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Recovery of Petroleum Hydrocarbons from Oily Sludge Landfilled Soil

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ABSTRACT

Three types of experiments, based on the physical properties of oily sludge landfilled soil, were conducted to recover total petroleum hydrocarbons (TPH) from the soil. These experiments included gravity separation, solvent extraction using water, and air floatation. The oil portion was not easily separated from the wet (raw) soil because water molecules aggregate the soil particles, despite the fact that the soil was sandy. However, the drying and grinding processes destroyed the aggregates, causing the TPH recovery to increase to approximately 60% when air floatation was used. The drying process decreased the specific gravity of the soil sample, thereby enhancing the overall recovery of TPH from the soil. Although thermal desorption and/or incineration are common choices for heavily dumped sites, physical separation can recover the oil portion instead of simply removing it.

Key words : Oily sludge, Heavy oil, Physical separation, Specific gravity, Air floatation

1. Introduction

The petroleum oil refinery process produces a large amount of oily sludge with a high concentration of total petroleum hydrocarbons (TPHs). The sludge also contains viscous oily emulsions. The main resources of the oily sludge are the crude oil storage tank, the bottom of the storage tank in the petroleum refinery plant, and the transporting equipment (Elektorowicz and Habibi, 2005, Hu et al., 2013, Liu et al., 2009). The oily sludge, which is itself toxic and also contains toxic heavy metals generated by the refinement or improvement processes, has a negative effect on the soil and surrounding ecosystems (Al-Mutairi et al., 2008). The viscous sludge can block soil pore and decrease its permeability (Suleimanov et al., 2005). Additionally, the emission of volatile organic carbons or the release of toxic substances contaminates both soil and groundwater (Wake, 2005). Therefore, soil that is contaminated by oily sludge should be treated properly.

There are several techniques to remediate the oily sludge-contaminated soil; these include incineration, solidification/stabilization (S/S), chemical treatment (solvent extraction or oxidation treatment), and landfarming (Hu et al., 2013). Incineration requires too much energy to be economically feasible (Habibi, 2004, Sankaran et al., 1998) and can destroy the soil structure. S/S consumes relatively little energy and requires shorter processing times; therefore, its operation cost is relatively low. However, this technique has a limited effect on the remediation of organic contaminated soil. In particular, the S/S process cannot guarantee long-term stability of the soil, and changes in the surrounding environment can cause the release of contaminants (Gussoni et al., 2004, Karamalidis and Voudrias, 2007, Malviya and Chaudhary, 2006). Chemical oxidation can convert the contaminants into non-toxic compounds; however, the high concentration of long-chain compounds requires a large amount of oxidants, and the partial oxidation of the parent compounds generates a more toxic intermediate. The solvent extraction process can recover oil, which is useful from an economic standpoint, but can produce hazardous toxic solvents during the extraction process (Ferrarese et al., 2008, Hu et al., 2013). Landfarming, which is the most widely available method used to treat soil contaminated with oily sludge, is a simple process that is environmen-

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tally-friendly and cost-effective (Bhattacharyya and Shekdar, 2003, Bossert et al., 1984, Hejazi and Husain, 2004, Hu et al., 2013). However, the high concentration of oil used by this method can be toxic to microbes (Bhattacharyya and Shekdar, 2003, Hu et al., 2013). Most remediation techniques just focus on the removal of petroleum, not on the recovery of oil.

Alternatively, physical recovery processes can be cost-effective and safe because they do not require chemical agents, high temperatures, or high pressures (Lee et al., 2013). Gravity separation uses the difference in the specific gravity between water and soil coated with oil. Air floatation is achieved by generating tiny air bubbles, which adhere to the particles, causing the particles to float to the surface of the water. Solvent extraction using water without chemical agents can recover the oil portion from the soil.

Therefore, in this study, lab-scale experiments were carried out to evaluate the potential of the physical remediation of soil contaminated with large amount of oily sludge (without the use of chemical agents or high energy consumption) in point of petroleum recovery. Because the target site had very high concentration of TPH, therefore, if it is recovered, it can be reused for energy source. Gravity separation, solvent extraction with water, and air floatation (bubbling) tests were carried out to evaluate the effectiveness of the physical recovery techniques.

2. Materials and methods

2.1. Soil

Soil specimens were collected from an oily sludge dumping site in Balikpapan, Indonesia. The oily sludge at this site was dumped from a wax manufacturing plant without any appropriate treatment. The soil portion was 31 wt%, and the sludge in the soil was either coated on the soil particles or formed a solid aggregate comprised of the soil and sludge. The initial soil properties are shown in Table 1. The soil containing sludge was not mixed with water due to its strong hydrophobicity, where soil particles were coated by the oil or oily sludge; therefore, the surface of the soil is non-wettable. Solids larger than 2 mm were removed in order to investigate the size distribution of the soil particles in dried and wet conditions. To prepare the dried sample, the soil was dried in an oven at 70°C for 16 h. The main fraction (approximately 80%) is fine soil with a diameter < 0.149 mm in both the dried and wet conditions.

Table 1. Initial properties of soil with acidic oily sludge

Experimental Conditions	
Water contents of soil (%)	13.4
Water contents of sludge (%)	7.5
Specific weight of sludge	1.2
pH	7.2
EC (μS/cm)	674
TPH in soil (mg/kg)	22,295
TPH in fine soil (mg/kg)	24,387
TPH in sludge (mg/kg)	71,867
Weight of Soil : Sludge ratio (%)	31 : 69

2.2. Methods

2.2.1. Gravity separation

Gravity separation was carried out based on two basic properties of the oily sludge: the difference in the specific density between oil and tap water and the hydrophobicity of the oily sludge. The soil was sieved (using a 2-mm sieve) and dried at 70°C for 1~6 h. The water contents at each drying time were then evaluated. 30 g of soil and 300 mL of tap water were mixed in a 500 mL beaker (solid/liquid ratio: 1/10) with a mechanical stirrer, and the soil portion that was suspended on the tap water surface was collected. The collected soil was dried at 70°C for the analysis.

2.2.2. Solvent extraction

The specimens used to evaluate the extraction efficiency were dried at 70°C for 1~6 h; each sample contained a different water content. The raw specimen was used to compare with dried specimens. Both specimens were sieved with the 2-mm sieve, and then 5 g of soil and 50 mL of tap water were mixed in a 250 mL flask (S/L ratio is 1/10) for 30 min at 150 rpm. After the mixing, the soil was separated from the mixture by filtering. The separated soil was dried and the residual TPH concentration was analyzed according to the SM 5520F method, which is the standard analysis method in Indonesia. All experiments were carried out in duplicate.

Chemical extraction experiments were also conducted to compare the TPH recovery efficiency. The solid to liquid

(S/L) ratio is 1/10 too, and the mixture was shaken at 150 rpm for 30 min. Four solvents that are well-known TPH extractants (i.e., methanol, ethanol, butanol, and hexane) were used as extracting agents.

2.2.3. Air floatation

Particle size is an important factor for air flotation. To decrease the particle size, the specimen was dried at 70°C for 16 h, and the original and dried soils were grinded for 5, 10, 15, and 30 s with a grinder. 30 g of grinded soil was put in a 1 L beaker and mixed with 300 mL of tap water (S/L ratio: 1/10). The soil and water mixture was aerated with a blower. The air floatation process was continued until soil was no longer suspended. The suspended soils were skimmed off and the weight of the suspended soils was measured after drying at 70°C. The weight of the soil on the bottom of the beaker was also measured, and the remaining TPH concentration in the bottom soil was analyzed according to the SM 5520F method.

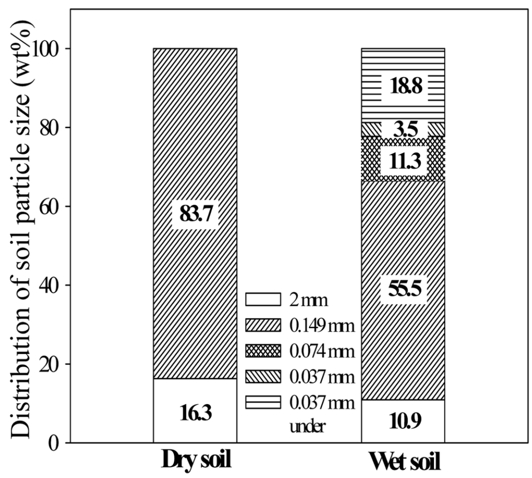

Fig. 1. Distribution of particle size. The dried soil was prepared by drying for 16 hours at 70°C.

3. Results and discussion

3.1. Gravity separation

The gravity separation results are summarized in Table 2. The water contents decreased from 11 to 4 wt% as the drying time increased from 1 to 6 h. The suspended soils increased from 1.4 to 23.5 wt%, which indicates that the drying process enhanced the recovery efficiency. Drying the soil decreased the specific gravity of the soil (due to the removal of water). This process also increased the hydrophobicity of the soil. This result suggests that gravity separation after drying can recover high concentrations of TPH from soil coated with oil by taking advantage of the difference in the specific gravity (without using any chemical agents). Karr et al. (1985) reported physical separation between toxic oily sludge and a water mixture using the physical properties of the oily sludge (Karr, 1985); in their process, the act of drying removed water, which has a relatively high specific gravity compared to the oil portion, leading to a decrease in the overall specific gravity (Khamehchiyan et al., 2007). The water content after drying decreased, the hydrophobic non-volatile portion of the remaining oil, and the dried sample became more hydrophobic, which can enhance the separation. In general, the concentration of TPH in fine soil is higher than it is in coarse soil (Na et al., 2007, Suleimanov et al., 2005, Urum et al., 2004); also in the case of our specimen, almost TPH existed in soil particles that were smaller than 0.149 mm. The TPH concentration in 2 mm and 0.149 mm soils, almost same both TPH concentration in Fig. 1. It means that the recovery of TPH is possible using physical separation, because high concentration of TPH is certain portion of soil.

3.2. Solvent extraction

The results of the tap water extraction test are shown in

Table 2. Efficiency of gravity separation using tap water according to drying time at 70°C

Drying time (h)	Settled soil (%)	Suspended soil (%)	Water contents (%)	Mass balance (%)
1	87.4	1.4	11.3	100.2
2	87.9	2.1	9.6	99.6
3	89.2	3.0	7.9	100.1
4	87.6	7.3	6.9	101.8
5	82.8	15.3	6.0	104.2
6	74.5	23.5	4.5	102.6

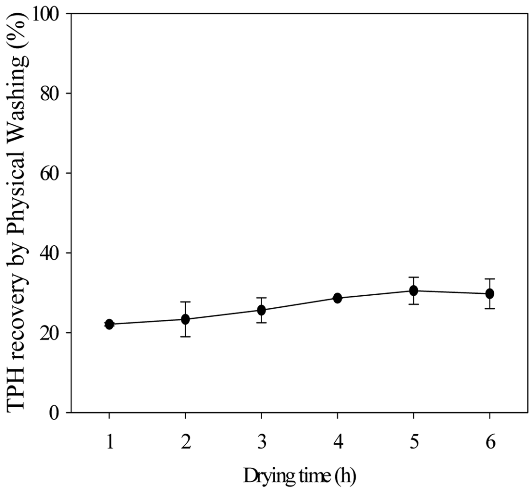

Fig. 2. Recovered total petroleum hydrocarbon concentration after physical washing using tap water according to drying time. Soil samples were dried for 1~6 hours at 70°C, and S/L ratio is 1/10.

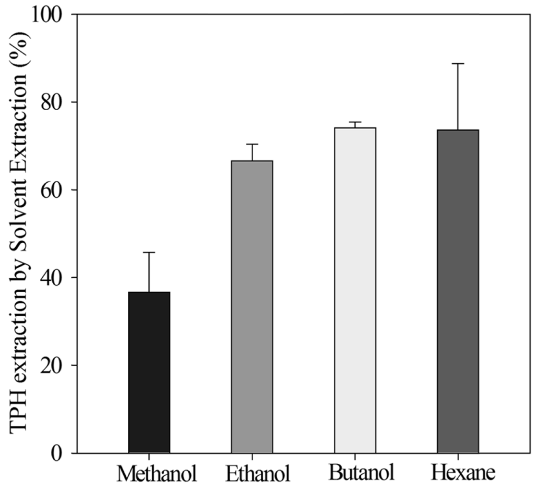

Fig. 3. Recovered total petroleum hydrocarbon concentration in solvent after solvent extraction. Soil to solvent ratio was 1/10.

Fig. 2. The average concentration of TPH after washing was 16,318 mg/kg and the tap water extraction of TPH was about 30%. Consequently, the tap water contents slightly influenced the solvent extraction of TPH, but this effect was not significant. The dry state solvent extraction is more efficient than wet state soil, however, the saturation in the recovery of TPH was observed with the increase in drying. Therefore, it is enough to dry the soil until some portion of water content.

The oil portions are hydrophobic; therefore, a hydrophobic solvent can enhance the extraction of TPH from the soil. The most efficient solvent was hexane, which can extract 73% of TPH from the soil (Fig. 3). Hexane is one of the most commonly used solvents for TPH extraction or recycling (Wu et al., 2011) because it is strongly hydrophobic. Additionally, alcohols with a longer hydrophobic chain extracted more TPH (Fig. 3). The organic solvent extraction recovered 1.5 times as much TPH compared to the tap water extraction. However, the toxicity of the residual organic solvents and the safety concerns associated with their remedial actions should be solved in order to improve the applicability of solvent extraction.

3.3. Air floatation

The oil portion was negligibly separated from raw soil, regardless of the grinding time (Fig. 4), while the amount of oil that was separated from the dried soil increased with

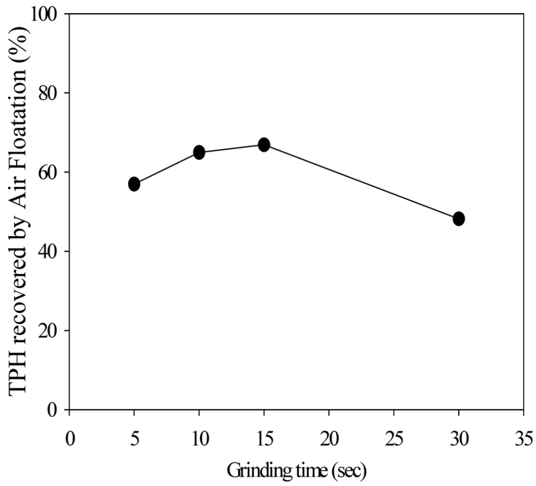

Fig. 4. Recovered total petroleum hydrocarbon concentration after the air floatation according to grinding time (5, 10, 15, 30 seconds) after drying for 16 h at 70°C.

longer grinding times. In the wet soil, water molecules acted to aggregate the soil particles. These aggregates had a higher specific gravity due to the fact that they consisted of a larger number of soil particles, which caused them to settle to the bottom of the reactor. Additionally, the presence of water in the soil decreased the overall hydrophobicity of the soil. Therefore, the wet soil with oily sludge was not separated. In the grinded raw soil, TPH was not recovered in Fig. 4. In the case of raw soil, not all of the soil particles were separated and recovered because some portion of the soil existed as a mixture in the middle of the reactor, therefore TPH and soil recovery efficiency is very low.

In the dried soil, the oily portion recovery was enhanced with increased grinding time; this trend is very similar with what was observed during gravity separation. Approximately 60% of the soil was separated by air flotation; this value represents a 2.6 times increase compared to what was obtained by gravity separation. Grinding decreased the particle size, and the particles with a lower specific gravity and a smaller size were well-suspended by air bubbling (Khamehchiyan et al., 2007). Additionally, the oily fine soil was suspended in tap water by the bubbling process because the hydrophobic aggregates of soil and oily sludge were broken by grinding, which increased the hydrophobicity surface of the oily fine soil flocs. The almost TPH is contained in fine soil (smaller than 0.149 mm), these make possibility of TPH recovery using physical treatment. Also, approximately 66% of TPH was recovered from the sample that was grinded for 15 s, which is more efficient compared to the solvent extraction test using water (approximately 30%). However, this recovery efficiency is still lower than what was obtained via organic solvent extraction. The grinding over 15 sec increased the temperature of soil and oily sludge, the sludge was slightly molten, and the molten oily sludge aggregated the small soil particle to larger one. That is the reason for the decrease in the recovery.

4. Conclusion

In this study, three physical separation processes were evaluated for the remediation and recovery of soil from an oily sludge landfill site. In the target sample, most total petroleum hydrocarbons (TPHs) exist in fine soil with a particle size less than 0.15 mm; therefore, these volume recovery can be achieved by suitable physical recovery methods. Air floatation can recover approximately 66% of TPH after drying and grinding. However, this TPH recovery efficiency is lower than what can be achieved via organic solvent extraction. Additionally, the residual TPH was still present at a concentration of 4,000 mg/kg, which should be lowered to below the suggested value. Although the remaining TPH concentration did not reach the target concentration, air floatation can reduce the volume of oily sludge-mixed soil by 25% by using physical separation which dry soil mixed with tap water, and also can recover TPH. Moreover, the soils must be returned to the original site for reuse, therefore, the solvent with toxicity including hexane or butanol are not recommended. Therefore, physical separation can reduce the cost and process times of the treatment process. It can also minimize the exposure of toxic solvents to the original site and reusing of crude oil sludge in sites. Moreover, physical processes are used as a pretreatment before bioremediation, thermal desorption, or solvent extraction, these processes can lower the concentration of the contaminants and volume of the contaminated soils. Also, the high concentration of TPH can recover using physical separation, and then could reduce the cost.

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References

Al-Mutairi, N., Bufarsan, A., and Al-Rukaibi, F., 2008, Ecorisk evaluation and treatability potential of soils contaminated with petroleum hydrocarbon-based fuels, *Chemosphere,* **74**(1), 142-148.

Bhattacharyya, J. and Shekdar, A., 2003, Treatment and disposal of refinery sludges: Indian scenario, *Waste Manage. Res.,* **21**(3), 249-261.

Bossert, I., Kachel, W.M., and Bartha, R., 1984, Fate of hydrocarbons during oily sludge disposal in Soil, *Appl. Environ. Microbiol.*, **47**(4), 763-767.

Elektorowicz, M. and Habibi, S., 2005, Sustainable waste management: Recovery of fuels from petroleum sludge, *Can. J. Civ. Eng.,* **32**(1), 164-169.

Ferrarese, E., Andreottola, G., and Oprea, I.A., 2008, Remediation of pah-contaminated sediments by chemical oxidation, *J. Hazard. Mater.,* **152**(1), 128-139.

Gussoni, M., Greco, F., Bonazzi, F., Vezzoli, A., Botta, D., Dotelli, G., Natali Sora, I., Pelosato, R., and Zetta, L., 2004, 1 h Nmr spin-spin relaxation and imaging in porous systems: An application to the morphological study of white portland cement during hydration in the presence of organics, *Magn. Res. Imaging,* **22**(6), 877-889.

Habibi, S., 2004, A New Electrokinetic Technology for Revitalization of Oily Sludge.

Hejazi, R.F. and Husain, T., 2004, Landfarm performance under arid conditions. 1. Conceptual Framework, *Environ. Sci. Technol.,* **38**(8), 2449-2456.

Hu, G., Li, J., and Zeng, G., 2013, Recent development in the treatment of oily sludge from petroleum industry: A review, *J. Hazard. Mater.,* **261**, 470-490.

Karamalidis, A.K. and Voudrias, E.A., 2007, Cement-based stabilization/solidification of oil refinery sludge: Leaching behavior of alkanes and pahs, *J. Hazard. Mater.,* **148**(1-2), 122-135.

Karr, L.A., 1985, Physical, Chemical, and Toxicological Properties of Navy Oily Sludge. Final Report, October 1983-September 1984.

Khamehchiyan, M., Hossein Charkhabi, A., and Tajik, M., 2007, Effects of crude oil contamination on geotechnical properties of clayey and sandy soils, *Eng. Geol.*, **89**(3-4), 220-229.

Lee, C.D., Yoo, J.C., Yang, J.S., K., J., and Baek, K., 2013, Extraction of total petroleum hydrocarbons from petroleum oil-contaminated sandy soil by soil washing, *J. Soil & Groundwater Env.*, **18**(7), 18-24.

Liu, J., Jiang, X., Zhou, L., Han, X., and Cui, Z., 2009, Pyrolysis treatment of oil sludge and model-free kinetics analysis, *J. Hazard. Mater.*, **161**(2-3), 1208-1215.

Malviya, R. and Chaudhary, R., 2006, Factors Affecting Hazardous Waste Solidification/Stabilization: A Review, *J. Hazard. Mater.,* **137**(1), 267-276.

Na, S., Park, Y., Hwang, A., Ha, J., Kim, Y., and Khim, J., 2007, Effect of ultrasound on surfactant-aided soil washing, *Jpn. J. Appl. Phys,* **46**(7S), 4775.

Sankaran, S., Pandey, S., and Sumathy, K., 1998, Experimental investigation on waste heat recovery by refinery oil sludge incineration using fluidised-bed technique, *J. Environ. Sci. Health, Part A*.

Suleimanov, R., Gabbasova, I., and Sitdikov, R., 2005, Changes in the Properties of Oily Gray Forest Soil During Biological Reclamation, *Biol. Bull.,* **32**(1), 93-99.

Urum, K., Pekdemir, T., and Copur, M., 2004, Surfactants treatment of crude oil contaminated soils, *J. Colloid Interface Sci.,* **276**(2), 456-464.

Wake, H., 2005, Oil refineries: A review of their ecological impacts on the aquatic environment, *Estuarine Coastal Shelf Sci.*, **62**(1-2), 131-140.

Wu, G., Li, X., Coulon, F., Li, H., Lian, J., and Sui, H., 2011, Recycling of solvent used in a solvent extraction of petroleum hydrocarbons contaminated soil, *J. Hazard. Mater.,* **186**(1), 533-539.