

EFFECTS OF SURFACTANTS ON THE FENTON DEGRADATION OF PHENANTHRENE IN CONTAMINATED SEDIMENTS

Sang-Hyun Jee, Seok-Oh Ko[†] and Hae-Nam Jang^{*}

Department of Civil Engineering, Environmental Research Center, Kyunghee University, Suwon, Korea

^{*}Kumho Institute of Construction Technology, Seoul, Korea

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Abstract : Laboratory batch experiments were conducted to evaluate the Fenton degradation rates of phenanthrene. Fenton reactions for the degradation of phenanthrene were carried out with aqueous and slurry phase, to investigate the effects of sorption of phenanthrene onto solid phase. Various types of surfactants and electrolyte solutions were used to evaluate the effects on the phenanthrene degradation rates by Fenton's reaction. A maximum 90% removal of phenanthrene was achieved in aqueous phase with 0.9% of H₂O₂ and 300 mg/L of Fe²⁺ at pH 3. In aqueous phase reaction, inhibitory effects of synthetic surfactants on the removal of phenanthrene were observed, implying that surfactant molecules acted as strong scavenger of hydroxyl radicals. However, use of carboxymethyl-β-cyclodextrin (CMCD), natural surfactant, showed a slight enhancement in the degradation of phenanthrene. It was considered that reactive radicals formed at ternary complex were located in close proximity to phenanthrene partitioned into CMCD cavities. It was also shown that Fenton degradation of phenanthrene were greatly enhanced by addition of NaCl, indicating that potent radical ion (OCl⁻) played an important role in the phenanthrene degradation, although chloride ion might be acted as scavenger of radicals at low concentrations. Phenanthrene in slurry phase was resistant to Fenton degradation. It might be due to the fact that free radicals were mostly reacting with dissolved species rather than with sorbed phenanthrene. Even though synthetic surfactants were added to increase the phenanthrene concentration in dissolved phase, low degradation efficiency was obtained because of the scavenging of radicals by surfactants molecules. However, use of CMCD in slurry phase, showed a slight enhancement in the phenanthrene degradation. As an alternative, use of Fenton reaction with CMCD could be considered to increase the degradation rates of phenanthrene desorbed from solid phase.

Key Words : Phenanthrene, Advanced oxidation process, Surfactant, Sediment, Carboxymethyl beta cyclodextrin (CMCD)

INTRODUCTION

Sediments are a major problem in aquatic ecosystem management and restoration. Nutrients, heavy metals, and toxic chemicals are found in much higher concentrations in sediments than in the overlying water column.

Among many pollutants, polycyclic aromatic hydrocarbons (PAHs) generated by a number of industrial activities are accumulated in sediments and pose severe environmental problems. Many PAHs are potential or proven carcinogens and highly hydrophobic. For these reasons, PAHs are often strongly bound to particles causing sediment contamination.

A number of different technologies are available for the removal of PAHs in contaminated sediments. Advanced oxidation processes (AOPs)

[†] Corresponding author
E-mail: soko@khu.ac.kr
Tel: +82-31-201-2999, Fax: +82-31-202-8854

have been widely used to enhance oxidation kinetics, resulting from the formation of the hydroxyl radicals, a powerful and non-specific oxidant. In Fenton process, hydroxyl radicals are produced by the reaction of hydrogen peroxide and ferrous iron and show excellent efficiency in the degradation of PAHs in aqueous solution. However, PAHs in the presence of sediments are highly partitioned into solid phase because of the hydrophobicity of PAHs and high content of organic matter in sediments. Particle-associated PAHs may be incapable of reacting with aqueous phase radicals, because radicals react with dissolved species much faster than they cross the solid-liquid interface and react with sorbed PAHs.¹⁾ Therefore, sorption of PAHs to sediments may result in decreased PAH removal rates. Correspondingly, sorption-desorption kinetics of PAH to sediments need to be understood to predict degradation rates of PAH by AOPs. Increase of PAH mass in the aqueous phase using some additives is also necessary to enhance the oxidative degradation rate of PAH.

In this study, the effect of sorption to sediment particles on PAH oxidation by radicals was evaluated. The sediment-water distribution of model PAH compound, phenanthrene, was examined. Generally, it has been known that surfactants could increase the PAH concentration in aqueous phase. Therefore, oxidation experiments were carried out with several synthetic and natural surfactants to increase the PAH mass in aqueous phase and degradation rate of PAH. Degradation rates of phenanthrene using Fenton's reagent were evaluated for aqueous and slurry conditions.

MATERIALS AND METHODS

The sediment samples used in this study were collected from Buan, Chunbuk, Korea. All samples were stored in amber glass containers and refrigerated at 4°C until used. Sediment pH was determined by equilibrating 10 g of sediment with 10 mL of water on end-over-end shaker for 1 day. A pH meter and electrode

(Orion 720A-plus) was used to measure pH of sediment samples. Total organic matter content was determined by drying sediment samples in 105°C oven for 24 hr followed by ignition in a 550°C oven for another 24 hr. Losses resulting from drying and ignition were determined gravimetrically. Phenanthrene (Aldrich, ≥99%) was used as model PAH. Hydrogen peroxide(30 wt%), ferrous sulfate, Triton X-100, Sodium Dodecylsulfate (SDS), Dodecyltrimethylammonium bromide (DTAB), and carboxymethyl-β-cyclodextrin (CMCD) was obtained from Aldrich Co. All other chemicals were of analytical grade, unless specified. Phenanthrene concentration was analyzed using a HPLC (Younglin, Inc.) equipped with autosampler, UV/VIS detector(254 nm), and X-terra C18 column (5 μm, 4.6× 250 mm, Waters, Inc.). Mixture of acetonitrile and water (70:30) was used as mobile phase and its flow rate was 1 mL/min. The oven temperature was maintained 30°C.

To measure the rate of chemical transformation of phenanthrene in aqueous phase by Fenton's reagent, phenanthrene solution was added to bottle (250 mL). Aliquots of a stock solution of hydrogen peroxide with an original concentration of 30% were injected into the bottle to give several concentrations. Then, ferrous sulfate solution was added. The pH in the experiment systems was adjusted with few drops of H₂SO₄ and NaOH solutions. After predetermined time, a fraction of sample solution was taken and added to quenching solution (MeOH) to stop further reaction.²⁾ Sample solution was passed through pasteur pipet filled with glass wool to remove particulates and the filtrate was analyzed for phenanthrene concentration. To evaluate the effects of surfactants, various concentration of surfactant was added. Sediment sample was artificially contaminated with phenanthrene and its initial concentration was about 3 g/kg-sediment.

RESULTS AND DISCUSSION

Fenton reaction of phenanthrene in aqueous solution

In preliminary experiments, it was observed that oxidation rates of phenanthrene by hydrogen peroxide (3%) alone were negligible (shown in Figure 1). A result for the Fenton's oxidation of phenanthrene was shown in Figure 2. Different concentrations of hydrogen peroxide and ferrous sulfate were used and the pH was adjusted to 3.0. About 90% of phenanthrene degradation was achieved within 1.5 hours and the rates were found to be dependent upon the ferrous ion concentration. The amounts of iron precipitates generated by Fenton's reaction ($H_2O_2 = 0.9\%$, $Fe^{2+} = 300\text{ mg/L}$, phenanthrene = 0.8 mg/L) was measured by filtration after pH adjustment to medium value (8.0) and found to be about 130 mg/L .

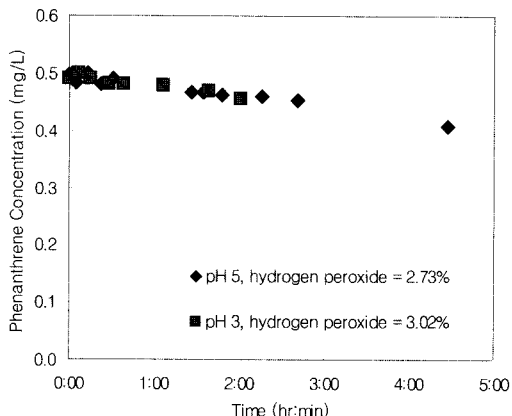


Figure 1. Effect of hydrogen peroxide on phenanthrene degradation.

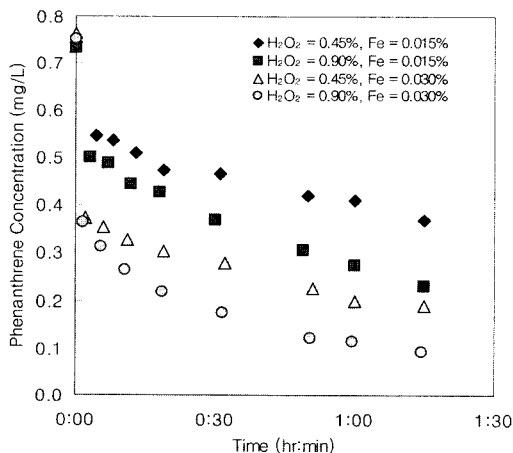


Figure 2. Fenton degradation of phenanthrene as a function of Fe^{2+} and H_2O_2 concentration.

As surfactant solution added into phenanthrene contaminated, micelles were formed. Aqueous phenanthrene was partitioned into hydrophobic cores of micelles, resulting in enhanced solubilization of phenanthrene. Fenton reaction for the phenanthrene degradation was examined in the presence of different types of surfactant micelles, as shown in Figure 3. Solution pH was adjusted to 3.0 and concentration of H_2O_2 and Fe^{2+} was 0.9% and 300 mg/L , respectively. When nonionic surfactant, Triton X-100, was added, phenanthrene degradation rate was decreased, compared with that in the absence of surfactant. Additionally, Triton X-100 concentration was gradually decreased due to the reaction with radicals generated by Fenton reaction (data not shown here). This result indicated that hydroxyl radicals having non-specific characteristics were scavenged by both phenanthrene and surfactant micelles. Although total amount of PAH degraded by Fenton reaction could be increased due to its solubility enhancement by micellar solubilization, slower degradation rate was obtained in the presence of surfactant micelles.

It could be expected that head groups of SDS (anionic surfactant) form complexes with ferrous iron (cationic ion) and thus generate radicals adjacent to palisade layer of micelles, resulting in enhanced degradation of phenanthrene partitioned

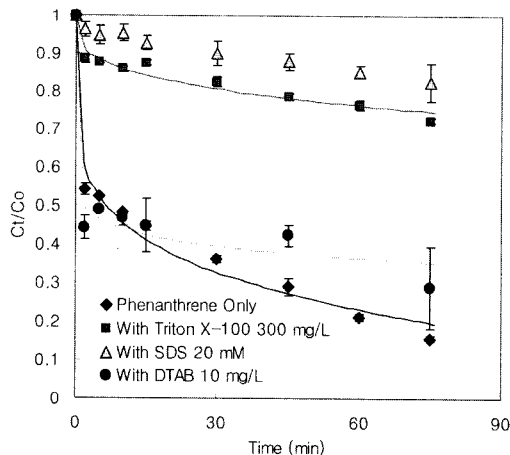


Figure 3. Effect of surfactant types on the Fenton degradation of phenanthrene. Initial phenanthrene concentration = 0.75 mg/L .

into micelle cores. However, low degradation of phenanthrene were observed, indicating that SDS did not form efficient complexes with soluble irons. In the case of cationic surfactant (DTAB), although higher rate was observed compared with other surfactant types, still lower degradation were obtained than those without surfactant addition. More detailed investigations for the Fenton degradation of PAHs are necessary in terms of surfactant types, concentrations, interactions between soluble irons and other ionic species.

In addition to synthetic surfactants, use of carboxymethyl- β -cyclodextrin (CMCD) on the Fenton degradation of phenanthrene was evaluated. CMCD, a natural biosurfactant, has been suggested as washing or flushing agent to remove heavy metals and organic contaminants, simultaneously.³⁾ While hydrophobic organics is partitioned into hydrophobic cavity of CMCD, heavy metal combines with the oxygen atom at the edge of CMCD, forming the ternary complexes (PAH-CMCD-iron).⁴⁾ It can be expected that Fenton reagent, Fe^{2+} form complexes with CMCD and generated hydroxyl radicals adjacent to PAH partitioned into CMCD cavity, resulting in direct reactions between radicals and PAHs. Figure 4 proved that addition of CMCD enhanced the Fenton degradation rate of phenanthrene.

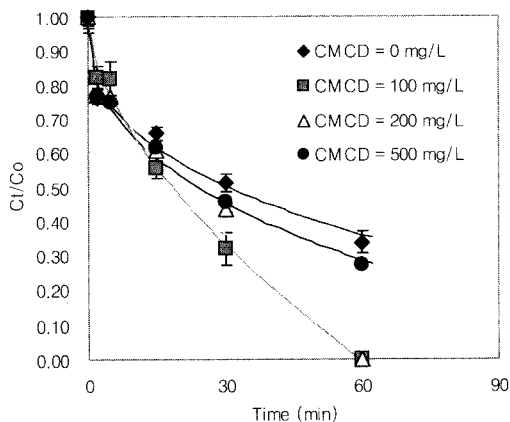


Figure 4. Fenton degradation of phenanthrene as a function of CMCD concentration. Initial phenanthrene concentration \cong 0.75 mg/L.

Therefore, natural surfactant would be more appropriate solubility enhancing agent than synthetic surfactant that acted as active scavenger of radicals.

Additionally, effect of chloride ion on the PAH degradation was evaluated. As shown in Figure 5, higher degradation rates of phenanthrene were observed as NaCl concentrations increased. Although Cl^- ion was known to be scavenger of hydroxyl radicals²⁾, it was considered that chloride ions could form hyperchlorite radicals (OCl^\cdot) and contribute to the further degradation of phenanthrene.⁵⁾

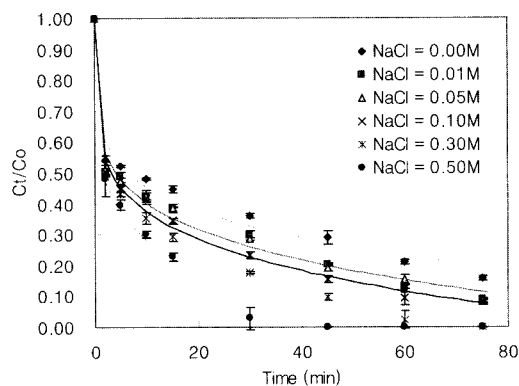


Figure 5. Effect of NaCl concentration on the Fenton degradation of phenanthrene. Initial phenanthrene concentration \cong 0.75 mg/L.

Fenton degradation of phenanthrene-contaminated sediment slurry

As mentioned above, PAH such as phenanthrene has high hydrophobicity and thus show strong affinity to solid phases. Therefore, to remove PAHs sorbed onto solid phase, desorption of PAHs from solid phase has to be preceded by using natural or synthetic surfactants. In this section, Fenton reaction of phenanthrene in the presence of solid phase was investigated to evaluate the relative oxidation efficiency of PAH, the effects of solid phase on the Fenton oxidation, and to find out appropriate method to enhance the treatment efficiency of PAH-contaminated sediment slurry.

Sorbents used in this study was kaolin (Aldrich)

and a sediment collected from Buan, Chunbuk, Korea. Batch experiments were conducted and solid/liquid ratio was 1:5. For kaolin slurry, phenanthrene concentration decreased to about 50% after 75 min when Fenton oxidation was occurred under the condition of pH 3.0, H_2O_2 0.9% and Fe^{2+} 300 mg/L (shown in Figure 6). At the same condition, the degradation rate of phenanthrene in the presence of kaolin was lower than that in the aqueous phase. This indicated that solid phase prevented hydroxyl radicals from approaching to the sorbed phenanthrene. Effects of solid phase on the phenanthrene degradation were much more evident in Buan sediment. As shown in Figure 7, the removal rate was about 20%,

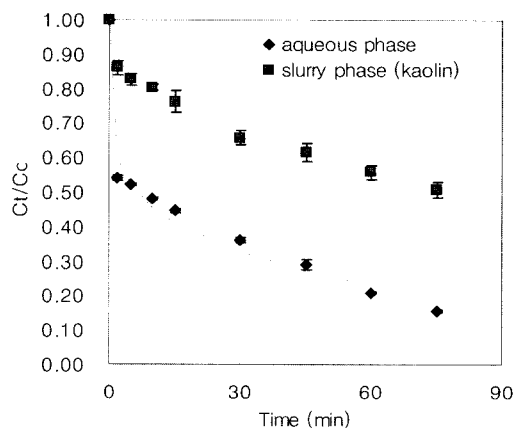


Figure 6. Effect of kaolin on the Fenton degradation of phenanthrene. Initial phenanthrene concentration ≈ 0.75 mg/L.

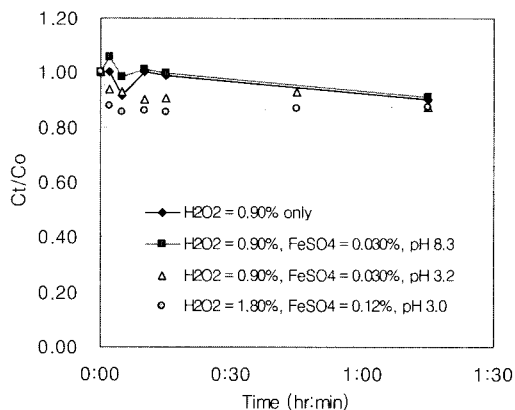


Figure 7. Fenton degradation of phenanthrene in Buan sediment slurry. Phenanthrene concentration was about 3 g/kg-sediment.

implying that sorption onto solid phase and existence of soil organic matter decreased oxidation efficiency of phenanthrene.

As surfactant molecules were added into the slurry, sorbed phenanthrene was desorbed and thus its concentration in aqueous phase increased. Degradation of phenanthrene in kaolin slurry was evaluated in the presence of surfactants. As shown in Figure 8, addition of Triton X-100 into the slurry resulted in lower degradation rate. It indicated that hydroxyl radicals, nonselective oxidants, scavenged by surfactant molecules could not efficiently attack phenanthrene partitioned into micelles. This result could be expected from the results that obtained from the Fenton oxidation of phenanthrene in aqueous and micellar phase described in above section.

However, the use of carboxymethyl- β -cyclodextrin (CMCD) on the Fenton degradation of phenanthrene in kaolin slurry showed a slight enhancement in the degradation of phenanthrene. As mentioned above, Fe^{2+} form complexes with CMCD and generated hydroxyl radicals adjacent to sorbed PAH partitioned into CMCD cavity, resulting in direct reactions between radicals and sorbed PAH. Figure 9 proved that addition of CMCD enhanced the Fenton degradation rate of

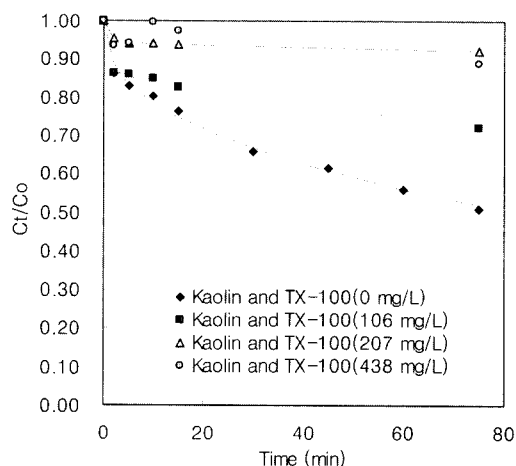


Figure 8. Fenton degradation of phenanthrene in kaolin slurry with addition of surfactant. Initial phenanthrene concentration in aqueous phase ≈ 0.75 mg/L.

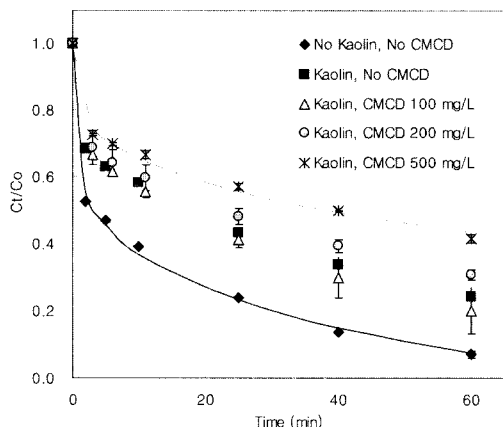


Figure 9. Effect of CMCD concentration on the Fenton degradation of phenanthrene in kaolin slurry. Initial phenanthrene concentration = 0.75 mg/L)

phenanthrene in slurry phase. Therefore, natural surfactant, such as CMCD would be more appropriate solubility enhancing agent than synthetic surfactants.

CONCLUSIONS

In order to evaluate their potential for the treatment of contaminated sediments, Fenton's reactions were investigated. Effects of addition of synthetic and natural surfactant to the aqueous and slurry phase on the Fenton's reactions were also evaluated.

In Fenton system with aqueous phase, about 90% phenanthrene degradation was achieved, at pH 3.0, 0.9% of H_2O_2 and 300 mg/L of Fe^{2+} . The low phenanthrene degradation rates were attained in the presence of synthetic surfactant solutions, indicating that hydroxyl radicals were non-specifically scavenged by organic compounds. In contrast, added CMCD enhanced Fenton degradation rates of phenanthrene by forming ternary complex including ferrous iron and organic pollutant, which enable hydroxyl radicals generated in close proximity to phenanthrene to directly attack the pollutants partitioned into CMCD cavity.

Fenton's reactions for the soil slurry showed lower efficiency than those for aqueous phase,

indicating that hydroxyl radicals could not easily attack the sorbed phenanthrene. Addition of synthetic surfactant to increase aqueous phase concentration of phenanthrene did not show enhanced Fenton's degradation, because of the non-specific characteristics of radicals. Meanwhile, it was expected that CMCD redistributed the phenanthrene (increase of aqueous phase concentration) and efficiently degrade phenanthrene partitioned into CMCD cavity. The use of CMCD could be a good alternative for the removal of hydrophobic organic pollutant in sediments.

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