

# Remediation of Petroleum Hydrocarbon-contaminated Soil Slurry by Fenton Oxidation

C. Pongcharoen, K. Kaiyavong and T. Satapanajaru

**Abstract**—The objective 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 some factors 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 results demonstrated that the optimum condition was that the molar ratio of  $H_2O_2:Fe^{3+}$  was 200:1, the pH was 4.0 and the rate of reaction was increasing rapidly from starting point to 7<sup>th</sup> hour and destruction kinetic rate ( $k$ ) was  $0.24\ h^{-1}$ . Approximately 96% of petroleum hydrocarbon was observed (initial total petroleum hydrocarbon (TPH) concentration =  $70 \pm 7\ g\ kg^{-1}$ )

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

## I. INTRODUCTION

SOIL contamination by petroleum hydrocarbons, a very important environmental problem, has been attracting considerable public attention over the past decades [1]. Petroleum hydrocarbons are a mixture of chemical substances caused during human activities by using petroleum products in industrial and agricultural production. Although petroleum is one of the dominant energy sources to maintain the economic and social development 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 to many living organisms [4]. The presence 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 petroleum hydrocarbons, how to remedy, treat and control this contamination efficiently is becoming a technical problem in 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 ingredients and active agents. It can also be an effective pretreatment step for enhancing bioremediation by reducing overall toxicity to indigenous 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 as one of the most powerful oxidizing reactions available and can be used to destroy a wide variety of organic compounds in 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 Amphor Meung (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 from serviced 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 of ferric iron whereas changing the dose of hydrogen peroxide to obtain the optimal ratio of hydrogen peroxide to iron [8]. In the experiment, each tested was performed in triplicate.

The molar ratio of  $\text{H}_2\text{O}_2:\text{Fe}^{3+}$  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 catalyst 1.765, 0.441 and 0.221 M ( $\text{Fe}_2(\text{SO}_4)_3$ ) were added. The molar ratio of  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  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  $\text{HNO}_3$  / 0.1 M  $\text{NaOH}$  solution and performed with the molar ratio of  $\text{H}_2\text{O}_2:\text{Fe}^{3+}$  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  $\text{H}_2\text{O}_2:\text{Fe}^{2+} = 200:1$  and  $\text{pH} = 4$ ). 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  $70 \pm 7 \text{ g kg}^{-1}$ .

### 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 ratio of  $\text{H}_2\text{O}_2:\text{Fe}^{3+}$  test is presented in Fig. 1. The best condition of the TPH removal efficiency was obtained at the molar ratio of  $\text{H}_2\text{O}_2:\text{Fe}^{3+}$  was 200:1 (removal efficiency of 91.07 %) and the lowest level of removal was recorded when the ratio of  $\text{H}_2\text{O}_2:\text{Fe}^{3+}$  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, and pH 7.0.

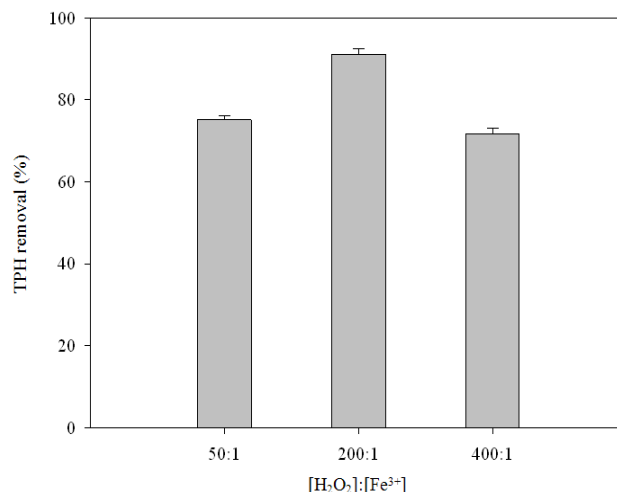


Fig. 1 Effect of  $[\text{H}_2\text{O}_2]:[\text{Fe}^{3+}]$  on TPH mass removal. Reported values are the mean one standard deviation ( $n = 3$ )

### 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 low pH values ( $<2$ ), the reaction is slowed down due to the formation of complex iron species, formation of oxonium ions  $[\text{H}_3\text{O}_2]^+$  and consumption of OH radicals by the generated hydrogen ions.

At high pH ( $>4$ ), the generation of  $\text{OH}^\cdot$  radicals is slower because of the formation of the ferric-hydroxo complexes and the decomposition of  $\text{H}_2\text{O}_2$  [9]- [11].

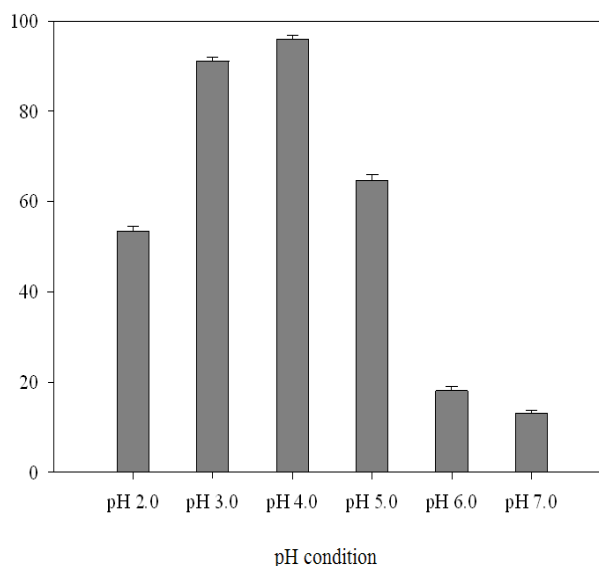


Fig. 2 Effect of pH condition on TPH mass removal. Reported values are the mean one standard deviation ( $n = 3$ )

#### 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  $\text{H}_2\text{O}_2:\text{Fe}^{3+}$  molar ration of 200:1. The TPH concentration in soil was  $78.80 \text{ g kg}^{-1}$ . 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 7<sup>th</sup> hour. In the 8<sup>th</sup> hour, the rate of reaction in the process decreased slightly until the 12<sup>th</sup> hour. The first order TPH destruction kinetic rate ( $k$ ) was observed as

$$-d[\text{TPH}]/dt = k[\text{OH}][\text{TPH}] \quad (1)$$

Since free radical reactions are very fast, it is assumed that a steady-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  $0.24 \text{ h}^{-1}$ .

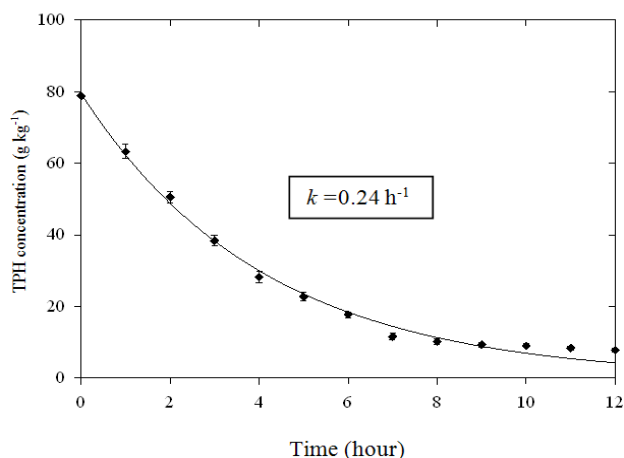


Fig. 3 TPH concentration in soil at the different time point during Fenton-like oxidation process

#### IV. CONCLUSIONS

This study reported the capability of a Fenton reaction, using  $\text{Fe}^{3+}$  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.

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#### REFERENCES

[1] S. Peng, Q. Zhou, Z. Caia, and Z. Zhanga, "Phytoremediation of petroleum contaminated soil by *Mirabilis Jalapa L.* in a greenhouse plot experiment," *Journal of Hazardous Materials*, vol. 168, pp. 1490-1496, Mar. 2009.

- [2] W. Duan, G. Chen, Q. Ye, and Q. Chen, "The situation of hazardous chemical accidents in China between 2000 and 2006" *Journal of Hazardous Materials*, vol. 186, pp. 1489-1494, Dec. 2010.
- [3] E. Okstad, E. Jersin, and R.K. Tinmannsvik, "Accident investigation in the Norwegian petroleum industry – Common features and future challenges" *Safety Science*, vol. 50, pp. 1408 – 1414, Jan. 2011.
- [4] N. Merkl, R. Schultze-Kraft, and C. Infante, "Phytoremediation in the tropics - influence of heavy crude oil on root morphological characteristics of graminoids" *Environmental Pollution* 138, vol. 138, pp. 86-91, Feb. 2005.
- [5] K. Das, and A.K. Mukherjee, "Crude petroleum-oil biodegradation efficiency of *Bacillus subtilis* and *Pseudomonas aeruginosa* strains isolated from a petroleum-oilcontaminated soil from North-East India" *Bioresourc Technology*, vol. 98, pp. 1339-1345, May. 2006.
- [6] E.J. Jonera, D. Hirmannb, O. H.J. Szolarb, D.Todorovicb, C.Leyvala, and A.P. Loibnerb, "Priming effects on PAH degradation and ecotoxicity during a phytoremediation experiment" *Environmental Pollution*, vol. 128, pp. 429-435, Sep. 2003.
- [7] M. Lu, Z. Zhang, W.Qiao, Y.Guanb, M. Xiao, and C.Peng, "Removal of residual contaminants in petroleum-contaminated soil by Fenton-like oxidation" *Journal of Hazardous Materials*, vol. 179, pp. 604-611, Mar. 2010.
- [8] M. Lu, Z. Zhang, W. Qiao, X. Wei, Y. Guan, Q. Ma, and Y. Guan, "Remediation of petroleum-contaminated soil after composting by sequential treatment with Fenton-like oxidation and biodegradation" *Bioresourc Technology*, vol. 101, pp. 2016-2113, Nov. 2009.
- [9] R. Baciocchi, M.R. Boni, and L.D. April, "Hydrogen peroxide lifetime as an indicator of the efficiency of 3-chlorophenol Fenton's and Fenton-like oxidation in soils" *Journal of Hazardous Materials*, B96, pp. 305-329, 2003.
- [10] L. Di Palma, In situ chemical oxidation of environments combined with hazardous materials. In: Lens, P., Grotenhuis, T., Malina, G., Tabak, H. (Eds.), *Soil and Sediment Remediation: Mechanisms, Technologies and Applications*. IWA Publishing, London, pp. 200–222, 2005.
- [11] J.H. Langwaldt, Stimulated in situ soil treatment: biodegradation coupled to Fenton's reaction. In: Lens, P., Grotenhuis, T., Malina, G., Tabak, H. (Eds.), *Soil and Sediment Remediation: Mechanisms, Technologies and Applications*. IWA Publishing, London, pp. 223–247, 2005.
- [12] Venny, S. Gan and H.K. Ng, "Inorganic chelated modified-Fenton treatment of polycyclic aromatic hydrocarbon (PAH)-contaminated soils" *Chemical Engineering*, vol. 180, pp. 1-8, Oct. 2011.