Effect of the Ratio of Crude Oil to Soil Organic Matter on H_2O_2 Decomposition and Oxidation of Crude oil in Contaminated Soils

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Abstract:
Chemical oxidation with Fenton's reagent (H_2O_2) was applied to two soils contaminated with TPH (total petroleum hydrocarbons as crude oil). Soil YA contains 2.69% TPH and 11.31% soil organic matter (SOM); the TPH/SOM ratio is 0.24:1.0. Soil XI contains 8.97% TPH and 5.93% SOM, i.e. the TPH/SOM ratio is 1.51:1.0. The results indicate that in soil with a low TPH/SOM ratio (containing a higher percentage of SOM), SOM could be removed easily and consume H_2O_2 more effectively than crude oil, and O_2 gas may be a major product of the H_2O_2 decomposition. However, in the soil with a high TPH/SOM ratio, a low initial rate of O_2 generation was obtained, and the SOM may need to be modified to improve the removal of the crude oil in that soil.

Keywords: ratio of crude oil to soil organic matter; H_2O_2 decomposition; O_2 gas generation; crude oil contaminated soil; Fenton oxidation

Introduction

Fenton's reagent is the product of a reaction between hydrogen peroxide (H_2O_2) and ferrous iron (Fe^{2+}) that produces the hydroxyl radical (•OH). Fenton's reagent has attracted considerable attention because the high reactivity of the hydroxyl radical readily degrades a wide variety of pollutants (in reaction with alkanes, $k=10^7$-10^9 M^{-1} s^{-1}; in reaction with alkenes and aromatics, $k=10^9$-10^{10} M^{-1} s^{-1}) [e.g. Lindsey et al. (1)]. Fenton's oxidation technology has been applied in the pilot- and full-scale removal of crude oil from soil at several contaminated sites in recent years [e.g. Vitolins et al. (2); e.g. Tsai et al. (3)]. However, [e.g. Tyre et al. (4) reported low oxidation efficiencies under high soil organic matter (SOM) concentrations, indicating that the catalytic efficiency for the decomposition of H_2O_2 and target pollutants depends on the specific characteristics of the soil organic matter]. The oxidation of SOM usually results in huge costs from the large-scale consumption of hydrogen peroxide [e.g. Yeh et al. (5)]. Therefore, it is necessary to develop a technique for the oxidation of crude oil with minimal SOM removal.

[e.g. Romero et al. (6) reported that at uniform initial H_2O_2 concentrations, greater H_2O_2 decomposition is obtained if the concentration of soil organic matter (SOM) is increased.] [e.g. Petigara et al. (7) reported that hydroxyl radicals (•OH) were a major product of H_2O_2 decomposition in soils containing low amounts of SOM but they were a minor product in soils containing high amounts of SOM]. Therefore, SOM can be one of the factors that control the rate of H_2O_2 decomposition and hydroxyl radical formation, which are responsible for contaminant oxidation [e.g. Goi et al. (8)]. These reports focus on the formation of hydroxyl radicals at low H_2O_2 concentrations (40 μM to 1.0 mM) [e.g. Lindsey et al. (1)]; [e.g. Petigara et al. (7)]. Less is known about how ratio of TPH/SOM affects O_2 gas production from H_2O_2 decomposition in the remediation of soils. More importantly, the effect of the initial rate of O_2 gas generation on oxidation of crude oil in soils remains unclear. In this study, the rate of O_2 gas generation in two soils was investigated when eight successively higher H_2O_2 concentrations were applied. The effects of soil composition, such as the TPH/SOM ratio on oxidation of crude oil, H_2O_2 decomposition, and O_2 gas generation, were investigated. The relationship of O_2 gas generation and the oxidant utilizations were evaluated.

Materials and Methods

Chemicals

Liquid hydrogen peroxide (30% by weight) was purchased from Paini Reagent Company (Zhengzhou, China). Citric acid (analytical grade $C_6H_8O_7$) was purchased from National Medicine Group Chemical Reagent Factory (Beijing, China).

Soil Samples Contaminated with Crude Oil

A soil sample, designated soil YA, was collected from an oil well in the city of Yan'an, China. Another

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soil sample, designated soil XI, was taken from near an oil storage station in the city of Xi`an, China. The two soil samples had been exposed to crude oil contamination for approximately two years. The soil samples were sieved through a 2-mm mesh to remove impurities and then homogenized using a rotary shaker that rotated at 12.5 rpm for 48 h.

The two samples contain different original TPH concentrations: 26.9 and 89.7 g TPH per kg of dry matter in soils YA and XI, respectively. The pH values of soils YA and XI were 7.67 and 8.01, respectively. The dry matter of soils YA and XI were 0.923 and 0.920 (w/w), respectively, and their SOM concentrations were 14.0% and 14.9% by weight, respectively.

The total SOM was assumed to consist of two parts: TPH (total petroleum hydrocarbons as crude oil) and the SOM. It was determined that soil YA contains 2.69% TPH and 11.31% SOM, whereas soil XI contains 8.97% TPH and 5.93% SOM. The TPH/SOM ratios were calculated as 2.69/11.31 = 0.24 for soil YA and 8.97/5.93 = 1.51 for soil XI.

Experimental Design

The procedure for the modified Fenton oxidation was as follows: 5 g of soil and 40 mL of deionized water were mixed in a 250-mL serum vial, and a 10-mL iron catalyst with a pH of 7.5 was added to the slurry. The iron catalyst was made from 5.8 mM Fe (II) and citric acid as iron chelating agents based on a previous study [e.g. Xu et al. (9)]. Then, H_2O_2 at eight concentrations (300, 500, 700, 900, 1,100, 1,300, 1,500, and 1,700 mM) was added to the slurries at pH 7.5. The suspensions were then mixed for 1 min using a magnetic stirrer. The oxidation reaction was allowed to occur in open bottles over the course of 2 days until no residual H_2O_2 was measured. However, the volume of O_2 gas generated during the Fenton reaction was measured by the drainage gas-collecting method in a closed system. Three separate experiments were conducted: the first to measure H_2O_2 and SOM concentrations, the second to measure TPH concentrations, and the third to measure O_2 generation. Control reactions were performed in parallel using deionized water in place of oxidants. Each treatment consists of three replicates performed at room temperature in dark conditions.

Extraction and Analysis

The soil samples were mixed with acetone and water at an acetone/water ratio of 4:1 (v/v) and a solid/liquid ratio of 1:10 $g.mL^{-1}$. The resulting slurry was sonicated for 15 min and shaken at room temperature for 1 h. Then, 25 mL of petroleum ether was added to the flask and shaken at room temperature for 1 h (175 rpm, Gerhardt Laboshaker). Finally, the extraction medium of TPH was mixed with 200 mL of deionized water two times to separate the petroleum ether and acetone phases. The floating petroleum ether phase was transferred to the sample bottle and analyzed for TPH by GC.

Detailed analysis for TPH (1-μL extracts) was performed using an Agilent HP 6890 gas chromatograph (GC) with an HP-5 column (30 m × 0.25 mm × 0.50 μm) and a flame ionization detector (FID). Nitrogen was used as carrier gas (3.5 $mL.\ min^{-1}$). The injection temperature was 300°C. The ratio of split was 5:1. The column was held at 40°C for 0.50 min and ramped at 15°C per min to 150°C. The temperature was then increased at 10°C per min to a final temperature of 290°C and held for 5 min [e.g. Saari et al. (10)]. This enabled a complete run within 28.83 min. The GC was started and ended with injection of pure petroleum ether and a TPH mixed standard (purchased from Agilent Technology).

The dry weight was calculated based on the weight difference of the samples before and after drying in an oven for 24 h at 105°C. The SOM content was determined using the weight difference before and after drying in an oven for 24 h at 550°C. The pH was measured in the supernatant of a suspension containing a ratio of 1 g soil to 2.5 mL of liquid in 0.01 M $CaCl_2$ [e.g. Sutton et al. (11)]. Hydrogen peroxide in the supernatant was measured by iodometric titration using 0.1 N sodium thiosulfate [e.g. Quan et al. (12)]. The volume of O_2 gas generated was measured by the drainage gas-collecting method, and CO_2 produced was removed by 1 M NaOH [e.g. Xu et al. (13)].

Results and Discussion

The Effect of TPH/SOM on Oxidation of Crude Oil in Contaminated Soils

Figure 1 shows the removal of SOM and TPH at the eight H_2O_2 concentrations in the two soils. The TPH removal was calculated as the initial amount of crude oil (TPH) in the soil minus the amount remaining after treatment. This value indicates the amount of TPH that was mineralized in the 5-g samples of soils YA and XI, which contain 26.9 and 89.7 mg TPH per g dry matter, respectively. The results indicate that the amount of TPH removal depends on the H_2O_2 concentration and the ratio of TPH/SOM. There was a significant difference between the crude oil removals in soils YA and XI with the increase of H_2O_2 concentration. Specifically, only 29-69 mg of crude oil was removed from soil YA and 36 to 186 mg from soil XI (Figure 1 a). Low SOM removal in soil XI (high TPH/

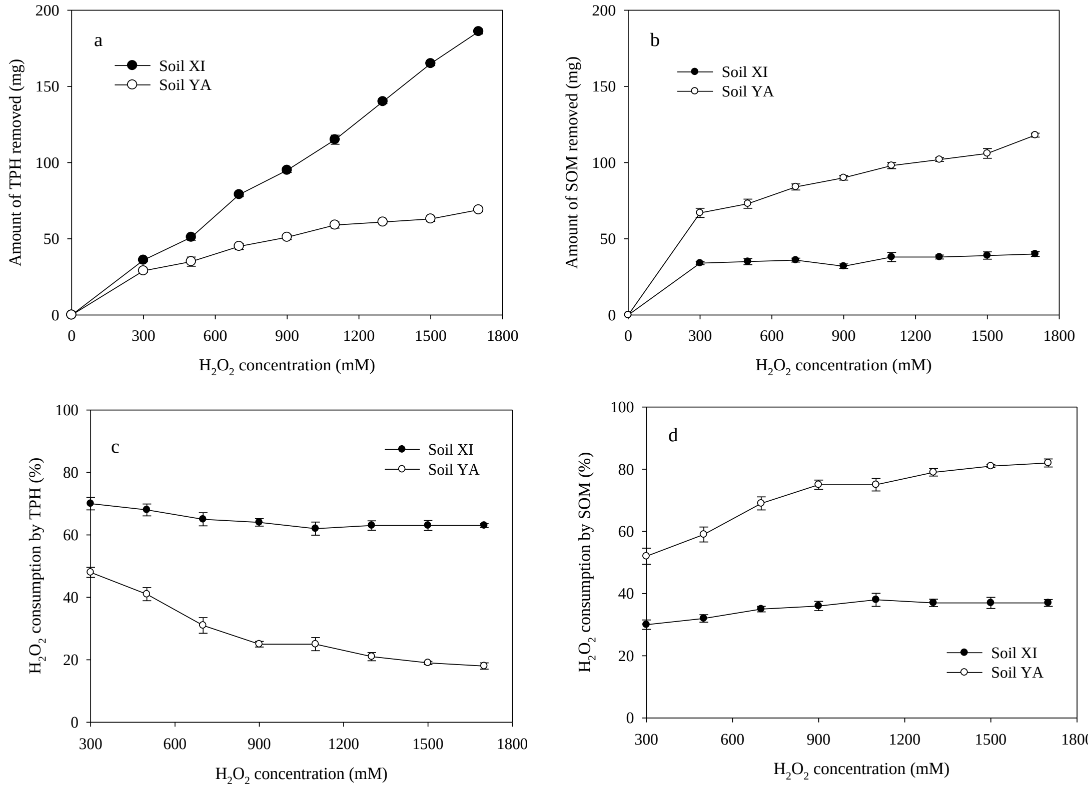

Figure 1. Removal of SOM and TPH in the two studied soils. (a) SOM, (b) TPH, (c) H_2O_2 consumption by TPH, (d) H_2O_2 consumption by SOM. Initial Fe^{2+} concentration was 5.8 mM, pH=7.5.

SOM ratio of 1.51) was accompanied by high crude oil removal. However, high SOM removal in soil YA (low TPH/SOM ratio of 0.24) was accompanied by low crude oil removal, indicating that the removal of crude oil was reduced by SOM. The finding that SOM reduced the oxidation efficiency of contaminants in soil was similar to previously reported results [e.g. Lindsey et al. (1); e.g. Sun et al. (14); e.g. Sutton et al. (15)]. [e.g. Jonsson et al. (16) reported that the hydroxyl radicals are consumed by SOM before they have an opportunity to react with polycyclic aromatic hydrocarbons (PAHs)]. [e.g. Romero et al. (5) also reported that excess H_2O_2 was added due to the consumption by SOM].

When the H_2O_2 concentration is increased from 300 to 1,700 mM, 34-40 mg of SOM was removed from soil XI and 67 to 118 mg for soil YA (Figure 1 b). The SOM in soil YA (low TPH/SOM ratio of 0.24) was removed easily and consumed H_2O_2 more effectively (70% to 60% of H_2O_2 was consumed by SOM; Figure 1d) than crude oil (30% to 40% of H_2O_2 was consumed by TPH; Figure 1c). The SOM in soil YA was more sensitive to high concentrations of H_2O_2 than that in soil XI (high TPH/SOM ratio of 1.51). Therefore, in the field applications on a soil with a low TPH/SOM ratio (such as soil YA), a relatively low H_2O_2 concentration may be a suitable choice. A large amount of TPH was removed from soil XI, where more H_2O_2 (52-80%) was consumed, because less H_2O_2 (48-20%) was consumed by the SOM in that soil. Therefore, crude oil was readily oxidized by the H_2O_2 in soil XI (high TPH/SOM ratio of 1.51).

The Effect of TPH/SOM on H_2O_2 Decomposition in Contaminated Soils

After 3 h of the Fenton reaction, 60-80% of H_2O_2 was rapidly consumed in soil YA (high percentage of SOM) as shown in Figure 2a. However, less crude oil (29-69 mg) was removed from soil YA, as noted above. However, only 25-42% of H_2O_2 was consumed in soil XI (Figure 2c), which exhibited a very slow rate of H_2O_2 decay and a higher rate of crude oil removal (36-186 mg). These results indicate that high percentage of SOM improved the decomposition of H_2O_2 in the slurries. [e.g. Romero et al. (6)] arrived at a similar conclusion: greater H_2O_2 decomposition is obtained in soil with a high amount of SOM.

Furthermore, a faster rate of H_2O_2 decay is associated with greater initial production of oxygen: 80 to 120 mL of O_2 gas was produced in soil YA in 30 min (Figure 2b), 30-70 mL of O_2 gas was measured in soil YA after 10 min of reaction time (Figure 3a); whereas 20 to 80 mL of oxygen was generated in soil XI (Figure 2d), O_2 gas was only 10-30 mL in soil XI

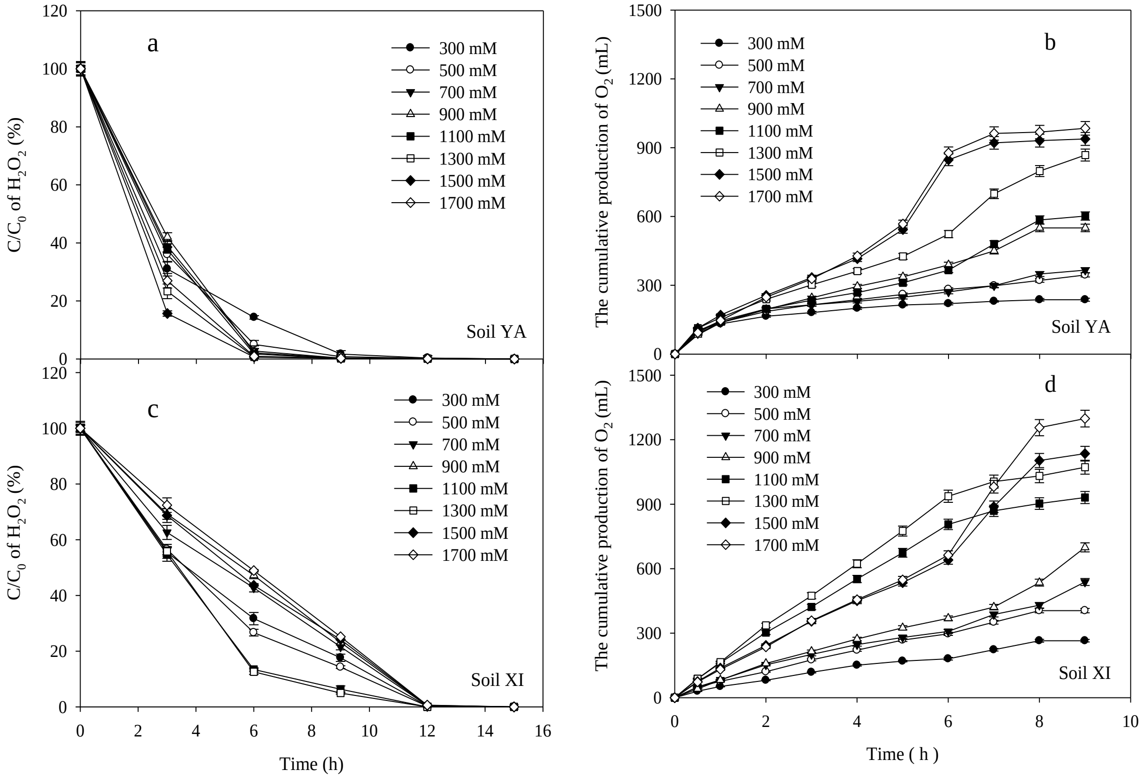

Figure 2. Decomposition of hydrogen peroxide in the two studied soils. (a) H_2O_2 decay in soil YA, (b) O_2 generation in soil YA, (c) H_2O_2 decay in soil XI, (d) O_2 generation in soil XI,. Initial Fe^{2+} concentration was 5.8 mM, pH=7.5.

in 10 min (Figure 3a). The rate of initial O_2 gas generation from soil YA (high percentage of SOM) was in the range of 280-400 mL/h, which is twice the rate of O_2 gas generation from soil XI (100-200 mL/h). The greater generation of gases may have prohibited H_2O_2 infiltration into the soil sample, which reduced the removal of crude oil during the actual remediation process because gas bubbles decreased H_2O_2 hydraulic conductivity.

An increase in TPH removal from 36 to 186 mg was observed in soil XI (low percentage of SOM) due to slow H_2O_2 decomposition and low initial O_2 generation. In contrast, an increase in SOM removal from 67 to 118 mg was observed in soil YA (high percentage of SOM) with rapid H_2O_2 decomposition and high initial O_2 generation. Therefore, these results indicate that rapid initial O_2 generation was obtained to reduce removal of crude oil when H_2O_2 was applied to the soil containing high percentage of SOM.

Figure 2a and Figure 2c indicate that there was minimal consumption of H_2O_2 in the two soils containing 900 mM of H_2O_2 after 3 h of reaction time. In soil YA, 58% of the H_2O_2 was consumed, whereas only 31% was consumed in soil XI, which has a lower percentage of SOM. A minimal initial rate of O_2 gas generation was achieved when 900 mM of H_2O_2 was added, which is in agreement with the decomposition of hydrogen peroxide discussed above. In soil YA, 246 mL of O_2 gas was produced per hour, which was higher than that in soil XI (90 mL/h). Therefore, the rates of H_2O_2 loss and O_2 gas generation in soils are dependent on the TPH/SOM ratio and H_2O_2 concentrations.

Figure 3b shows the molar ratio of produced O_2 to initial moles of H_2O_2 for each soil. In soil YA (high percentage of SOM), the H_2O_2 more easily decomposed to oxygen, resulting in a stoichiometric coefficient (n) of 0.1-0.6, whereas the stoichiometric coefficient (n) of soil XI is 0.1-0.3. The amount of oxygen production fit the H_2O_2 reaction well (Figure 2a, c). In addition, the values of n decreased with increasing H_2O_2 concentrations. Values lower than 0.5 would indicate extensive oxidation of SOM [e.g. Romero et al. (17)]. However, our results indicate that the concentration of the SOM in soil XI with a low value of n decreased slightly after oxidation. One explanation is that the SOM in soil XI underwent oxidation and modification but was not mineralized, in agreement with the results of [e.g. Romero et al. (6)]. A high rate of removal of TPH in soil XI indicates that this modification of the SOM may improve the oxidation of crude oil.

Therefore, in soil XI (lower percentage of SOM), the H_2O_2 decayed more slowly, and O_2 gas was also

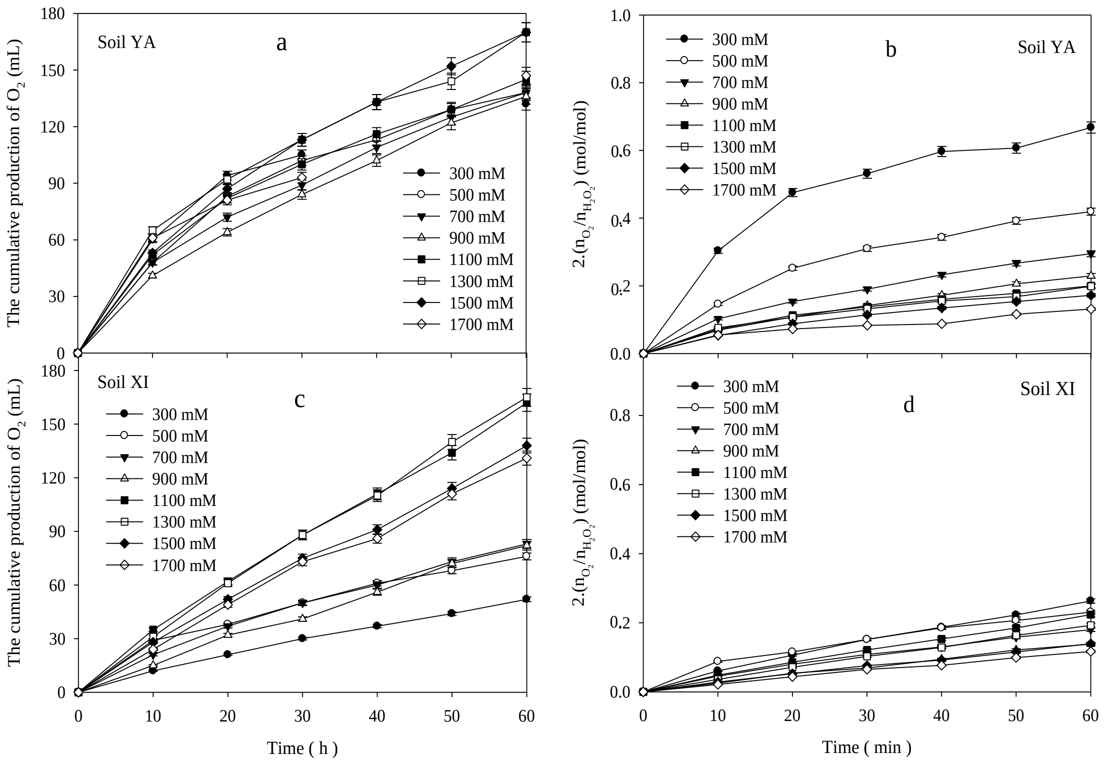

Figure 3. Initial O_2 generation from H_2O_2 decomposition in the two studied soils. (a) initial O_2 production in soil YA, (b) O_2/H_2O_2 in soil YA, (c) initial O_2 production in soil XI, (d) O_2/H_2O_2 in soil XI. Initial Fe^{2+} concentration was 5.8 mM, pH=7.5.

produced slowly for 10 min. The SOM in soil XI underwent oxidation and modification but was not mineralized, and greater TPH removal (from 36 to 186 mg) was observed in soil XI. However, during the remediation of soils with higher percentages of SOM (such as soil YA), the H_2O_2 decayed rapidly, and O_2 gas was produced rapidly for 10 min. This finding indicates that SOM may have improved H_2O_2 decomposition, and thus, the O_2 gas generation reduced hydroxyl radical formation in soil YA. This is a waste of the chemical [e.g. Yokoyama et al. (19)]. [e.g. Lindsey et al. (1) reported that fulvic acid and humic acid also reduced hydroxyl radical formation under most conditions], which is consistent with our results. In this case, a large amount of H_2O_2 may be wasted when high concentrations are applied.

Ratio of Crude Oil Removed to H_2O_2 Consumed

A significant increase in O_2 gas generation in both soils was observed with the increase in the H_2O_2 dosage when the H_2O_2 concentration exceeded 900 mM (Figure 4a). In soil YA (high percentage of SOM), the cumulative production of O_2 gas increased from 130 to 170 mL in 60 min; these values were higher than those in soil XI (80-160 mL). However, no increase in TPH removal per gram of H_2O_2 (remained at approximately 60 mg) was observed when H_2O_2 concentrations increased from 1100 mM to 1700 mM in soil XI whereas in soil YA, the amount of crude oil removed decreased with the increase of H_2O_2 concentration (Figure 4b). These results indicate that O_2 gas can be a major product to limited crude oil oxidation at high H_2O_2 concentrations (above 900 mM). Evidently, the chain reactions scavenge hydroxyl radicals and act as a sink for H_2O_2 depletion; which is agreement with Yokoyama results [e.g. Yokoyama et al. (19)]. [e.g. Seol et al. (18) also reported that an excessive usage of H_2O_2 relative to iron catalysts ($Fe^{2+}/H_2O_2<1/330$) tends to lower the efficiency of contaminant removal by iron chelation in a citric acid system], which is consistent with our results.

The soil exhibiting higher rates of H_2O_2 loss (soil YA) generally yields more O_2 gas due to the presence of a more rapid, competing H_2O_2 decomposition process. Although the rates of •OH formation in these soils can be significant, the faster competing process ultimately limits the overall yield of •OH. In contrast, in the soil exhibiting slow rates of H_2O_2 decay (soil XI), the yield of O_2 gas can be quite low, and •OH may be a major product.

Conclusions

Crude oil in soil was readily oxidized by H_2O_2 in the soil with a higher TPH/SOM ratio (low percentage

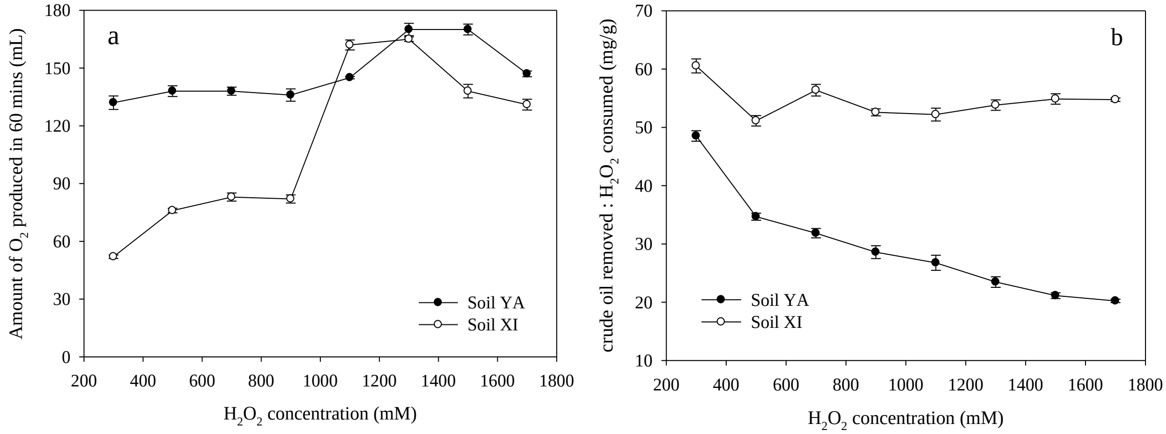

Figure 4. Effect of O_2 production on H_2O_2 utilization. (a) O_2 production and (b) H_2O_2 utilization. Initial Fe^{2+} concentration was 5.8 mM, pH=7.5.

of SOM) because the SOM is oxidized and modified but not mineralized. This modification of the SOM may improve the oxidation of crude oil. In addition, less O_2 was produced and more •OH was formed during the process of H_2O_2 decomposition for the soil with high ratio of TPH/SOM. This study provides environmental engineering researchers and practitioners with updated information about the effects of the crude oil to SOM ratio on H_2O_2 decomposition and oxidation of crude oil in contaminated soils. The slight destruction of SOM may produce free organic matter with the ability to bind iron. Further experiments are required to investigate how the oxidation of SOM influences concentrations of iron bound to soil matrix.

Acknowledgments

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