

Short communication

## Soil remediation by an advanced oxidative method assisted with ultrasonic energy

Roberto Flores\*, Georgina Blass, Vanessa Domínguez

*Instituto de Investigaciones Electricas, Calle Reforma 113, Colonia Palmira, Cuernavaca 62490, Mexico*

Received 14 September 2006; accepted 15 September 2006

Available online 20 September 2006

### Abstract

A new process for the remediation of soil contaminated with hydrocarbons is proposed. The innovation consists on coupling an advanced oxidative method, using a Fenton-type catalyst, with the application of ultrasonic energy. The use of ultrasonic energy not only assists the desorption of the contaminants from the soil, but also promotes the formation of  $\bullet\text{OH}$  radicals, which are the oxidant agents involved in the oxidation process. Different Fenton-like catalysts were employed in the present study; however, the highest removal of toluene and xylenes were obtained with iron sulfate and copper sulfate, respectively. Also, hydrogen peroxide was tested at different concentrations, and it was found that increasing its concentration enhanced the removal of all the contaminants. Finally, it was demonstrated that applying ultrasonic energy to the reacting system process noticeably enhanced the global efficiency of the process due to a synergistic effect in conjunction with the hydrogen peroxide concentration and type of catalyst.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Soil remediation; Advanced oxidation process; Ultrasonic energy; Fenton-type catalysts

### 1. Introduction

Soil contamination due to volatile organic compounds, such as diesel and gasoline, is mainly originated from leaks that occur in the underground tanks located in the gas stations [1]. The most common methods for remediation of contaminated soils present severe limitations [2–4]. For instance, excavations followed by landfills do not destroy the pollutants. The incineration generates polyaromatic hydrocarbons (PAHs) which are sometimes more toxic than the original pollutant; therefore, they must be also eliminated. *In situ* biological treatments show limitations for biorefractory compounds and low activity under frozen climatic conditions. Venting for remediation of soils contaminated with low volatility compounds requires very high operating temperatures, which is not economically feasible.

One practical alternative is the oxidation of the organic compounds using Fenton-type catalysts and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). In this case, the organic compounds are totally mineralized to  $\text{CO}$  and  $\text{CO}_2$ . The process consists on putting in contact

the polluted soil with an aqueous solution that contains a Fenton-type catalyst and  $\text{H}_2\text{O}_2$ . The reaction proceeds at almost room temperature, and compared to other processes, such as, venting and bioremediation, its treatment time is reduced from years and months to few days or less. The reaction mechanism is complicated, but the initial step is the generation of the  $\text{OH}\bullet$  radical, that happens through the catalytic reaction of  $\text{H}_2\text{O}_2$  with metallic Fenton-type salts, which are complex formed by Cu, Co, Fe, Mn, Ru, V, and Ti [5]. Among these metallic salts, one of the most employed for soil remediation is  $\text{FeSO}_4$ . Previous works, that used  $\text{FeSO}_4$  as catalyst to remediate soils contaminated with hydrocarbons, have reported that the removal of the pollutants improves as the  $\text{H}_2\text{O}_2$  and catalyst concentration augment [1,4,6–8]. They also reported that the mineralization reaction occurs in the aqueous solution after the hydrocarbons have been desorbed from the soil. Since the desorption process is very slow, this is the rate-determining step; therefore, an increase in the stirring rate would enhance the removal since the pollutants would be desorbed faster.

An alternative for accelerating the desorption of the hydrocarbons from the soil is the application of ultrasonic energy [2,9]. It was observed that the desorption % depended on the contaminant concentration, sonication time, particle size, soil pH, surfactant

\* Corresponding author. Tel.: +52 777 362 3811; fax: +52 777 362 3832.  
E-mail address: [rfv@iie.org.mx](mailto:rfv@iie.org.mx) (R. Flores).

concentration, and the intensity of the ultrasonic energy. It is believed that ultrasound waves at frequencies of 45 kHz produce local temperatures and pressures in the order of 5000 °C and 1000 atm [9]. This event causes tremendous turbulences and strong mixing which favors the desorption of compounds strongly absorbed in the surface of the soil. Additionally, due to the intense conditions in the liquid–gas interphase, the molecules of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O in the surroundings could break generating OH• radicals.

Based on the above principles, and in the presence of a Fenton-type catalyst, polluted water has been treated by oxidation assisted with ultrasonic energy to eliminate hydrocarbons and excellent reviews have been presented elsewhere [10–15].

In the present work, the oxidative method using Fenton-like catalyst coupled with the application of ultrasound energy is proposed for the remediation of hydrocarbon contaminated soils. It is expected that the application of ultrasound to the system will promote the formation of OH• radicals, will facilitate the desorption of the hydrocarbon from the soil, and will enhance the mineralization of the pollutant once it is in the liquid phase.

For testing the last statement, soils were contaminated with known amounts of toluene and xylene isomers. Then, samples were taken and treated with the above proposed method. The studied operating variables were the H<sub>2</sub>O<sub>2</sub> and catalyst concentrations in the aqueous solution, and the application of ultrasonic energy.

## 2. Experimental

### 2.1. Materials

Toluene (98 wt%) and xylenes (98 wt%) were purchased from Aldrich and used as received. Aqueous hydrogen peroxide (30 wt%), Iron sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O), iron chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O), and Copper sulfate (CuSO<sub>4</sub>·3H<sub>2</sub>O) were acquired from Baker and used as received. The water used in the experimentation was deionized by passing through an ionic exchange column. The soil employed in the present study was characterized according to the ASTM-D3682-91 Method, and the following composition in wt% of the major elements was obtained: Al, 7.12; Ca, 2.46; Fe, 3.56; K, 0.63; Mg, 1.17; Mn, 0.05; Na, 1.89; Si, 14.35. For the contamination of the soil, toluene and xylenes were dissolved in dichloromethane, and then mixed with soil. The slurry was kept in a closed chamber at 8 °C for 2 days to assure total evaporation of the dichloromethane, and then, the contaminated soil was stored in an amber vessel at the same temperature.

### 2.2. Procedure and apparatus

First, it was prepared 40 g of aqueous solution by dissolving the metallic Fenton-like salt in a known amount of deionized water, and then, a specified amount of the H<sub>2</sub>O<sub>2</sub> solution was added. Once the aqueous solution was prepared, it was mechanically mixed in a beaker with 20 g of contaminated soil. After the suspension looked visually homogeneous, the stirrer was removed, and the beaker was placed inside of an ultrasonic bath;

then, ultrasonic energy was supplied during 10 min. The ultrasonic energy was applied with a frequency of 47 kHz and an intensity of 147 W using a Cole Parmer 8890R-MTH ultrasonic bath. Therefore, the energy used in each experiment was around 16 kJ/g of polluted soil. Once the treatment time elapsed, the liquid phase was separated from the soil using vacuum filtration.

### 2.3. Qualitative and quantitative analysis

After the treatment, the remaining aromatic hydrocarbons were extracted from the soil as indicated by the EPA 3550B method. Then, the obtained solution was injected to a HP gas chromatograph Model 6890A equipped with an ionization flame detector and a RTX5 capillary column in order to perform the qualitative and quantitative analysis. To determine the remotion %, the polluted soil was characterized before and after the remediation treatment.

## 3. Results and discussion

Experiments mixing mechanically the contaminated soil with deionized water (without H<sub>2</sub>O<sub>2</sub> nor Fenton-like catalyst) did not present any removal of contaminants from the soil, meaning the hydrocarbons remained absorbed in the soil.

The effect of H<sub>2</sub>O<sub>2</sub> concentration was analyzed in absence of catalyst and applying ultrasonic energy. The results are reported in Fig. 1. It is observed that toluene was eliminated easier than xylenes except when no H<sub>2</sub>O<sub>2</sub> was added to the reacting system, since the removal was similar taking in consideration the experimental error. In absence of H<sub>2</sub>O<sub>2</sub>, it was eliminated 21% of toluene and 26% of xylenes, this removal was attributed only to the desorption of the hydrocarbon from the soil promoted by the application of ultrasonic energy due to the cavitation. This process provokes turbulence in the slurry, so the resistance to the mass transfer in the solid–liquid interphase is weakened, and the hydrocarbon could be moved to the liquid more easily. Also, the high temperature obtained by the expansion and implosive collapse of the microbubbles generated by the ultrasonic energy could enhance the breaking of physical bonds between the adsorbed hydrocarbon and the soil as already was explained elsewhere [2]. The removal of all hydrocarbons improved as the H<sub>2</sub>O<sub>2</sub> was added to the reacting system. So, it was considered that the cavitation may promote not only the desorption of the

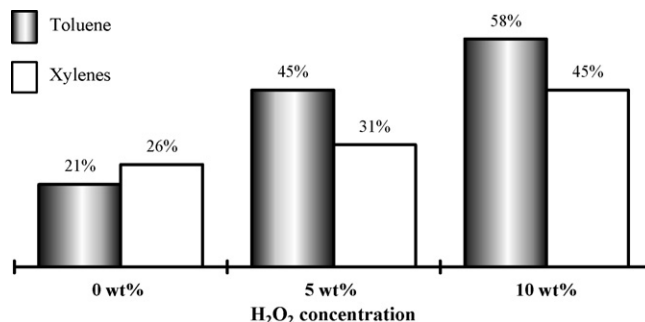


Fig. 1. Effect of H<sub>2</sub>O<sub>2</sub> concentration in absence of catalyst applying ultrasonic energy at 47 kHz.

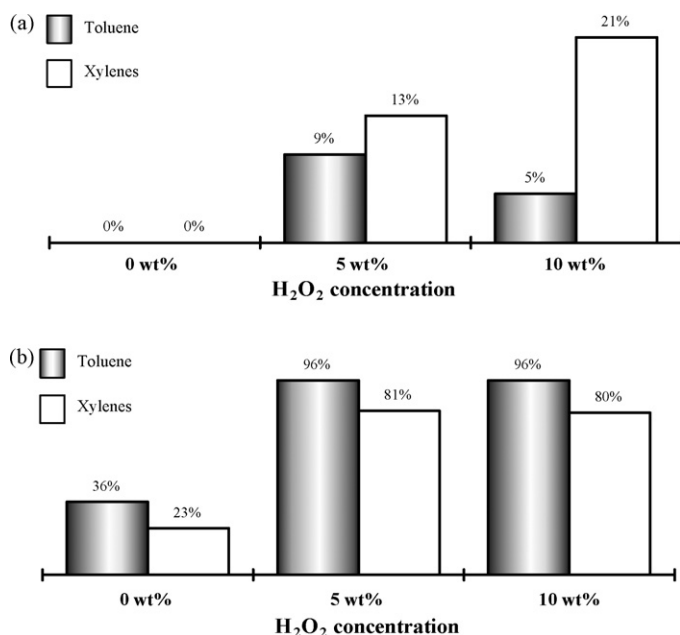


Fig. 2. Effect of H<sub>2</sub>O<sub>2</sub> using FeSO<sub>4</sub> as catalyst: (a) without applying ultrasonic energy; (b) applying ultrasonic energy at 47 kHz.

hydrocarbons from the solid matrix, but also the production of •OH radicals due to the decomposition of H<sub>2</sub>O<sub>2</sub>. Also, this last step could be catalyzed by the naturally occurring iron minerals contained in the soil as was explained elsewhere [1].

On the other hand, experiments using a FeSO<sub>4</sub> concentration in the aqueous solution of 25 mM and different concentrations of H<sub>2</sub>O<sub>2</sub> were performed without applying ultrasonic energy. The results are showed in Fig. 2(a). No removal of any contaminant was observed in absence of H<sub>2</sub>O<sub>2</sub> even though a Fenton-like catalyst was present in the reacting system. When H<sub>2</sub>O<sub>2</sub> was added to the system, certain amounts of contaminants were removed from the soil, and for this case, xylenes were removed easier than toluene. Increasing the concentration of H<sub>2</sub>O<sub>2</sub> from 5 to 10 wt% did not improve the elimination of toluene; in fact, a small decrease from 9 to 5% was observed, but it was associated to an experimental error that occurred when conducting the tests. In contrast, xylenes elimination increased from 13 to 21% when more H<sub>2</sub>O<sub>2</sub> was added to the system.

The same experiments using FeSO<sub>4</sub> and different concentrations of H<sub>2</sub>O<sub>2</sub> were repeated, but now, ultrasonic energy was supplied to the reacting system. The experimental results are displayed in Fig. 2(b). Toluene was removed easier than xylenes, and the removal of all the aromatics enhanced as the H<sub>2</sub>O<sub>2</sub> concentration increased. The former sentence could be attributed to the solubility of the aromatic hydrocarbon in water since the organic compound must be in the aqueous phase in order to be mineralized; therefore, the more soluble the hydrocarbon is in water the easier it is destroyed. Watts et al. [1] reported the solubilities of toluene and xylenes are 532 and 163–185 mg/L, respectively; therefore, more toluene than xylenes would be dissolved in the aqueous phase. In absence of H<sub>2</sub>O<sub>2</sub>, 36% of toluene and 23% of xylenes were removed from the soil. When a concentration of 5 wt% of H<sub>2</sub>O<sub>2</sub> in the aqueous solution was

employed, 96 and 81% of toluene and xylenes were eliminated from the soil, respectively. Further increase of H<sub>2</sub>O<sub>2</sub> concentration up to 10% wt did not augment the removal of hydrocarbons. Therefore, the addition of a Fenton-type catalyst to the system greatly improved the efficiency of the process compared to the experimental results achieved in absence of catalyst. This effect was attributed to the larger amount of •OH radicals available in the reacting system produced by the interaction between H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub> molecules and promoted with the ultrasonic energy. When compared these results to those presented in Fig. 2(a), it is clear the necessity of applying ultrasonic energy to obtain excellent removal of aromatic hydrocarbons from a contaminated soil. Also there is a synergistic effect between the H<sub>2</sub>O<sub>2</sub> concentration, presence of catalyst, and supply of ultrasonic energy. This could be explained in the following way: when only ultrasonic energy is applied to the slurry in absence of hydrogen peroxide and Fenton-type catalyst, the aromatic hydrocarbons are able to be partially desorbed from the soil; however, since their solubility is low in the aqueous phase, they are again deposited and absorbed in the soil after the experiment during the filtration step. On the other hand, when hydrogen peroxide is present in the liquid phase, the application of ultrasonic energy promotes its decomposition in •OH radicals by the naturally occurring iron minerals contained in the soil. Then, these radicals mineralize the hydrocarbons molecules that are already dissolved in the liquid phase because of the application of ultrasound. Since toluene solubility in water is higher, more toluene would be mineralized. Finally, when the Fenton catalyst is also added to the slurry, it will accelerate the decomposition of hydrogen peroxide into •OH radicals, and also, it will promote the formation of more of these radicals by decomposition of water molecules.

Others metallic Fenton-type catalysts were tested using various H<sub>2</sub>O<sub>2</sub> concentrations in the aqueous phase. The selected metallic salts were FeCl<sub>3</sub> and CuSO<sub>4</sub>. Their efficiencies in the process were compared with respect to the efficiency obtained using FeSO<sub>4</sub>, and the results are reported in Fig. 3.

In absence of H<sub>2</sub>O<sub>2</sub>, no removal of hydrocarbon was detected when FeCl<sub>3</sub> was employed as Fenton catalyst. On the other hand, the elimination of the hydrocarbons from the soil was greater when CuSO<sub>4</sub> was used compared to the efficiency obtained employing FeSO<sub>4</sub>. When using FeSO<sub>4</sub>, the elimination of toluene and xylenes were 36 and 23%, respectively, and when adding CuSO<sub>4</sub>, the elimination increase up to 53% for toluene, and 49% for xylenes.

When the concentration of H<sub>2</sub>O<sub>2</sub> in the aqueous solution was 5 wt% and FeCl<sub>3</sub> was employed as Fenton catalyst, around 40% of toluene was removed from the soil, but all the xylenes remained in the soil. When CuSO<sub>4</sub> was added to the aqueous solution with the same concentration of H<sub>2</sub>O<sub>2</sub>, the removal of toluene and xylenes increased compared to the results obtained in absence of H<sub>2</sub>O<sub>2</sub>; 74 and 78% of toluene and xylenes were eliminated, respectively. However, when these results were compared to those obtained using FeSO<sub>4</sub> as Fenton catalyst keeping constant the other experimental conditions, it is observed that the performance of the process is better working with FeSO<sub>4</sub>.

Increasing the concentration of H<sub>2</sub>O<sub>2</sub> to 10 wt%, provoked a drastic enhancement in the performance of the process that

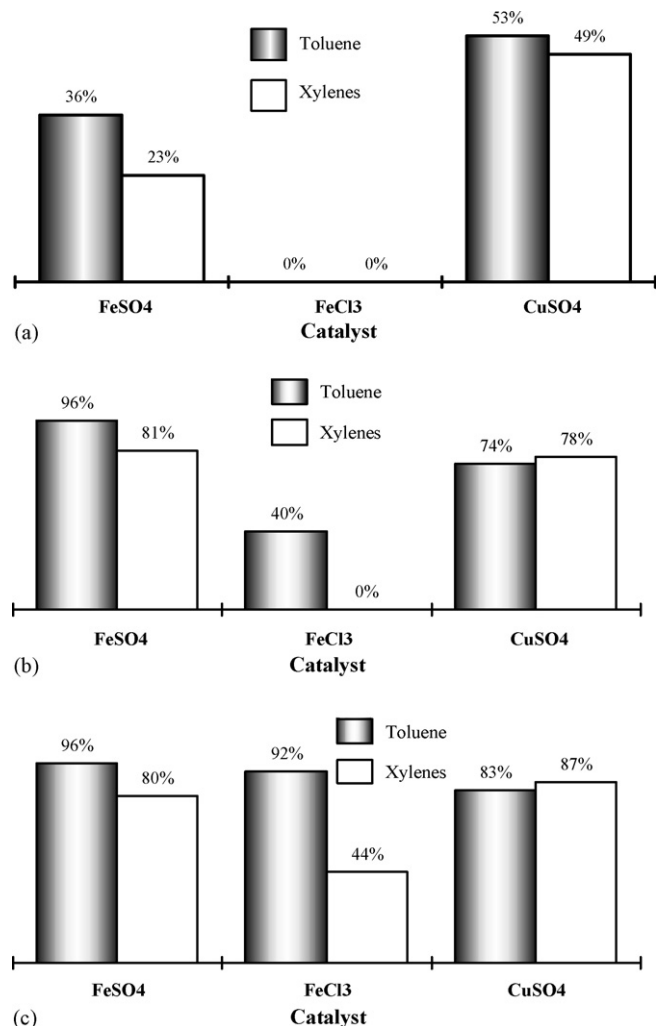


Fig. 3. Effect of type of catalyst applying ultrasonic energy at 47 kHz: (a) without H<sub>2</sub>O<sub>2</sub>; (b) using a 5 wt% H<sub>2</sub>O<sub>2</sub> aqueous solution; (c) using a 10 wt% H<sub>2</sub>O<sub>2</sub> aqueous solution.

employed FeCl<sub>3</sub> as Fenton catalyst. The removal of toluene increased up to 92%, and around 44% of xylenes were finally eliminated from the soil. On the other hand, the process that used CuSO<sub>4</sub> as catalyst also showed an improvement, but it was less intense. The removal of xylenes from the soil increased up to 83%, and the elimination of xylenes rose up to 87%. Comparing the results obtained with all the catalysts using a concentration of H<sub>2</sub>O<sub>2</sub> of 10wt%, it is observed that the removal of toluene is higher using FeSO<sub>4</sub> as catalyst; however, CuSO<sub>4</sub> displayed a better yield for the elimination of xylenes.

#### 4. Conclusions

A novel process for remediation of soil contaminated with hydrocarbon compounds has been proposed. This process combines the chemical oxidation using a Fenton-like catalyst with the application of ultrasonic energy. Experimental results showed that the application of ultrasonic energy was manda-

tory in order to obtain considerable removal of contaminants from the soil. Also, it was proved that the incorporation of a Fenton-type catalyst, particularly CuSO<sub>4</sub> and FeSO<sub>4</sub>, enhances the efficiency of the process when hydrogen peroxide is also present. Moreover, it was determined that FeSO<sub>4</sub> gave better results for the removal of toluene, and CuSO<sub>4</sub> was more effective for the elimination of xylenes. Finally, it was established that there is a synergistic effect between the studied variables for the improvement of the hydrocarbon elimination from the soil, but in order to be mineralized, the hydrocarbon must be dissolved in the liquid phase. Ultrasonic energy not only assists in desorbing the hydrocarbon from the soil, but also promotes the formation of the •OH radicals, which are the oxidant agents, from the decomposition of hydrogen peroxide and water molecules; hydrogen peroxide, provides the major source of the •OH radicals; and the presence of a Fenton-type catalyst increases the formation rate of the oxidant agent.

#### References

- [1] R.J. Watts, D.R. Haller, A.P. Jones, A.L. Teel, A foundation for the risk-based treatment of gasoline-contaminated soils using modified Fenton's reactions, *J. Hazard. Mater. B* 76 (2000) 73–89.
- [2] D. Feng, C. Aldrich, Sonochemical treatment of simulated soil contaminated with diesel, *Adv. Environ. Res.* 4 (2000) 103–112.
- [3] K. Kato, M. Kawaguchi, A. Kuriyama, Polluted soil remediation apparatus, polluted soil remediation method, pollutant degrading apparatus and pollutant degrading method, US Patent no. 6,538,170 B2 (2000).
- [4] S.H. Kong, R.J. Watts, J.H. Choi, Treatment of petroleum-contaminated soils using iron mineral catalyzed hydrogen peroxide, *Chemosphere* 37 (1998) 1473–1482.
- [5] F. Gozzo, Radical and non-radical chemistry of the Fenton-like systems in the presence of organic substrates, *J. Mol. Catal. A: Chem.* 171 (2001) 1–22.
- [6] F.K. Kawahara, B. Davila, S.R. Al-Abed, S.J. Vesper, J.C. Ireland, S. Rock, Polynuclear aromatic hydrocarbon (PAH) release from soil during treatment with Fenton's reagent, *Chemosphere* 31 (1995) 4131–4142.
- [7] V.S. Millioli, D.D.C. Freire, M.C. Cammarota, Petroleum oxidation using Fenton's reagent over beach sand following a spill, *J. Hazard. Mater.* 103 (2003) 79–91.
- [8] R.J. Watts, S. Kong, M. Dippre, W.T. Barnes, Oxidation of sorbed hexachlorobenzene in soils using hydrogen peroxide, *J. Hazard. Mater.* 39 (1994) 33–47.
- [9] T.J. Mason, A. Collings, A. Sumel, Sonic and ultrasonic removal of chemical contaminants from soil in the laboratory and on a large scale, *Ultrason. Sonochem.* 11 (2004) 205–210.
- [10] Y.G. Adewuyi, Sonochemistry: environmental science and engineering applications, *Ind. Eng. Chem. Res.* 40 (2001) 4681–4715.
- [11] Z. Laughrey, E. Bear, R. Jones, M.A. Tarr, Aqueous sonolytic decomposition of polycyclic aromatic hydrocarbons in the presence of additional dissolved species, *Ultrason. Sonochem.* 8 (2001) 353–357.
- [12] S. Toma, A. Gaplovsky, J.L. Luche, The effect of ultrasound on photochemical reactions, *Ultrason. Sonochem.* 8 (2001) 201–207.
- [13] I. Hua, M.R. Hoffmann, Optimization of ultrasonic irradiation as an advanced oxidation technology, *Environ. Sci. Technol.* 31 (1997) 2237–2243.
- [14] P.R. Gogate, P.A. Tatake, P.M. Kanthale, A.B. Pandit, Mapping of sonochemical reactors: review, analysis, and experimental verification, *AIChE J.* 48 (2002) 1542–1560.
- [15] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, *J. Hazard. Mater. B* 98 (2003) 33–50.