The impact of ultrasonic power and time for the removal of Total Petroleum Hydrocarbon from low permeability contaminated soils

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Abstract. Ultrasonic was widely studied in soil or sediment with several types of contaminants, both heavy metals and organic matter. Ultrasonic may enhance the desorption or leaching of contaminants from the soil and play an important role in the formation of radicals (•OH) that involved in the oxidation of hydrocarbon contaminants in the soil. This research has consisted of a tube reactor made from stainless steel in 21 cm × 21 cm × 18 cm of volume. According to previous research, ultrasonic power not only increases the desorption process or leaching contaminants from the soil but also plays an important role in the formation of radicals (•OH) which are oxidizers involved in the oxidation process. The main reactor has a dimension of 21 cm × 21 cm × 18 cm. The system used was a bath system, where the transducer was attached under the bath (reactor) so that it indirectly produces sonication. Contaminated soil has low permeability and obtained from conventional petroleum mining in Grobogan Regency, Central Java. Initial concentrations of TPH was 334100 mg / kg. Based on the optimum time experiment, it can be seen that the TPH removal was significant at the initial 15 minutes of sonication. At optimum conditions, TPH efficiency removal at 160 watts of power, 48 kHz of frequency, 1: 9 (gr/ml) of soil / liquid ratio was 61.03%.

1. Introduction
Petroleum hydrocarbons contaminated soil have serious problems with the environment, soil ecology, human health, and requires effective soil remediation technology [1]. The contaminants are processed and reduced to the concentration of Total Petroleum Hydrocarbons (TPH) having a final value requirement of less than 1% in accordance with the Minister of Environment Decree Number 128 of 2003 concerning Biological Procedures and Technical Requirements for Petroleum Waste and Contaminated Soil. Alternative techniques for processing contaminated soil are physical and chemical remediation, one of them is soil washing. However, one of the disadvantages of this technology is the use of surfactants which have an impact on toxicity, environmental balance, and biodegradability [1]. Therefore, the other alternative technology is ultrasonic irradiation. Ultrasonic has been shown to be an effective method for removing adsorbed material in soil particles, separating soil from water in high suspension concentrations, decreasing the stability of the
water/oil emulsion [1]. The decay of cavitation bubbles and shock waves (shockwaves) by ultrasonic is known to break down aggregate soil particles and support the release of contaminants that adhere to the soil [1,2]. The success rate of this ultrasonic method can be influenced by several factors such as soil type, soil liquid ratio, temperature, wave frequency, and energy/power used [3].

Soil clay (clay) has a low permeability value, making it difficult to treat. The desorption of chemical compounds on finer soil such as clay is more difficult than with coarser soil particles [4]. Song also stated that the desorption of contaminants in clay or dust type soil takes longer than the soil with a larger fraction such as sand. However, according to some studies, ultrasonic has been proven to be able to process the soil with a fine texture if the required ultrasonic energy is available. Some studies reveal the ultrasonic effects on contaminated soil. However, only a few studies have discussed the comparison of the effects of ultrasonic time and power on desorption of TPH contaminant in low-probability soil. In this study, experiment was carried out by comparing the efficiency of contaminant reduction in several treatments. They are ultrasonic irradiation of various power and ultrasonic time.

2. Methods

2.1 Soil Preparation

Contaminated soil sampling using a disturbed grab sampling method with a depth of 0-15 cm. Samples of petroleum contaminated soil come from around the petroleum mining site that has been contaminated for decades (aged-oil contaminated soil) located in Grobogan Regency with location coordinates that are 7°11'36,28 '' S and 111°11'42,26 '' E. Then, contaminated soil was prepared before the experiment. Soil preparation begins with silencing the soil for several days (7-14 days) and contacting it with open air without being exposed to direct sunlight so that air-dried soil was obtained. After drying, the soil was filtered on a sieve measuring 2 mm / 10 mesh. The soil that does not pass through the sieve was crushed again using the pestle and filtered again. After that, the soil was homogenized by the cone & quartering technique.

2.2 Ultrasonic Reactor

The main reactor has a dimension of 21 cm × 21 cm × 18 cm. In the ultrasonic bath system, the ultrasonic transducer is attached under the bath (reactor) so that it indirectly produces sonication. Bath itself can be used as a reaction container to receive ultrasonic waves. Figure 1 shows the scheme of an ultrasonic reactor.
2.3 Soil Characteristics
The quality of physical and chemical characteristics such as water content, pH, a conductivity of several other parameters, are the factors that significantly reduce the petroleum contaminants [6,7]. The physical parameters really affect the effectivity of the ultrasonic remediation. The soil coefficient of permeability value is low. The petroleum contaminated soil used in this study is categorized as sandy silt loam. The physical and chemical characteristics of the soil can be seen in Table 1.

| Parameter       | Values       |
|-----------------|--------------|
| Soil Properties |              |
| Gravel          | 5.2 %        |
| Sand            | 15.81 %      |
| Silt            | 45.46 %      |
| Clay            | 33.53 %      |
| Permeability    | $2.81 \times 10^{-5}$ cm/s |
| pH              | 9.30         |
| N Total         | 0.130 %      |
| C Organic       | 4.64 %       |
| Oil & grease    | 8.77 %       |
| TPH             | 3.41 %       |

The surface area of soil particles is a significant factor that affects the physical and chemical kinetics on the processing of the contaminated soil. Along with the increased surface area, the adsorption capacity and biological activity. The sand and silt particles have a relatively smaller surface area compared to clay fraction. The silt fraction, or commonly referred to dust or loam, is a fine fraction with a size range of 0.05-0.02 mm. The clay fraction is the finest size fraction with a size less than 0.002 mm. Soil texture is one of the important parameters in the soil washing process because the larger the size of the soil particles the easier it is to be drained by water [8]. Compared to sand, the clay structure tends to be more complex and a lot of layers and micropores between soil matrices, which means there are more contaminants that adsorbed and trapped [4].

2.4 Ultrasonic Process and Analysis
The sample of the contaminated soil that has been dried and filtered is mixed with a washing solution (deionized water) with soil ratio: 1: 3 and 1: 12 of liquid for both mechanical shaking only and mechanical shaking + ultrasonic irradiation. After the suspension looks homogeneous, a reactor was placed in ultrasonic with the desired frequency and power for a certain period of time. The ultrasonic test was done by three times of replications in each combination. The sample will be stirred with a stirrer for 10 minutes with a rotation speed of 113 rpm, and samples are collected in every 1 minute for TPH and oil & grease measurements on the soil and water, then a TPH elimination plot was made per time unit of the process. After the soil samples have reached the equilibrium conditions, the liquid phase is separated for 20 minutes by centrifugation at 3000 rpm, then filtered (filtration) to separate the soil (solids) and liquid. After that, the soil was drying by air dried for ±3 days. Then analyzed by liquid-liquid extraction to determine the balanced concentration.

2.5 Hydrocarbon Compounds Analysis with GC-MS
The separation of soil with liquid is done by filtration, and then extracted and analyzed by TPH compounds on the soil with GC-MS. The principle of GC is to separate organic compounds by passing the gas flow through the stationary phase. The mooring time (retention time) on the GC shows the identity of the compound that can give qualitative information, which is the presence or absence of certain compounds and qualitatively can show the number of each compound in a mixture. The GC device usage results in a separation of compounds in hydrocarbon fraction so that degradation can be
detected by looking at the growth or loss of various peaks which are the identities of hydrocarbon compounds. The injector temperature is 250 °C, detector temperature is 300° C and column temperature is 40°/ 2 minutes, 10° C / minute, 200° C/ 1 minute, and 290 °C/ 10 minutes.

3. Results and Discussion

3.1 Effects of ultrasonic time on TPH

Based on the optimum time experiment, it can be seen that the degradation of TPH was significant at the initial 15 minutes of sonication. As the ultrasonic process continued, more oil was transferred to the solvent (deionized water) until they reached the maximum release capacity. Referring to these results, it is likely that at that time a desorption and re-adsorption process of contaminants into soil particles has occurred, or it can be referred to reaching the equilibrium phase. However, it still needed to be proven by calculating the desorption capacity through desorption isotherm. The balance between oil re-adsorption and the injection of oil into the solution/emulsion occurred very quickly [9].

The initial TPH value was 32437 mg/kg then degraded to 22296 mg/kg at 13 minutes. This means that there was 45.48 % of degradation. The degradation of TPH can be seen in Figure 2. The test results have shown that time gives a positive impact on the desorption of petroleum hydrocarbon, and it is confirmed by the Wilcoxon signed-rank test.

![Figure 2. Graphic of the degradation of TPH (70 minutes)](image)

Based on statistical testing with the Wilcoxon signed-rank test, the obtained P value was 0.000061 or can be written as p value < 0.05. This means that H_0 is rejected by the difference in the average TPH value before the ultrasonic process and after the ultrasonic process. Based on the optimum time test results, the optimum time for ultrasonic remediation used in the next test in this study is 10-15 minutes. This result was also supported by Li et al., (2013). The research by the optimum time for the ultrasonic remediation was 15 minutes, where the desorption process was able to reach the equilibrium point at that time.

The reduction of TPH increases at 1 to 5 minutes [10]. However, the ultrasonic remediation at more than 5 minutes, no significant change occurred, and finally the reduction of TPH degraded at 8 minutes. So, it can be concluded that the processed sample of soil with longer ultrasonic, does not provide a greater reduction of the contaminants compared to the shorter processed samples. During processing (sonication), oil was desorbed into the slurry phase and resulting in a mixture of solution/emulsion between water and oil [11]. The efficiency of the ultrasonic period is important to do because it will affect the economic factor (costs required) related to the energy used.
3.2 Effect of power and intensity on TPH removal

Power setting in ultrasonic irradiation can regulate how strong the vibration occurs, so the process occurred in the form of how strong the collisions occurred between particles. Power is closely related to ultrasonic intensity. Intensity is directly related to ultrasonic wave amplitude. In general, increased intensity can increase the sonochemical effect in a liquid medium, therefore, the greater the power used, then the cavitation effect will become better [11]. The intensity produced by the transducer is equal to the electrical power divided by the transducer surface area. That is, the higher the power, the higher the intensity [12]. Ultrasonic intensity values based on power values can be seen in Table 2.

| No | Power (watt) | Intensity (Watt/cm²) |
|----|-------------|---------------------|
| 1  | 70          | 0.79                |
| 2  | 100         | 1.13                |
| 3  | 130         | 1.47                |
| 4  | 160         | 1.81                |

Degradation of TPH concentration based on the time during the occurred irradiation process can be seen in Figure 3.

According to Figure 3, it can be seen that the concentration of TPH undergoes degradation during the ultrasonic irradiation process that occurred up to a point. The removal efficiency at the power of 70 watts, 100 watts, 130 watts, and 160 watts are respectively 30.80%, 33.44%, 44.53%, and 61.03%. Power and intensity are closely related to the desorption process and degradation of the contaminants in the slurry phase when ultrasonic is applied [1,10].

If the frequency used is in a high range, the intensity needed will also be greater. This means that the greater the power, then the possibility in contaminant removal will also be greater [11]. Based on the results of this study, 70 watts of power was actually sufficient as a condition to produce cavitation effects in a liquid medium for 48 kHz of frequency.

ANOVA test results for power variables towards TPH contaminant, obtained calculated F value of 4.319, while the F table value is 2.75. Therefore, the calculated F > F table, then H₀ is rejected and H₁ is accepted. Then it can be concluded that the difference in power gives a significant effect on the degradation of TPH.

The degradation in the value of the contaminant can be explained by the main mechanism that plays the most role, i.e. desorption. The results indicate that desorption is an important mechanism that
has the potential to reduce TPH from the soil. The available energy must be sufficiently large and strong enough so that cavitation can occur, then the adsorbed contaminants can be desorbed into the solution. The size of soil particles affects the energy needed. Because sand has a smaller surface area, the energy needed is also lower, and on the opposite, loam or clay type soil, has a larger surface area, and so the energy needed to remove contaminant is greater. Ultrasonic processing can be successfully applied to treat coarse as well as fine soil when sufficient energy is available. However, fine soil has a low hydraulic conductivity which is like to inhibit the transfer and desorption of contaminant values [13]. Figure 4 shows the removal efficiency of oil & grease and TPH at various powers during certain times.

Based on Figure 4 it can be seen that the highest contaminant removal happens at the ultrasonic process with 160 watts of power. When viewed, there are differences in the equilibrium time between the four powers. Where the lowest power (70 watts) has an equilibrium time that tends to be longer than ultrasonic irradiation at other power. The minimum power needed for organic decontamination processes including hydrocarbon petroleum is 100-600 watts [14]. As previously explained, power will affect intensity. In order to occur a reaction that is cavitation formed, the intensity is 0.35 watts/cm². This means that even with 70 watts of power, cavitation can occur. Removing oil contaminants occur at 100 watts of power usage [3]. In this study, it means that the best intensity used so that the remediation process runs optimally is 1.81 watts/cm².

3.3 Mixing Effect
Mixing can help the dissolution process because it is capable to distribute soil to all sections of the solution so that larger the area of contact between the solid and liquid phase. Mass transfer and oxidation of hydrocarbon compounds only occurred in the solution or slurry phase in order to achieve the dispersion process of the contaminant into the solvent. The dispersion effect is investigated by comparing the remediation process with mechanical stirring alone to ultrasonic process that equipped with mechanical stirring. Ultrasonic waves are able to produce a droplet with a very small size, and that creates emulsion between two phases [15]. After the sonication process, the two phases can be separated easily, due to its density differences. Figure 5 shows the oil & grease concentration and TPH in two different processes (mechanical stirring alone and ultrasonic process equipped with mechanical stirring).
Figure 5. The differences in the degradation of TPH concentration between two processes (us+ mixing and mixing only)

An experiment to prove the effect of stirring was done in one hour with the mixing speed 113 rpm both with mechanical mixing alone and mechanical mixing equipped with ultrasonic. Based on Figure 5, it can be seen that the removal of the contaminant’s concentration occurred in the ultrasonic process equipped with mechanical mixing where the removal is 50.81% for oil & grease and 28.12% for TPH. Meanwhile, the percentage of contaminants in the mechanical stirring only process is 0.87% for oil & grease and 0.96% for TPH. TPH removal percentage on ultrasonic + mechanical stirring tends to be small. This is because the contaminants removal efficiency was occurred at 10-15 minutes sonication, as a result after one hour of sonication, the degradation of contaminants concentrations is not significant and even tends to increase due to the re-adsorption process.

The mechanical mixing process can create better turbulence and mixes, thus contributes to making physical contact between the contaminated soil particles and washing solution [16]. As a result, the pollutants that bind weakly with soil particles, are able to be released from the soil surface. Meanwhile, the pollutants that bind strongly with soil pore matrices will be more difficult to desorb if using mechanical mixing alone. Ultrasonic/mechanical mixing produces higher removal efficiency due to the desorption of both macroscale and microscale which not only remove the contaminants from the soil surface but also the pollutants that trapped in the pores of soil particles [17]. This argument is also supported by the research conducted by [16] whose results have shown that the removal efficiency of heavy metals with HCl washing solution was higher in ultrasonic/mechanical mixing processes compared to mechanical mixing alone or ultrasonic alone.

3.4 Analysis of the contaminants with GC MS

GCMS test (gas chromatography- mass spectrophotometry) is used to find out the organic compounds contained in the soil sample. GCMS test is used to confirm the occurred breakups of the organic compounds through the ultrasonic remediation process. Another goal is to find out the characteristics of the contaminants contained in the soil sample. Figure 6 (a) and (b) show hydrocarbon compounds before and after ultrasonic remediation.
The compounds in contaminated soil are classified as aged petroleum hydrocarbon because the soil has been contaminated for a long range of time. Most of the compounds detected are alkane compounds or also known as a saturated hydrocarbon. Based on the literature, ultrasonic cavitation has the potential of increasing the destruction and degradation of compounds, which when viewed from the carbon chains, are partially stable. Changes of hydrocarbon compounds can be seen in Figure 6. Compared to the initial GC MS graphs, there is a slight movement of peak up to retention time that reaches 60 minutes. The results of the degradation of petroleum by ultrasonic might strengthen the degradation of some chains of organic compounds into a relatively simple form and tends to be volatile. GC MS profile before and after ultrasonic remediation changes with a peak that tends to decrease in the final GC results. TPH component undergoes a change due to the pyrolysis of long-chain organic molecules, turned into intermediate compounds that have a lighter molecular weight [18]. In his research, it was seen that all peaks of n-alkanes degraded. This indicates that ultrasonic processing is not selective in degrading TPH.

In this study, after the remediation process, short-chain and volatile compounds like C$_2$, C$_8$, C$_{10}$ were found, which were not previously found at the initial condition before remediation. Most of the compounds were still aliphatic, but the number of aromatic compounds were increasing. It is likely that the degraded aliphatic compounds that had enough energy to achieve stability formed the aromatic groups.

Some of the organic compounds (long-chain hydrocarbon) that destructed can occur due to the production of hydroxyl radicals [9]. This usually occurs at 200-400 kHz of middle frequency.
Whereas in this study, the used frequency was low at 48 kHz. Hence, the destruction change of hydrocarbon compounds is not significant. However, the energy released from ultrasonic cavitation under the condition of 48 kHz of frequency is sufficient to achieve affinity of hydrocarbon molecules and increasing the desorption.

4. Conclusion
The results of this study and statistical analysis showed that the time and power of ultrasonic irradiation had a significant effect on the contaminants removal (oil & grease and TPH) in petroleum-contaminated clay. According to the optimum time test, the degradation of contaminants occurred at the initial 15 minutes while the rest is relatively stable and even had an escalation that can be happened due to the re-adsorption process. The highest contaminations removal occurred at 160 watts of power with an intensity of 1.89 watts/cm² with a removal efficiency of 63.15%

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