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Remediation of Petroleum Hydrocarbon-contaminated Soil Slurry by FentonOxidation

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***Abstract*—**Theobjective of this study was to evaluate the optimal treatment condition of Fenton oxidation process to removal contaminant in soil slurry contaminated by petroleum hydrocarbons. This research studied somefactors that affect the removal efficiency of petroleum hydrocarbons in soil slurry including molar ratio of hydrogen peroxide (H_2O_2) to ferrous ion(Fe^{2+}), pH condition and reaction time.The resultsdemonstrated that the optimum condition was that the molar ratio of H_2O_2:Fe^{3+} was 200:1,the pHwas 4.0and the rate of reaction was increasing rapidly from starting point to 7^{th} hour and destruction kinetic rate (k) was 0.24 h^{-1}. Approximately 96% of petroleum hydrocarbon was observed(initialtotal petroleum hydrocarbon (TPH) concentration = 70±7gkg^{-1})

***Keywords*—**Contaminated soil, Fenton oxidation, Petroleum hydrocarbon, Remediation.

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I. Introduction

SOIL contamination by petroleum hydrocarbons, a very important environmental problem, has been attracting considerable public attention over the past decades [1]. Petroleum hydrocarbonsare a mixture of chemical substances caused during humanactivities by using petroleum products in industrial and agriculturalproduction. Although petroleum is one of thedominant energy sources to maintain the economic and socialdevelopment of a country, petroleum has become one of the most important types of organic pollutants. There are increasingly wide pollution of sources including leakage of fuel by transportation and traffic accidents, land disposal of residual lubricants, inappropriate storage of oils, and discharge or leakage of organic solvents at industrial sites, particularly oil exploitation and abstraction[2],[3].Total petroleum hydrocarbons (TPHs) are one of the most common groups of persistent organic contaminants in the environment and are known to be toxic tomany living organisms [4]. Thepresence of petroleum hydrocarbons in soils is not only an adverse factor for human health,but also a negative impetus for plant growth and development[5],[6].

With the expanding of the soil contaminated by petroleumhydrocarbons, how to remedy, treat and control this contamination efficiently is becoming a technical problemin the environmental protection.

Chemical methods have been shown to oxidize and mineralize organics. Chemical oxidation may not only destroy target compounds,but also reduce toxicity associated with formulation ingredientsand active agents. It can also be an effective pretreatmentstep for enhancing bioremediation by reducing overall toxicity toindigenous microorganisms, allowing them to participate in the remediation process [7].

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The use of Fenton's reagent(Fe^{2+} + H_2O_2) to oxidize various compounds is one of the most studied chemical oxidation processes. It is recognized asone of the most powerful oxidizing reactions available and canbe used to destroy a wide variety of organic compoundsin aqueous waste, soils, and ground water [8]. In this regard, the objective of this study was to evaluate the optimal treatment condition of Fenton-like oxidation process to remove contaminant in soil contaminated by petroleum hydrocarbons. This research studied some factors that affect the removal efficiency of petroleum hydrocarbons including molar ratio of hydrogen peroxide (H_2O_2) to ferric iron(Fe^{3+}), pH condition and reaction time.

II. Materials and Methods

A. Contaminated Soil

The clean soil was from the adjacent areas of agricultural areas in AmphorMeung (Trad, Thailand), from which gravels and large organic scraps were removed.The soil was air-dried and ground to pass through a 2mm laboratory test sieve. Then this soil was mixed and homogenized with benzene 95 fuel, which was obtained fromserviced gas station (Bangkok, Thailand) in the ratio of soil to benzene 95 at 1:1.Contaminated soil was incubated for a week. The initial concentration of total petroleum hydrocarbon (TPH) in soil was investigated. Contaminated soil (10 g) was extracted by toluene (20ml). The concentration of TPH was determined by UV/VIS spectrophotometer (UV-Spectrophotometer model SHIMADZU UV-1700) at 400 nm. Soil slurry was prepared by using 1:2 (w/v) ratio of contaminated soil to DI water.

TABLE I
Characteristics of Soil Samples

Characteristic	Concentration
Sand (%)	46
Silt (%)	20
Clay (%)	34
Organic matter (%)	3.26
Water content (%)	16
pH	4.6
CEC (cmol kg^{-1})	5.5
Nitrogen (mg kg^{-1})	1630
Phosphorous (mg kg^{-1})	32
Potassium (mg kg^{-1})	52

B. Effects of the molar ratio of H_2O_2:Fe^{3+} test

Batch experiments were performed to obtain the optimal molar ratio of hydrogen peroxide to ferric iron. In view of the high contamination level, it cannot be expected that the Fenton oxidation treatment might be completed with various dose of hydrogen peroxide. Hence this study was applied a relatively small fixed dose offerric ironwhereas changing the dose of hydrogen peroxide to obtained the optimal ratio of hydrogen peroxide to iron [8].In the experiment, each tested was performed in triplicate.

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The molar ratio of H_2O_2:Fe^{3+} were tested in 40 ml centrifugal tubes. Briefly, a mass of 10g of contaminated soil was weighed into a tube and then 20 mL of distilled water and 0.1 mL of the desired amount of the catalyst1.765, 0.441 and 0.221 M ($Fe_2(SO_4)_3$) were added. The molar ratio of H_2O_2:F^{2+} was ranged from 50:1 to 400:1. The test tubes were shaken at 150 rpm for 24 h. At 24 h, centrifuge tubes were removed and centrifuged at 4000 rpm. Then, the supernatant liquid was removed and soil was extracted by toluene. The residual TPH concentration was investigated.

C. Effects of pHs

Ten grams of contaminated soil was added by 20 ml of DI water in 40 ml centrifugal tube. The various pH was adjusted to 6 different conditions (pH 2, 3, 4, 5, 6 and 7) with 0.1 M HNO_3 / 0.1 MNaOH solution and performed with the molar ratio of H_2O_2:Fe^{3+} was 200:1.The test tubes were shaken at 150 rpm for 24 h. At 24 h, centrifuge tubes were removed and centrifuged at 4000 rpm. Then, the supernatant liquid was removed and soil was extracted by toluene. The residual TPH concentration was investigated.

D. Rate of reaction test

The subsequent experiment was studied about the rate of reaction (*k*) based on the optimum condition found above (The molar ratio of H_2O_2:F^{2+} = 200:1 and pH = 4). After adding soil and Fenton reagent in centrifugal tubes, the tubes were shaken at 150 rpm for 12 h. At preselected time, centrifuge tubes were removed and centrifuged at 4000 rpm. Then, the supernatant liquid was removed and soil was extracted by toluene. The residual TPH concentration was investigated.

III. Results and Discussion

A. Contaminated soil characteristic

The soil texture and major physico-chemical characteristics of soil were showed in table 1. The soil was a sandy clay loam type, with 46, 20 and 34 % of sand, silt and clay,respectively.The total petroleum hydrocarbon (TPH), which was observed, was 70±7g kg^{-1}.

B. Effect of iron levels on contaminant removal

The ratio of hydrogen peroxide to ferrous ions is known to be an important determinant in the efficacy of Fenton oxidation. The removal of TPH in the molar ratioof H_2O_2:Fe^{3+} test is presented in Fig. 1. The bestcondition of the TPH removal efficiency was obtained at the molar ratio of H_2O_2:Fe^{3+} was 200:1(removal efficiency of 91.07 %) and the lowest level of removal was recorded when the ratio of H_2O_2:Fe^{3+} was 400:1(removal efficiency of 71.76%).

This same trend was observed by Lu *et al.* (2010)[8]. Their results indicated that the optimal treatment condition in removal of residual contaminants in petroleum-contaminated soil by Fenton-Like oxidation was: the molar ratio of hydrogen peroxide to iron = 200:1, andpH7.0.

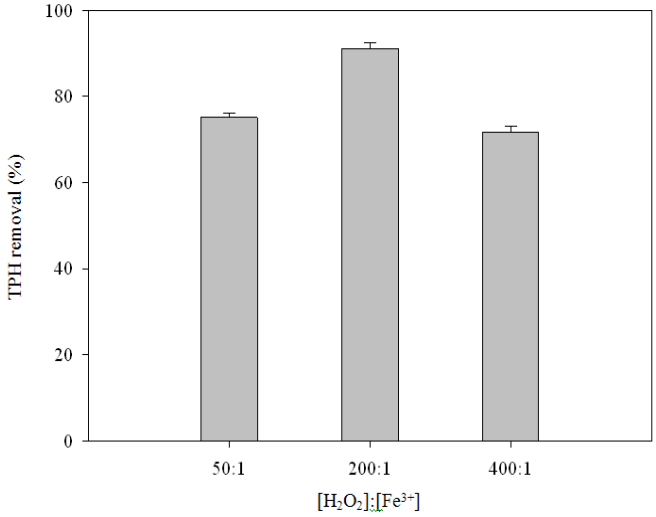


Fig. 1 Effect of $[H_2O_2]$:$[Fe^{3+}]$ on TPH mass removal. Reported values are the meanone standard deviation (n = 3)

C. Effect of pH condition on contaminant removal

The result of the pH condition tests demonstrated that the most efficiency was at pH 4.0(removal efficiency of 96.02 %). The pH condition, which was higher or lower than pH 4.0, was less efficiency. The pH catalyst seemed to be less efficiency drastically when the pH was increased (removal efficiency of 18.06 and 12.99 % at pH 6.0 and 7.0, respectively). The removal of TPH in the pH condition test is presented in Fig. 2.

At too lowpH values (<2), the reaction is slowed down due to the formationof complex iron species, formation of oxonium ions $[H_3O_2]^+$andconsumption of OH radicals by the generated hydrogen ions.

Athigh pH (>4), the generation of OH^- radicals is slower because ofthe formation of the ferric-hydroxo complexes and the decompositionof H_2O_2[9]- [11].

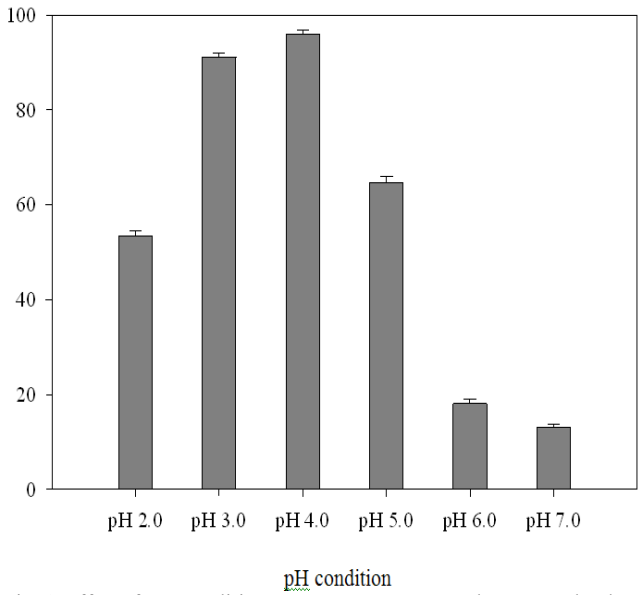


Fig. 2 Effectof pH condition on TPH mass removal. Reported values are the mean one standard deviation (n = 3)

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D.Kinetic Rate of removal

The experiment of the rate of removal was tested based on the optimum process conditions found above: pH 4.0 and H_2O_2:Fe^{3+} molar ration of 200:1. The TPH concentration in soil was 78.80 g kg^{-1}. The result of this experiment was presented in Fig. 3. It was found that the rate of TPH removal in soil increased rapidly at the starting point (after adding a Fenton reagent and shaking a sample) to the 7th hour. In the 8th hour, the rate of reaction in the process decreased slightly until the 12th hour. The first order TPH destruction kinetic rate (k) was observed as

$$-d\,[\mathrm{TPH}]/dt = k[\mathrm{OH}][\mathrm{TPH}] \qquad (1)$$

Since free radical reactions are very fast, it is assumed that asteady-state OH concentration was achieved as soon as the Fenton reaction started. Therefore, the steady-state OH^- concentration was assumed to be constant [12]. So, the TPH destruction kinetic rate (k) in this study was 0.24 h^{-1}.

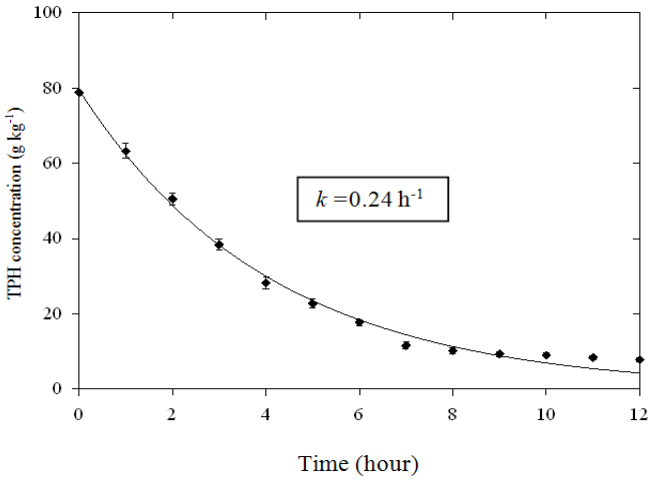


Fig. 3 TPH concentration in soil at the different time point during Fenton- like oxidation process

IV. Conclusions

This study reported the capability of a Fenton reaction, using Fe^{3+} as the catalyst, could eliminate contaminant in a highly petroleum-hydrocarbon contaminated soil. However, a Fenton oxidation needs to use an appropriate quantity of reagent and pH to obtain the most efficiency in removing TPH concentration. In the optimum condition in this study, Fenton reaction could remove TPH in soil slurry approximately 96 % within 12 h.

Acknowledgment

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