

Oil Extraction From Oil Sludge and TPH Elimination of Solids/Water by Ozonation

Misri Gozan¹

¹ Industrial Bioprocess Engineering Research Group, Chemical Engineering Department, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok 16424, Indonesia

Correspondence: Misri Gozan, Industrial Bioprocess Engineering Research Group, Chemical Engineering Department, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok 16424, Indonesia. Tel: 62-21-786-3516. E-mail: mgozan@che.ui.ac.id

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Abstract

About 1.1 million barrels of oil sludge are generated yearly in Indonesia by many oil and refinery industrial activities. Oil is strongly bound with solid particles in the sludge. Oil in the sludge may range from benzene, phenols to polycyclic aromatic hydrocarbons which are classified as toxic, mutagenic and carcinogenic for human and pollute the environment. Oil extraction is a favorable option because of environmental and economical reasons. Oil sludge from an oil field in Sumatra, Indonesia was extracted at low temperature (40–70 °C) resulting in Total Petroleum Hydrocarbon (TPH) around 1–2%. After addition of 10,000 ppm REKLIN G04 surfactant, TPH extraction was improved to 9%. After decantation, effluent water containing \pm 15,000 ppm TPH was ozonated for 60 minutes resulting in TPH reduction to \pm 5 ppm. After ozonation, TPH of discharge solids was only 7–40 ppm. Fingerprint by gas chromatography showed removal of light fraction of oil after ozonation.

Keywords: oil sludge, ozonation, surfactant, extraction, TPH, fingerprint

1. Introduction

Large amounts of oil sludge are generated during the cleaning of tanks, oil storage, maintenance of related facilities and processing operations prior to the sale of crude oil into the sea terminal. Disposed oil sludge normally contains toxic substances such as aromatic hydrocarbons (benzene, toluene, ethyl benzene and xylene), poly-aromatic hydrocarbons (Swoboda-Colberg, 1995).

In general, oil sludge is a complex water-in-oil (W/O) emulsion, typically including 30–50% of oil or total petroleum hydrocarbon (TPH), 30–50% of water and 10–12% of solids by mass (Ramaswamy et al., 2007). Total Petroleum Hydrocarbons (Ayotamuno et al., 2007) without adequate treatment can be a pollutant to the environment, especially on the ground.

Landfill, soil bioremediation and incineration are among common disposal methods for oil sludge. Disposal to landfill requires a lot of land that must be adequately insulated to prevent leaching of toxic compounds in the soil. Bioremediation applications with fertilizer and bacteria can lead to the accumulation of pollutants such as toxic metals. Oil sludge burning has limitations such as transportation and the release of toxic gas that evaporates into the environment. Toxic heavy metals can not be removed during the combustion process and will accumulate as solid particulates in the combustion zone (Dominguez et al., 2005). The objective of the research described in this paper is to find a more clean yet efficient method for treating oil sludge using ozonation and surfactant system.

Ozone is one of the alternative technologies that focus on achieving oxidation through chemical reactions. Ozone is very reactive and can oxidize compounds such as persistent mineral hydrocarbons. Ozone is readily generated when oxygen is exposed to electrical discharge. O atom ($E^{\circ}_{O/H_2O} = 2.42$ V) can be generated via dissociation of O_2 and boosts the rate of production of OH. (Bruggeman et al., 2009; Malik et al., 2001). Furthermore, O atom can directly react with contaminants and also takes part in the reactions with O_2 resulting in the formation of O_3 , $E^{\circ}_{O_3/O_2} = 2.07:07$ V (Malik et al., 2001). Ozone as a strongly oxidizing allotropic form of oxygen reacts best when it can act as an electron transfer acceptor for the oxidation of metal ions, as an electrophile for the oxidation of phenol and other activated aromatics, and as a dipole addition reagent by addition to carbon-carbon multiple

bonds. Ozone is unstable and decomposes through a cyclic chain mechanism to produce hydroxyl radicals in neutral and basic solutions (Glaze, 1987). Moreover, with the presence of H_2O_2 in plasma system, ozone can react with HO_2^- giving OH^- (Bruggeman et al., 2009; Malik et al., 2001; Joshi & Thagard, 2013).

In general, advanced oxidation processes (AOP) have typically been used for the decomposition of organic material, color and disinfectants. For example, aromatic hydrocarbon oxidation completely unraveled with a longer time than the other aliphatic hydrocarbons such as dodecane (Kornmuller et al., 1997). An oil emulsion can be characterized as hydrocarbon compounds. For the processing of oil-water emulsion, ozonation has not been studied so far. However, application of advanced oxidation may be a viable option for the degradation of the oil-water emulsion (Suthi, 2001). Various studies using surfactant or biosurfactant showed significant improvement of oil extraction solely (Yan et al., 2012) or in combination with other treatment such as ultrasonic (Zhang et al., 2012). Surfactants are amphiphilic molecules comprise distinct hydrophobic and hydrophilic moieties – a polar or ionic group connected to a long hydrocarbon tail (linear, branched or containing aromatic rings). In aqueous solutions and at critical micelle concentration (CMC), surfactants begin to form aggregates that are in dynamic equilibrium with the monomers in the bulk aqueous solution. Many factors affecting effectiveness of surfactant (Yazdi, 2011).

2. Method

2.1 Materials

Oil sludge was obtained from an oil pit field in eastern Sumatera, Indonesia. The surfactant (REKLING04) was a rhamnolipid base and obtained from PT Rekayasa Lingkungan, Jakarta-Indonesia. Chemicals such as Toluene, KI, H_2SO_4 and $Na_2S_2O_3$ are from Merck.

2.2 Procedure

Experiments were conducted in lab scale to determine optimum conditions for oil extraction from oil sludge. Oil sludge, additional water (Sludge:water 1:1) and surfactant were put into 500 mL flasks. This mixture (500 mL) remained for settling 4 hours. Then, the lower stream was collected into a water-solid flask. The upper stream, together with surfactant, went to a second settling flask. In this tank, agitation and heating were applied for 120 minute, prior to sedimentation. Variation of temperature (40, 50, 60 and 70 °C) and surfactant concentration (0–15,000 ppm) were conducted and sampling were taken at minute 15, 30, 60 and 120. The lower stream of centrifuge comingled in the water-solid tank, while upper stream went to a centrifugation step for 10 minute. Part of centrifugal output was collected as recovered oil. The lower stream of centrifuge comingled in the water-solid flask. Water-solid stream was then ozonated for 1 hour. Sampling was carried out at minute 0, 15, 30, and 60. After settlement and filtration, water in the upper stream and solid were collected and analysed for TPH and Total Suspended Solids (TSS). The setup of oil extraction procedure is illustrated in Figure 1.

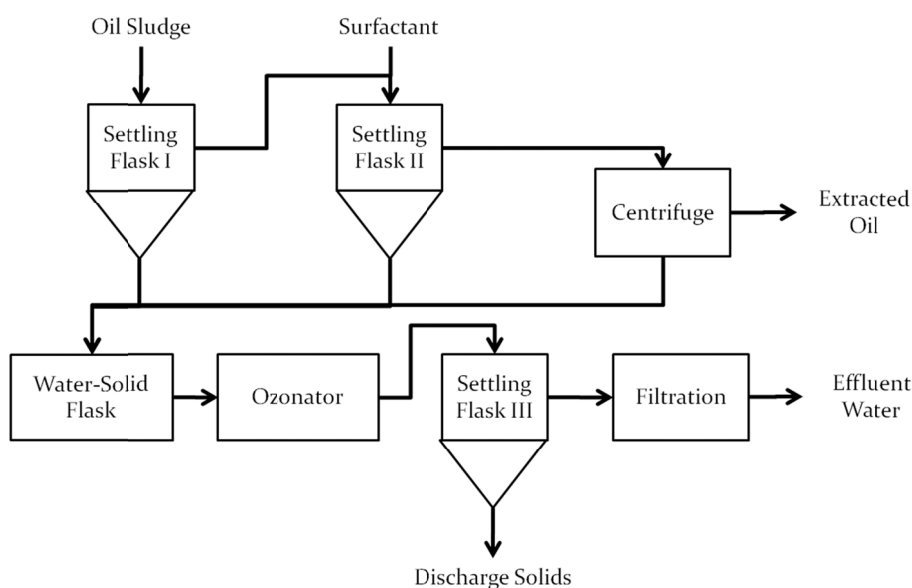


Figure 1. Process flow scheme of oil extraction by surfactant and ozonation

2.3 Analysis

Total Petroleum Hydrocarbon (TPH) analysis for discharged solids and effluent water were done by extraction with toluene, then filtration in filter paper with addition of sodium sulphate and measurement with Spectrophotometer HACH DR 3900. Fingerprint Analysis of Recovered Oil and Discharged Solids were conducted by Gas Chromatography-Flame Ionisation Detector 30 m \times 0.25 mm film thickness 0.25 μ m fused silica capillary columns, coated with methyl silicone (GC-FID, Shimadzu 14B series). Detector (FID) and injector temperatures were kept at 250 and 280 $^{\circ}$ C, respectively. The oven temperature was programmed from 60 to 280 $^{\circ}$ C at 4 $^{\circ}$ C/min with an initial hold time of 1 min and final hold time of 15 mins. Helium at a linear velocity of 2 mL/min was used as carrier gas.

Ozonator productivity testing was conducted by iodometric titration. Ozone is generated flowed into KI solution that oxidizes iodide ions into iodine solution. Iodine formed is then titrated with sodium thiosulfate solution so as to obtain the capacity of ozone produced.

3. Results

3.1 Heating

Oil sludge, water and surfactant were put into 500 mL flasks. Temperature, surfactant concentration and centrifugal speed were varied. Below centrifugal speed of 2700 rpm only less than 1% oil was recovered. Hence, for the rest of experiments, centrifugal speed of 2750 rpm was applied.

Oil sludge, water and surfactant were mixed in various temperature from 40 to 70 $^{\circ}$ C. Samples were taken at minute 15, 30, 60 and 120. After TPH analysis, oil recovered was depicted in Figure 2. In the beginning of mixing almost all samples showed around 1% of oil extraction. It was still in this percentage until 2 hours of experiments at sample with temperature 40 and 50 $^{\circ}$ C. At temperature 60 and 70 $^{\circ}$ C the oil extraction increased to around 2%. The peak oil extraction was achieved after 30 minute heating and mixing. The stable oil extraction of around 2% at temperature 60 $^{\circ}$ C lead to use these temperature as default for next experiments.

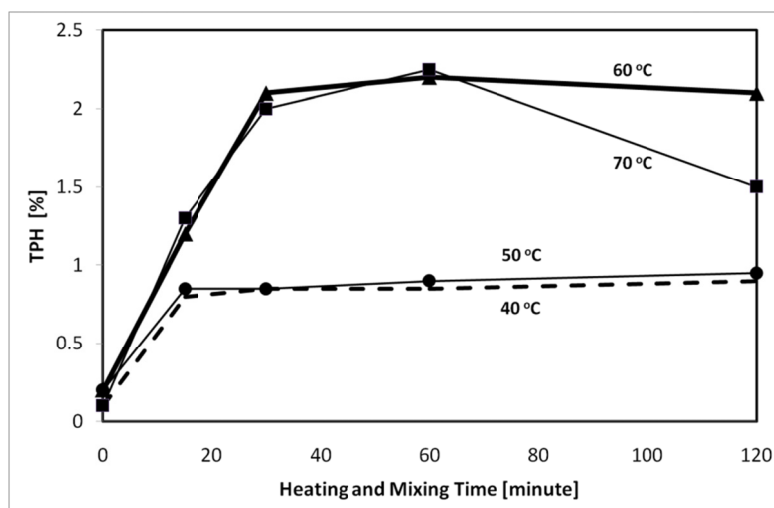


Figure 2. Effect of mixing temperature and heating time on oil extraction

3.2 Surfactant Concentration

Surfactant as deemulsifier was given to the mixture of oil sludge and water at concentration of 200; 500; 1,000; 10,000 and 15,000 ppm. Samples were taken at minute 15, 30, 60 and 120. For every sampling, 30 minute of settling time were applied before upper sample were then undergone TPH analysis. Oil recovered was depicted in Figure 3. There was surfactant added for control samples. No significant different between 10,000 and 15,000 ppm surfactant was observed after 60 minute. There is no more increase in oil extraction observed after 60 minute. The highest oil extraction was ca. 9%.

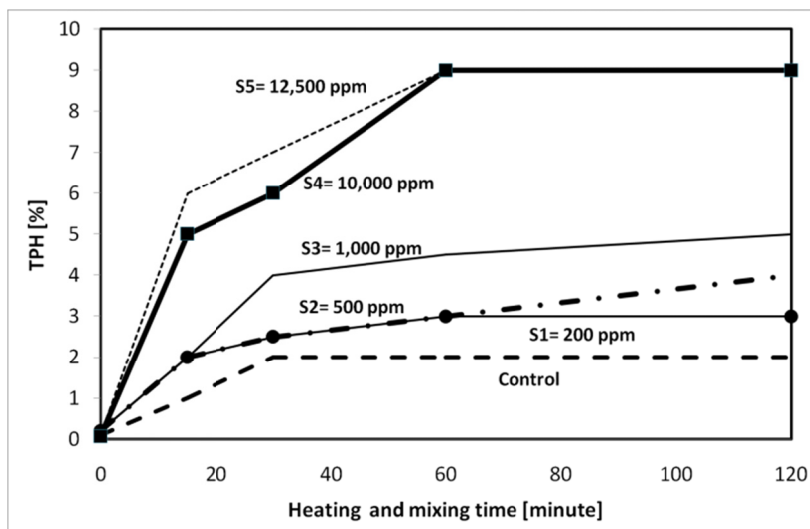


Figure 3. Surfactant effect on oil extraction. Heating was applied at 60 °C

3.3 Ozonation

Experiments on ozonation were aimed to reduce the TPH or oil content in the water effluent and discharge sands. After mixing with 10,000 ppm surfactant and heating at 60 °C, oil content in the upper part was decanted. Remaining water and solids were then stirred while 0.35 gram ozone/hour was applied. Samples were taken at minute 15, 30, 45 and 60 of ozonation. Figure 4 shows the TPH/oil content. It was clearly observed that after 45 minute the TPH content was almost not found.

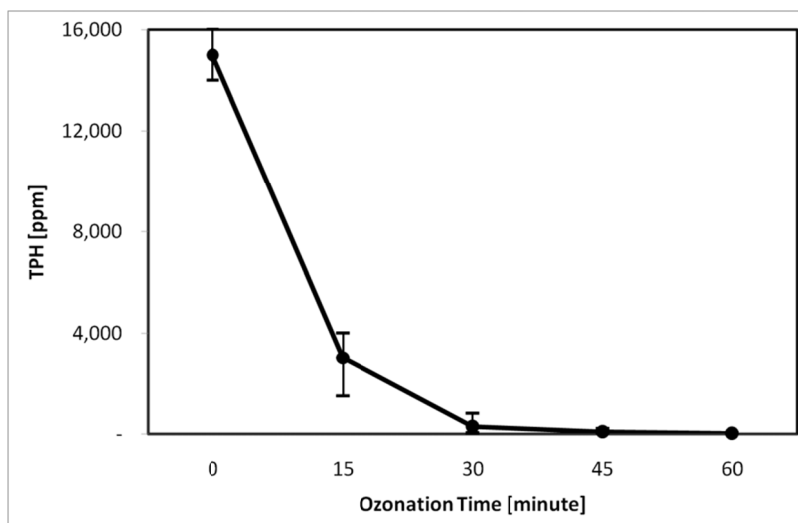


Figure 4. Oil content along with ozonation

To observe the effect of ozonation on hydrocarbon fraction, samples were analysed with GC as it is shown in Figure 5. The fraction of hydrocarbons was slightly changed. Before ozonation, fingerprint was predominated by lighter hydrocarbon. After 30 minute ozonation, heavier fractions were observed.

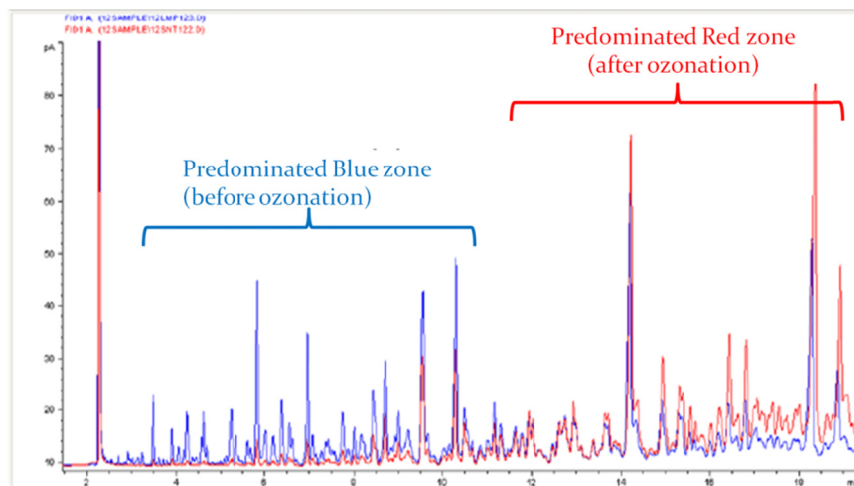


Figure 5. Oil finger print before and after ozonation

3.4 End Product Characterization

At the end, extracted oil, discharge solids and water effluent were characterized as depicted in Table 1.

Table 1. Characterization of end products: extracted oil, discharge solids and Effluent water

| | BSW¹ in Extracted Oil [%] | TPH in Discharge Solids [ppm] | TSS in Effluent Water [ppm] | Oil in Effluent Water [ppm] |
|-------------|--|---|---|---|
| Experiments | 0.5–0.9 | 7–40 | 10–57 | 4–5 |
| Regulation | na | Na | 200* | 25* |

¹ BSW = Basic Sediments and Water, ASTM D-96.

² KEP-42/MENLH/10/1996.

4. Discussions

4.1 Effect of Heating

This initial experiments were aimed to determine optimum conditions for separation of oil, water and sands. Heating the oil sludge mixture was expected to increase oil solubility, thus improve oil extraction. However, only slight increase, from 1 at temperature 40 °C to 2% TPH at the highest extraction. Increasing the temperature to 70 °C did not significantly increased the oil extraction. Instead, the oil extraction after 2 hours in the sample dropped to 1.5%. This might be due to evaporation of volatile hydrocarbons at slightly high temperature. The highest oil extraction was achieved at temperature 60 °C until 2 hour experiment.

4.2 Effect of Surfactant

Addition of surfactant and heating at 60 °C, evidently enhanced the oil extraction. The highest oil extraction was at TPH 9% by using 10,000 ppm REKLIN G04 surfactant. Oil extraction obviously also depends on the initial oil content of the sludge. The concentration of surfactant that should be given to the system would also affected by the oil content in the sludge. Addition of surfactant to 12,500 ppm did not show any significant effect. However, no more addition of surfactant was done to avoid reemulsion. CMC (Critical Micelle Concentration) is the critical threshold surfactant concentration in a solution. If the concentration is exceeded CMC it will lead to the formation of micelle reemulsion (Opawale & Burges, 1998). The surfactant used in this experiments was of Rhamnolipids, which are a class of glycolipid bio-surfactants usually produced by specific bacterial strains (Mulligan, 2005). The CMC of Rhamnolipids has been reported between 10 and 230 ppm (Nitschke et al., 2005). However, our results showed that REKLIN G04 surfactant gave the highest extraction far beyond this concentration range. Nevertheless, addition of rhamnolipids into oil sludgemay affect the adsorption energy of hydrocarbons with solid particles and lower the energy required for desorption (Zhang et al., 2012), and thus the

organic compounds could be easily removed at the ozone application.

4.3 Effect of Ozonation on Oil Content of Water Effluent and Discharge Solids

Immediately after 0.35 gram ozone/hour application the TPH content was reduced significantly. After 45 minute the TPH content was almost not found. Ozone attacked lighter hydrocarbon fractions easier than the heavier ones. GC fingerprints confirmed that lighter fractions (0–16 minute, or atom C1 to C12) in the left part of Figure 5 were strongly degraded. Then after 16 minute retention time (heavier hydrocarbons, C12 to C39) we could see no significant degradation. Formation of hydroxyl radicals is the vital oxidants that dominate the plasma oxidations in water application of ozone. Their reactions with organic compounds may be differentiated into three different mechanisms: abstraction of hydrogen atom; electrophilic addition to unsaturated bond and electron transfer. In the case of saturated aliphatic hydrocarbons or alcohols, hydrogen abstraction is primary for organic abatement with yielding H₂O and an organic radical (Jiang et al., 2014). As for olefins or aromatic hydrocarbons, C-centered radical with a hydroxyl group at the α-C atom can be formed with OH radical addition to unsaturated double carbon–carbon bonds of organic compound. Besides, reduction of hydroxyl radicals to hydroxide anions by an organic substrate is of particular interest in the cases where hydrogen abstraction or electrophilic addition reactions may be disfavored by multiple halogen substitution or steric hindrance (Lukes, 2001). Ozone oxidation strength decreases with the number of branch and length of hydrocarbons. Higher intensity of ozone dose might be needed to eliminate the heavier fraction of hydrocarbons.

4.4 Environmental Compliance of Effluent Water and Discharge Sands

The main goal of oil extraction from oil sludge is to have as much as possible oil, while it is desirable to have less than 1% BSW in the extracted oil. In the other hand, due to stringent environmental regulation, effluent water from oil waste treatment must contain less than 25 mg/L Oil and Grease, and less than 200 mg/L TSS (KEP-42/MENLH/10/1996). All those expectation and regulation have been fulfilled by the method of extraction and ozonation.

5. Conclusion

Oil extraction of oil sludge was studied in these lab experiments. Using no surfactant, only low percentage of TPH was observed. The extracted oil increased significantly after application of heating (60 °C) and surfactant REKLIN G04. Elimination of TPH was achieved by using ozone resulting in TPH reduction to almost zero in both effluent water and discharge solids. Fingerprint by gas chromatography showed removal of light fraction of oil after ozonation.

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