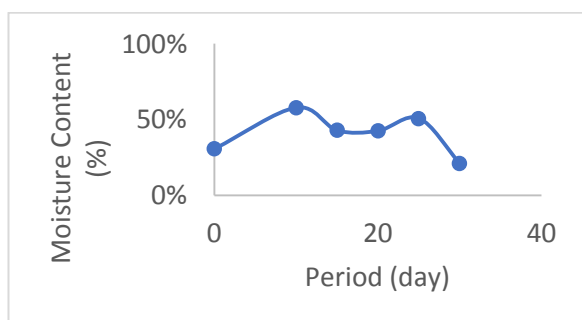


Figure 3. Relation between moisture content in retentate and bioremediation period

Kinetic Modeling of Bioremediation Process

Bioremediation process of petroleum refinery waste degrades hydrocarbon compounds within samples into mainly carbon dioxide and water. Concentration of the produced water (C) was calculated as additional moisture content as bioremediation proceed (moisture content of the original sample prior to processing was deducted from those of the processed ones). The relation between C and bioremediation period (t) was utilized to determine the kinetic model of bioremediation process based on rate law of reaction, as well as Michaelis-Menten model.

Rate Law of Reaction

Integrated rate laws for each reaction order (in terms of product) are as follows [7]:

$$\text{Zero order} \quad : \quad C = C_0 + kt \quad (1)$$

$$\text{First order} \quad : \quad \ln C = \ln C_0 + kt \quad (2)$$

$$\text{Second order} \quad : \quad C^{-1} = C_0^{-1} - kt \quad (3)$$

$$n\text{-th order} \quad : \quad C^{1-n} = C_0^{1-n} + (1-n)kt \quad (4)$$

In the above equations, C is concentration of produced water in mass fraction during bioremediation process, C_0 is the initial concentration (equal to 0), k is reaction rate constant, t is bioremediation period (day), and n is the order of reaction. Equation (1) – (3) were plotted as presented in Figure 4. It is clearly seen that the production of water during bioremediation process did not exactly follow either of zero, first, nor second order of reaction. This is because the R^2 values are all fall below unity, meaning that the plots do not fit the equations. Because of that, equation (4) was then plotted for n ranging from 0 to 3 (except for $n = 1$, where equation (2) was used), for which the $R^2 > 0$. The values of n and k were then calculated accordingly (Figure 5).

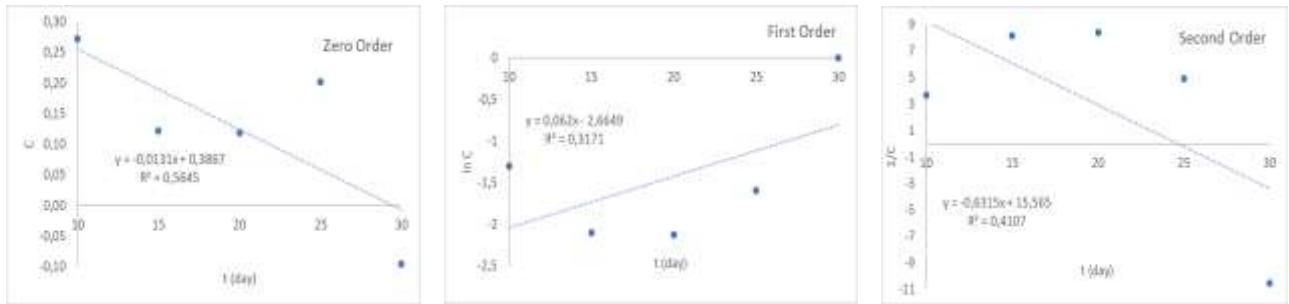


Figure 4. Fitting the rate laws of reaction into the kinetics of bioremediation process

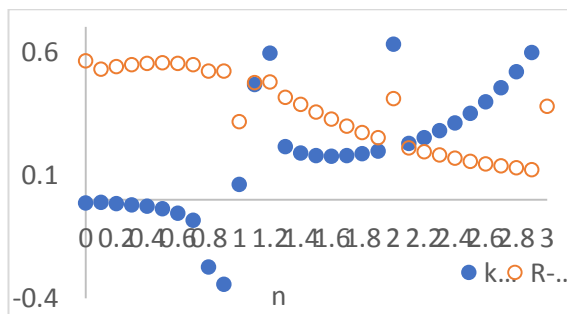


Figure 5. Comparison between k & R^2 values in determining the appropriate order of reaction

It was observed that the rate constants were negative for $n < 1$ and odd numbers > 1 . These k values were not particularly accounted in this study because rate constant must be positive in terms of product formation. The positive k raised exponentially with the increasing n , whereas the trend of R^2 was declining. As observed in Figure 5, the appropriate reaction order was chosen at $n = 1.2$ with the highest R^2 of 0.4771 for reasonably positive k at 0.5940 day^{-1} . Although the R^2 value is not high enough to validate the equation fit, the reaction order is very close to the one of TPH degradation by *Pseudomonas pseudoalcaligenes* at 1.1 [8]. *Pseudomonas* sp. was capable to effectively degrade many hydrocarbon compounds [9, 10].

Michaelis-Menten Model

Michaelis-Menten (MM) kinetics is widely used to describe the rate of enzymatic reactions (V), usually those involving microbes-containing substrate with concentration of $[S]$. Parameters in the equation below also include V_{\max} [g/ml/day] as the maximum reaction rate and K_M as the Michaelis constant [11]:

$$V = \frac{V_{\max} [S]}{K_M + [S]} \tag{5}$$

$$K_M + [S]$$

Rearrangement for linear regression results in the following equation:

$$\frac{1}{V} = \frac{K_M}{V_{\max}} \frac{1}{[S]} + \frac{1}{V_{\max}} \tag{6}$$

$$V V_{\max} [S] V_{\max}$$

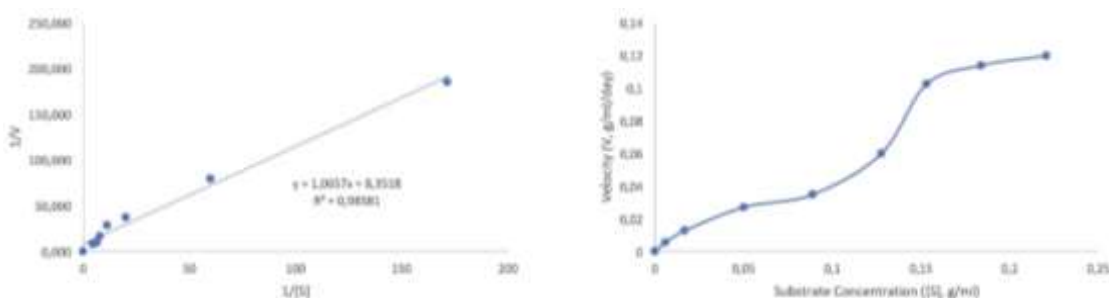


Figure 6. Prediction of Michaelis-Menten kinetics with linear regression (left) and predictive plotting (right)

The prediction of MM kinetics involved one set values of $[S]$ and V from the experiment at 0.05 g/ml and 0.027 g/ml/day, respectively. Initially it was assumed that this V value was approaching V_{max} . Few more points were then assumed at both upper and lower values of V and $[S]$ (the right plot in Figure 6), considering that numerically $K_M = [S]$ at $V = \frac{1}{2} V_{max}$ [11]. A plot according to equation (6) is presented in Figure 6 (left). A linear regression of the plot revealed that, in fact, the experimental value of V was far below calculated V_{max} . The predictive plotting was then adjusted while maintaining positive slope and intercept of the linear regression line, as well as R^2 pretty close to 1. Calculation based on the slope and intercept data obtained from the left plot in Figure 6 using equation (6) resulted in $V_{max} = 0.1197$ g/ml/day and $K_M = 0.1276$. The R^2 of linear regression is very close to 1, signifying the relation between reaction speed and substrate concentration [11].

Conclusion

This study has successfully implemented bioremediation process of petroleum refinery waste employing rice straw substrate with substrate-to-waste ratio of 1:20m/v. Organoleptic tests revealed that the initial odor and turbid yellow color of petroleum oil disappeared within less than 10 days, as the rotten smell of dark brown rice straw substrate started to be consistently sensed afterwards. The processed waste was safe for the environment with pH = 8.

The kinetics of TPH degradation as reflected by moisture content and modeled by rate law demonstrates a close proximity to the results of previous studies in terms of reaction order ($n = 1.2$) and rate constant ($k = 0.5940 \text{ day}^{-1}$). A prediction for Michaelis-Menten kinetic models provided values of maximum enzymatic reaction speed ($V_{max} = 0.1197$ g/ml/day) and Michaelis constant ($K_M = 0.1276$).

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