Journal of Engineering Science and Technology
EURECA 2014 Special Issue April (2015) 26 - 34

TREATMENT OF PALM OIL REFINERY EFFLUENT USING ADVANCED OXIDATION PROCESS

N. RAJESH*, C. S. LAI, D. VEENA, H. T. T. NGUYEN

School of Engineering, Taylor's University, Taylor's Lakeside Campus,
No. 1 Jalan Taylor's, 47500, Subang Jaya, Selangor DE, Malaysia
*Corresponding Author: Rajesh.Rajasekaran@taylors.edu.my

Abstract

Palm oil refinery effluent (PORE) is a type of wastewater that produces from palm oil industries. High demand and constant production of refined palm oil worldwide cause the volume of PORE to be continuously increase. PORE has high level of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) due to the presence of organic matters that are harmful to environment such as aquatic lives. Hence, it is essential to treat PORE before discharging back to environment. In this research, Fenton process from advanced oxidation process is used for treatment of PORE to reduce COD and BOD level as well as composition of organic matters. For the Fenton process, two chemicals are used to produce hydroxyl radicals, which have high oxidizing power to break down the organic matters present in PORE. Thus, COD and BOD level of PORE is reduced and safe to discharge to the environment. Besides Fenton process, physical treatment were conducted by only changing pH and temperature of raw PORE samples without adding chemicals in order to study characteristic of organic compounds. The experiment samples were tested the COD and BOD level. As a result, 0.5M of Fenton reagent obtained highest reduction of percentage of COD and BOD level which are 63.6% and 61.3% respectively. In addition, 30% reduction in COD and BOD level of PORE was obtained in the physical treatment.

Keywords: Palm Oil Refinery Effluent (PORE), Wastewater treatment, Advanced Oxidation Process (AOP), Fenton process, Hydroxyl radicals.

1. Introduction

Malaysia is one of the largest palm oil producers in the world and palm oil refinery effluent is the significant pollutant from the palm oil mill. A huge generation of palm oil refinery effluent (PORE) produces every year. High

Abbreviations	
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DOE	Department of Environment
FAS	Standard Ferrous Ammonium Sulfate
PORE	Palm Oil Refinery Effluent

demand of palm oil from worldwide causes the increment of PORE produced after the process. PORE is produced during the process of refinery of palm oil.

As a result, refined palm oil will be produced and PORE will be treated as wastewater from the refinery process. PORE contains 95-96% of water, 4-5% of total solids and 0.6-0.7% of oil [1]. PORE that produced from the refinery process contains of oil, grease and suspended solids. There are traces of organic matters presence in PORE. This is due to the use of chemicals during the refinery process. The COD and BOD level of the suspension is high because of the presence of organic matters. High level of COD and BOD could harm or cause death of the aquatic lives. Hence it results in the imbalance of the ecosystem. Thus, PORE has to be treated to meet the standard of DOE before discharging to the environment.

There are several treatment methods for PORE such as biological treatment, physical treatment and physical-chemical treatment. These treament methods aim to reduce COD and BOD level of PORE. An install of wastewater treatment is important for the continuous production of palm oil from refinery process. Currently, PORE is treated by using conventional method, which is biological method. The conventional treatment method needs microorganism to breakdown the organic matters contained in PORE. To grow the microorganism, an optimum environment must be created. For instance, temperature of the wastewater could not be higher than 30^{o}C. Hence, wastewater has to be cooled down to optimum temperature for microorganisms to grow before starting the treatment. In addition, pH level of wastewater has to be maintained at the optimum level. Besides, there will be time delayed on treatment when the microorganisms are dead.

There are many types of advanced oxidation processs available in literature namely Fenton process, ozonation process, hydrogen peroxide oxidation process, photocatalytic oxidation process. Fenton process from Advanced Oxidation Process was selected to treat PORE. Fenton process was discovered by H.J.H Fenton in year 1894. It is stated that hydrogen peroxide could decompose by using iron salt to form of hydroxyl radicals (*OH) to degrade organic matters. At present, Fenton reagent is often used in treatment of wastewater, which are from several industries such as olive oil production and dye, paper production, and pharmaceutical industries. Fenton reagent that used in this research consists of iron (II) sulphate and hydrogen peroxide. Fenton reagent generates OH radicals from hydrogen peroxide that have high oxidative power and it obtains general organic pollutant abatement [2].

Iron (II) sulphate acting as a catalyst of the Fenton process, catalyses and enhances the production of hydroxyl radicals. The rate of production of OH radicals directly reflects to the duration of decomposition of organic matters in wastewater. When the rate of production of hydroxyl radical is high, the duration needed to decompose organic matters in wastewater would be shorter. Fenton process chosen in this research could be used at ambient temperature and pressure, hence it is easy to conduct the experiments using Fenton reagent.

However, PORE must be maintained at pH 3 because the precipitation of ferric hydroxide will occur when the Fenton reagent operate at higher pH, whereas iron complex ions will be produced when it operates at pH lower than pH 3. Overall, it is an effective treatment in decomposing organic matters that are present in the wastewater.

By applying Fenton Process to treat PORE, organic matter content in PORE could be reduced before it discharges to the environment. Then, as the composition of organic matters is reduced, COD and BOD levels of PORE will be reduced. Thus, pollution of the water by PORE is expected to be minimised after treating PORE with Fenton reagent. In this research, optimum concentrations of Fenton reagent for the PORE treatment were established. Besides, physical treatments such as pH treatment and temperature treatment also were conducted in order to compare with the results of Fenton process. Furthermore, COD, BOD and HPLC testing of samples are conducted to determine the effectiveness of Fenton reagent and the physical treatments of PORE. The main objective of this research is to quantify the amount of decomposing organic matters in wastewater (PORE) by physical and chemical treatment.

2. Research Methodology

2.1. Overall research design

In the conduction of experiments, initial and final value of BOD and COD level in PORE was determined. For physical treatment, changes in pH and temperature of raw PORE were observed to study the effect of pH and temperature change on raw PORE. For chemical treatment, experiments were conducted at ambient temperature and pressure as well as maintained the pH of PORE at 3.0. By changing the concentration of the Fenton reagent, an optimum concentration of Fenton reagent would be obtained to decompose the organic matters in PORE effectively.

2.2. Treatment methods

2.2.1. Chemical treatment

Fenton reagent was used in this experiment to conduct chemical treatment of PORE. The main chemicals were iron (II) sulphate and hydrogen peroxide. Preparation of Fenton reagent was based on the selected ratio. In this project, the selected ratio for both chemicals was 1:2 indicating the ratio of iron (II) sulphate: hydrogen peroxide respectively.

First, iron (II) sulphate was dissolved in 500ml of PORE sample. Then, samples was adjusted to have pH 3.0 with sulphuric acid. After that, hydrogen peroxide was added into sample. The mixture was then left for 30 minutes for the reaction between PORE and Fenton reagent to be completed. The experiments were conducted with 0.1M increment from 0.1-0.5M of Fenton reagent. Then, each parameter was repeated until concurrence results were obtained.

2.2.2. Physical treatment

Physical treatment used in this work was conducted by adjusting the pH and temperature of PORE. This treatment was conducted with the absence of Fenton reagent. The purpose of conducting this treatment is to observe the effects of changing pH and temperature on decomposition of organic matters in PORE. In this treatment, pH range was from 2.0 to 10.0 for the increment of 2. Hence, there was a total of 6 samples of experiment including original sample of PORE without alteration of pH.

In the first step, initial pH of PORE was measured. Then, sulphuric acid/sodium hydroxide was added into the sample in order to reduce/increase the pH of PORE. After adding the acid/alkaline, final pH of PORE was determined.

Then, second physical treatment was about changing temperature of PORE. The range of temperature was 20-100^{o}C with 20^{o}C difference for each sample. The sample of PORE was heated to a desired temperature by Bunsen burner. After the heating process, samples were tested for COD and BOD values to determine the amount of organic matters that were present in the PORE.

2.3. Sample testing

2.3.1. COD testing

COD test was conducted to observe the effectiveness of Fenton reagent and the physical treatments in decomposing organic matters in PORE. The procedure of COD testing was referred to section 5.2 [3] - Closed reflux, titrimetric method for COD from the standard methods for the examination of water and wastewater. There were several reagents needed for this testing which are standard potassium dichromate digestion solution, sulphuric acid reagent, ferrion indicator solution, standard ferrous ammonium sulphate titrant (FAS). Thermoreactor Type ECO 8 instrument was used for COD testing. This COD testing required a blank sample for reference purposed. Blank sample needed distilled water as the sample of testing.

First step of the test was to wash the culture tube with sulphuric acid H2SO4 at 20% concentration, the aim was to prevent any contamination of the culture tube. Then, 2.5ml of sample in culture tube and potassium dichromate digestion solution was added. After that, 3.5ml of sulphuric acid reagent was added. Lastly, the testing tube was closed and gentle mixed by inverting the tube for several times. For this testing, sample heated to 150°C and left to reflux for two hours. Then, Ferroin indicator and FAS were added to the sample for titration after it cools to room temperature. The end point of titration was the colour changed of sample from blue-green to reddish brown.

There are some precautions needed to take in account during the testing. Face shield and glove was worn when handling the samples. The reason was there will be some gases releases during the heating process of the samples. Besides, the samples were heated to 150^{o}C which required glove to protect hands.

2.3.2. BOD testing

For BOD test, it was referred to section 5210B [4, 5], 5-Day BOD Test from Standard Methods for the Examination of Water and Wastewater. The duration of testing for BOD was five days for each sample. The model of instrument used for testing was Eutech Instrument (TN-100). Before conducting the test, the pH of sample of PORE was determined. Then, it was adjusted to the optimum range of pH 7.0-7.2 and sulphuric acid or sodium hydroxide can be used to adjust the pH of the sample.

Besides, optimum temperature, which samples needs to be adjusted to the temperature of 20 ± 3 °C [6]. After preparing the samples, BOD test was conducted. The samples were diluted for experimental testing. First, 1ml of diluted sample added into the bottle and dilution water will be added until the neck of bottle for further dilution. Next, aluminium foil was used to wrap the solution bottle for incubation purposed after gentle mixing. In this testing, blank solution which contains deionized water was used as reference of BOD test. The procedure to prepare blank solutions was identical as procedure to prepare BOD samples for PORE. Then, value of Dissolved Oxygen (DO) of sample was measured from day-0 to day-5.

2.4. Data analysis

For the data analysis, results from experiments and sample testing were collected for further analysis. Each parameter was repeated until concurrence value of results obtained. One of the main objectives of this work was to determine the effectiveness of Fenton reagent in decomposing organic matters. Hence, the data for initial and final reading of the treated sample such as COD and BOD were recorded. Then, all the results were tabulated in table forms in order to calculate the efficiency of Fenton reagent in decomposing organic matters.

3. Results and Discussion

Fenton Process is a type of Advanced Oxidation Process that utilizes iron (II) sulphate and hydrogen peroxide to produce free radicals. The free radicals that are produced during the Fenton process have high oxidizing potential to decompose organic compounds easily. It is an effective way to decompose organic compounds due to the unselectiveness of the free radicals. In this project, Fenton process was chosen to treat PORE and the effectiveness of Fenton reagent was evaluated. The effectiveness of Fenton reagent was determined by the COD and BOD testing.

3.1. Effect concentration of fenton reagent

Concentration of Fenton reagent was adjusted to treat PORE which is in the range of 0.1M to 0.5M. Besides, the ratio of iron (II) sulphate to hydrogen peroxide is 1:2 which was calculated in terms of mass [7]. Mass of hydrogen peroxide needed is higher compared to mass of iron (II) sulphate because hydrogen peroxide is the main component that produced free radicals. Besides, iron (II) sulphate acted as a catalyst in the Fenton process. Table 1 shows the results for Fenton process conducted to treat PORE and the COD and BOD results are expressed as mean values.

As can be seen in Table 1, the pH of each sample was set at 3 to ensure the Fenton process can be utilized fully in this treatment. Then, it shows that the COD value and BOD for each sample are reduced after the Fenton treatment. Form Table 1, 0.5M of Fenton reagent removed the highest amount of organic compounds in PORE. It reduced a total of 896 mg/L for COD and 865 mg/L for BOD levels. The reason is because the hydroxyl radicals produced from 0.5M Fenton reagent is the highest among the samples. Moreover, sample that used 0.1M of Fenton reagent reduced the least amount of COD and BOD level. From the data, it shows that sample reacted with 0.1M of Fenton reagent has only removed 448 mg/L of COD level and 446 mg/L of BOD level. Hence, difference of COD and BOD level between these two samples are 448 mg/L and 419 mg/L respectively.

Table 1. Results of PORE after treated with Fenton Reagent.

Parameters	Raw PORE	Concentration of Fenton Reagent (M)				
		0.1	0.2	0.3	0.4	0.5
pH	5.76	3.00	3.00	3.00	3.00	3.00
COD (mg/L)	1408	960	832	704	640	512
BOD (mg/L)	1359	913	794	680	577	494

During the Fenton process, the reagent that reacted with organic compounds in PORE would break down the organic compounds into carbon dioxide gas and water. Thus, COD and BOD level of samples after treatment reduces when concentration of Fenton reagent increases. Besides, there were bubbles formed during Fenton process. The release of gas during the process is due to the decomposition of organic compounds. Moreover, water and salts will be formed after the decomposition of organic compounds [8].

Since the formation of carbon dioxide, water and salts from the Fenton process, organic compounds content in PORE was reduced. It indicates that COD and BOD level of PORE was reduced. In addition, when concentration of Fenton reagent increases, the amount of gas released increases. This is because there were more available hydroxyl radicals that can attack the organic compounds readily. Hence, COD and BOD level of PORE would be reduced.

3.2. Effects of concentration of Iron (II) Sulphate and hydrogen peroxide

As a result, there are some deposition of salts after the Fenton process. The formation of salts caused by the high concentration of Fe^{2+} will produce Fe^{3+} (ferrous ions) that are less reactive towards hydroxyl peroxide. Moreover, there would be a recycling redox process between ferric ions and ferrous ions when it has overdosed. Hence, the effectiveness of Fenton reagent would be reduced. Besides, hydroxyl peroxide has to compete with ferrous ions in to become radical state and to decompose the organic matters. Thus concentration of iron (II) sulphate has to be selected carefully. In addition, when the concentration of iron is high, it will lead to salt deposition after the experiment. It causes additional cost for elimination of iron sludge [9]. Thus, concentration of iron is important and needed to perform further research to obtain an optimum concentration for effective of Fenton process. Besides, concentration of hydrogen peroxides is also a crucial factor. For instance, accessive hydroxyl radicals will form other structures with the organic compounds instead for decomposing it. Hence, concentration of hydrogen should not be overdosed as it will contribute to the ineffectiveness of decomposing organic compounds, decreasing the COD level.

3.3. Physical treatment

Besides Fenton process, physical treatment also conducted to study the characteristic of organic compounds in PORE. First, the organic compounds containing in PORE are mostly free fatty acids obtained after the degumming process from the refinery process of palm oil. There are four major fatty acids, which contains in crude palm oil which are palmitic acid, oleic acid, linoleic acid and stearic acid. The fatty acids are sensitive towards pH and temperature change because the bonds in fatty acid will be broken down and form a new product. Thus, this research is to study the influence of pH and temperature on the characteristic of fatty acid.

Furthermore, temperature treatment was applied for physical treatment in this research. The aim of temperature treatment was the same with pH treatment. Characteristic of organic compounds can be studied together by conducting these two treatments. After the treatment, COD and BOD level tests were conducted for the results of physical treatment. Table 2 and Table 3 show the results of the physical treatments.

Table 2. COD and BOD Results of pH Treatment.

pH	COD (mg/L)	Percentage of Reduction (%)	BOD (mg/L)	Percentage of Reduction (%)
3.0	576	25	532	23
5.0	672	12.5	641	7.2
5.76 (RAW)	768	-	691	-
7.0	480	37.5	450	34.9
9.0	512	33.3	483	30.1

For the pH treatment, 0.1M of sulphuric acid and sodium hydroxide were used to adjust the pH of the PORE. In this experiment, there was no Fenton reagent added inside the PORE because it was aimed to study the characteristic of PORE. From Table 2, it shows that pH does affect the composition of organic compounds. This is because the organic compounds will change structure when it at different pH. The pH of PORE increases, organic compounds would also increase the solubility and forms a layer of ‘soap’ [8]. Besides, changes of pH would cause organic compounds to change its structure into another type of organic compound [10]. Hence, the COD and BOD level of pH treatment has slight reduction which is less than 40% for overall pH treatment. Next, temperature treatment was conducted by heating up PORE with Bunsen burner. Table 3 shows the results of temperature treatment for this research.

From Table 3, it shows that percentage of reduction of organic compound in temperature treatment is less than 30%. This situation occurred due to the organic compounds contained in PORE will decompose into another stable compound. For instance, oleic acid will decompose and change its structure into stearic acid at high temperature. It is due to the oleic acid having weak stability in the double bond structure [11]. Besides, organic compounds could decompose into different type of organic compounds when the temperature is high [12]. Then, saturated organic compounds in the solution were increased. Consequently, composition of stearic acid was increased when composition of linoleic acid reduced. Hence, it shows that decomposition of linoleic acid led to the formation of another organic compound, which is stearic acid. As a result, COD and BOD level of PORE is reducing insignificantly because there is no reduction of organic compounds.

Table 3. COD and BOD results of Temperature Treatment.

Temperature (^{o}C)	COD (mg/L)	Percentage of Reduction (%)	BOD (mg/L)	Percentage of Reduction (%)
22 (RAW)	1248	-	1217	-
40	998	20	994	18.3
60	1064	14.7	986	19
80	928	25.6	936	23.1
100	1023	18	964	20.8

4. Conclusions

It was observed that at 0.5M of Fenton reagent the percentage of COD and BOD removal was 63.6% and 61.3% respectively. For 0.1M of Fenton reagent, the reduction of COD and BOD level was 31.8% and 32.8% respectively. Treatment with respect to pH, the highest reduction of COD and BOD was obtained at pH 7.0 and the percentage of reduction of COD and BOD level was 37.5% and 34.9% respectively. While for temperature treatment, the highest reduction of COD and BOD level obtained was at 80^{o}C and the reduction in COD and BOD level was 25.6% and 23.1% respectively. Hence, the physical treatment reduced lower percentage of COD and BOD because the organic compounds in PORE was not decomposed fully. Instead, some of the organic compounds changed to a more stable form. In a Nutshell, chemical treatment showed higher reduction of COD and BOD level because of organic compounds present in PORE was decomposed fully by the Fenton process.

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