

Oxidative Degradation of Pyrene Wastewater with Cetylpyridinium Chloride in Pyrite Suspension

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ABSTRACT

Degradation of polycyclic aromatic hydrocarbon (PAH) with surfactant in pyrite Fenton system was investigated in a closed batch reactor. Pyrene as one of the PAHs in the presence of cetylpyridinium chloride (CPC) as a cationic surfactant was gradually degraded in pyrite Fenton system by 96% in 180 min at initial pH 7 showing pseudo-first-order reaction kinetics (0.0194 min^{-1}), while pyrene in the absence of CPC decreased abruptly by 91% in 5 min, followed by slow decline showing second-order reaction kinetics. In a classic Fenton system, pyrene in the presence of CPC was degraded by 35% in 180 min at initial pH 3. Pyrite Fenton system provided continuous effective production of OH radical (OH•), resulted from slow but sustainable dissolution of ferrous ion from the pyrite surface. A main oxidant to degrade pyrene was the OH• in the presence of CPC. CPC was removed successfully (94%) in the pyrite Fenton system as well, producing carbon dioxide and ammonium as main final products. This study supports that the pyrite Fenton system can be a promising remediation technology to treat toxic wastewater containing PAHs and surfactants coming from soil washing processes.

Keywords: Pyrene, Cetylpyridinium chloride, Pyrite, Fenton reaction, OH•

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are representative environmental contaminants composed of two or more fused aromatic rings and are ubiquitous pollutants because they can be produced by natural incomplete combustion such as forest fires as well as anthropogenic sources like utilization of fossil fuel (Beltrán et al. 1998). They have attracted much attention because most of them are mutagen and carcinogen (Menzie et al. 1992). However, thermal desorption after excavation has been considered to require relatively expensive remediation cost while biological treatment has been reported to be limited because of its slow reaction kinetics and low bioavailability for PAHs resulted from their high hydrophobicity and low water solubility (Mueller et al. 1991, Silva et al. 2009). Therefore, soil washing with surfactant has been studied as one of the most promising technologies to remove PAHs efficiently (Mulligan et al. 2001).

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The washing process is efficient, but the contaminants are not degraded and the wastewater containing surfactants as well as contaminants can be produced during the treatment. The complex surfactant wastewater from PAH remediation process (i.e., soil washing) may be rather persistent to be treated by the conventional treatment processes because PAHs mixed with the surfactants composed of large molecules with complex organic groups are recalcitrant and unreactive in aquatic environments (Sáez et al. 2010). Several advanced oxidation processes (AOPs) using various methods such as ozone (Haapea and Tuhkanen 2006), photocatalyst (Wen et al. 2003), Fenton reagent (Saxe et al. 2000) to treat this kind of effluents have been focused (Rivas 2006). Fenton reaction among the processes applying various iron sources has been widely used for the oxidative degradation of organic compounds due to its high oxidative capacity (Duesterberg and Waite 2006, Smith et al. 2006). To initiate the Fenton reaction, Fe(II) catalyzes the decomposition of hydrogen peroxide to generate a strong and relatively non-specific oxidant, hydroxyl radical ($\text{OH}\cdot$) ($\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}\cdot + \text{OH}^-$) (Walling 1975). However, limitations in the Fenton reaction, i.e., reactive radical scavenging due to high concentration of aqueous Fe(II) and low operation pH (pH 3~4) to avoid iron precipitation ($\text{Fe}(\text{OH})_3$) should be overcome for the proper application to the contaminated soil and groundwater (Beltrán et al. 1998). To cope with the limitations, different types of Fenton systems using Fenton-like reaction (Matta et al. 2008) and modified Fenton reaction (Lee and Lee 2010) have been studied and developed. Another problem that should be dealt with during Fenton reaction based on contaminant degradation is the risk of incomplete degradation and the production of toxic intermediates. Fenton reactions have been known to cause poor mineralization and production of toxic transformation products (Lee et al. 1998, Lee and Hosomi 2001, Lundstedt et al. 2006). Various transformation products including oxygenated and hydroxylated PAHs, aldehydes, and carboxylic acids have been reported. The oxygenated PAHs have been known as more persistent and some of them have been proposed to be accumulated as final products potentially (Lundstedt et al. 2006). In addition, Lundstedt et al. (2007) reported that some oxygenated PAHs were even more toxic than their parent compounds. Limited study on transformation product study for PAHs also should be solved. For example, Sigman et al. (1998) reported that 1-hydroxyphrene, 1,6- and 1,8-pyrenequinone were detected as a pyrene by-products during photocatalytic reaction while Zeng et al. (2000) proposed that various aldehydes and long-chain aliphatic hydrocarbons. No research for integrated product study has been conducted to date.

In the present study, pyrite which is one of the most abundant metal sulfide occurring in the most ancient magnetic rocks and in more recent sedimentary deposits (Lowson 1982) was chosen to investigate the potential approach to mitigate the production of toxic oxy-PAH intermediates as well as to solve the expected limitations of Fenton reaction upon the treatment of PAHs. Pyrite has been successfully employed for the oxidative degradation of 2,4,6-trinitrotoluene (TNT) (Matta et al. 2008), trichloroethylene (TCE) (Che et al. 2011a), and carbon tetrachloride (CT) (Che and Lee 2011b).

The aim of this work was to apply the pyrite Fenton system to the treatment of recalcitrant complex surfactant wastewater discharged from soil washing processes. Pyrene was selected as a model PAH because it is a mutagen and has been reported to be found frequently in contaminated soils although it is not classified as a carcinogen (Schneider et al. 1996). A cationic surfactant, cetylpyridinium chloride (CPC), was selected as a model surfactant for the soil washing processes, since it is not biodegraded completely and more toxic than other surfactants with respect to plants and animals (Eng et al. 2006). The objectives of this study were to characterize the oxidative degradations of pyrene in CPC solution as well as CPC in pyrite Fenton system, to identify the major transformation products from the complex surfactant wastewater, and to elucidate the degradation mechanism of surfactant as well as PAH and their degradation pathway by pyrite Fenton reaction.

2. EXPERIMENTAL SECTION

2.1. Chemicals

Chemicals used in this study were cetylpyridinium chloride (CPC) (>99.0%, Sigma), pyrene (98%, Aldrich), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99%, Sigma), and hydrogen peroxide (H_2O_2 , 30 wt. %, Junsei). Nitric acid (60%, Junsei) was used for the remove of oxidized surface layer on pyrite. Sodium hydroxide (97 %, Sigma) and sulfuric acid (99.999%, Aldrich) was used to adjust initial suspension pHs of batch samples. Tert-butanol (t-butanol, >99%, Sigma) for $\text{OH}\cdot$ scavenger and chloroform (99.9%, Sigma) for superoxide radical ($\text{O}_2\cdot^-$) scavenger were used. Acetonitrile (CH_3CN , 99.9%, J.T.Baker) as an eluent for pyrene analysis by high-performance liquid chromatograph (HPLC), methanol (CH_3OH , 99.9%, Merck) for the preparation of stock solutions and samples, and ethanol (95%, Jin Chemical) for pyrite pretreatment were all HPLC grade. Acetone (99.9%, Merck), CH_3CN (described above), dichloromethane (DCM, 99.9%, Merck) for the extraction of pyrene (gas chromatograph/mass spectrometry (GC/MS) analysis) and the preparation of stock solution of pyrene and its transformation products were all HPLC grade. For pyrene transformation products study, 1-hydroxypyrene (1-HP, 98%, Aldrich), acetic anhydride ($\geq 98\%$, Sigma-Aldrich), sodium dichromate dehydrate ($\geq 99.5\%$, Sigma-Aldrich), basic alumina (0.063-0.200 mm, Merck), diisooctyl ester 1,2-benzenedicarboxylic acid (diisooctyl phthalate (DIOP), $\geq 99\%$, Aldrich), stearic acid ($\geq 98.5\%$, Sigma), and palmitic acid ($\geq 99\%$, Sigma), hexadecane (99%, Sigma-Aldrich), and octadecyl isocyanate (98%, Sigma) were purchased. For the analysis of CPC, orange G (Sigma), sodium acetate trihydrate (99%, Sigma-Aldrich), acetic acid (99.7%, Junsei) and chloroform ($\geq 99.0\%$, Sigma-Aldrich) were used. Distilled water was purified by ultrapure filtration system (ELGA PURELAB Classic system) to obtain $18 \text{ M}\Omega \cdot \text{cm}$ pure deionized water (DIW). DIW was used for characterization tests as controls (i.e., oxidative degradation of pyrene by pyrite Fenton reaction and classic Fenton reaction). DIW was used for the preparation of all solutions. All the chemicals were used without further purification.

Pyrite (FeS_2 , Zacatecas, Mexico) was purchased from Ward's natural science. It was grounded using a ceramic mortar and pestle. The smashed particles were passed through a $150 \mu\text{m}$ sieve, ultra-sonicated in ethanol for 5 min to remove fine particles, and washed with 1 M nitric acid to eliminate oxidized surface. The pyrite sample was rinsed with DIW and then with ethanol to dehydrate the surface and finally dried and stored in a closed glass vial, which is placed in an anaerobic chamber before use. Prepared pyrite was analyzed by X-ray diffraction (XRD) to investigate the purity and identity. It showed a good agreement with those in Joint Committee on Powder Diffraction Standards (JCPDS) diffraction data files (JADE 9, Materials Data, Inc.) (data not shown). 1,6-pyrenequinone (1,6-PQ) and 1,8-pyrenequinone (1,8-PQ) as pyrene degradation products were synthesized based on the method by Cho and Harvey (1976).

2.2. Experimental Procedures

Batch kinetic isotherm experiments were conducted at room temperature ($25 \pm 0.5^\circ\text{C}$) in aerobic condition for the characterization of pyrene degradation by the pyrite Fenton reaction using an amber borosilicate glass vial (nominal volume: 20 mL, Kimble) with open-top cap with three layered septum system (Lee and Batchelor 2003). CPC solution (1.8 mM) was prepared by dissolving exact amount of CPC (0.6444 g) in 1 L of deionized water (DIW) in large Erlenmeyer flasks. The initial solution pH of CPC was adjusted to 7 using NaOH (0.4 M). An exact amount of crystalline pyrene (0.0101 g) was then added into the flask wrapped in aluminum foil to avoid photodegradation and stirred with a magnetic stirrer for at least 48 hr. The solutions were filtered through a medium porosity fritted glass funnel to remove any

microcrystalline pyrene, resulting in 42.03 μM pyrene solution with CPC. An exact amount of pyrite (0.03 g) were weighed and kept into the reactors followed by the addition of 10 mL of CPC pyrene solutions, resulting in 3 g L^{-1} (i.e., 25 mM Fe(II)) pyrite suspension. Fenton reaction was initiated by spiking 10 μL H_2O_2 (i.e., 9.8 mM) into the vials and capped immediately. All the reactors were mounted on a tumbler and rotated at 7 rpm for 180 min. Similar batch experiments have been conducted also for classic Fenton reaction using ferrous sulfate heptahydrate (25 mM Fe(II)) to compare the kinetics of pyrene degradation with pyrite. During experiments, the probable losses of pyrene due to volatilization, photodegradation by sunlight, oxidative degradation by H_2O_2 , sorption on reactor wall and pyrite surface were examined using three controls (CPC + pyrene, CPC + pyrene + H_2O_2 , and CPC + pyrene + pyrite).

Batch mechanistic tests were conducted to measure Fe(II), Fe(III), and H_2O_2 concentrations in classic Fenton system as well as pyrite Fenton system to investigate the role of pyrite in Fenton reaction under the same experimental procedures and conditions described above. The degradation kinetics of pyrene was monitored during characterization experiments by measuring the aqueous pyrene concentration at each sampling time. An exact amount (100 μL) of t-butanol (1 M) was added to each sample vial to quench Fenton reaction and each sample was filtered using membrane filter (0.2 μm). All controls and samples were prepared in duplicate and analyzed within 24 hr. Unless stated otherwise, all experiments were conducted in aerobic condition.

CPC degradation was monitored by measuring aqueous CPC concentration at each sampling time based on the same procedures described above.

Pyrene transformation product study was conducted to investigate the fate of CPC as well as pyrene in pyrite Fenton system. All experimental procedures and reaction conditions were the same as described above. With respect to each sampling time, 7 mL of dichloromethane (DCM) was added to sample vial and vigorously mixed for 30 sec to extract residual pyrene after Fenton reaction. The DCM layer was collected to 125 mL round flask. After conducting 2 more times of extraction, collected DCM was concentrated to 1 mL and transferred to 24 mL of amber borosilicate glass vials. The residual DCM was mildly dried using N_2 (99.9%) gas stream. An exact amount (1 mL for CPC-pyrene, 500 μL for pyrene) of ethyl ether for gas chromatograph/mass spectrometry (GC/MS) analysis and methanol for high-performance liquid chromatograph (HPLC) analysis was added to dissolve the pyrene residue. Each sample prepared was injected to GC/MS and HPLC to quantify the transformation products.

2.3. Experimental Procedures

Appropriate amount of samples were withdrawn using a syringe at each sampling time and filtered using 0.2 μm membrane filters (Whatman). The filtered samples were mixed with 1 M t-butanol (i.e., OH radical quencher) into 2 mL GC amber vials and used for analysis with 24 hr. Pyrene concentration in aqueous solution was measured by a Varian ProStar HPLC (Varian Inc., Walnut Creek, CA) comprising a ProStar 210 binary pump, a ProStar 410 autosampler, and a ProStar 335 photodiode array detector. An aliquot amount (50 μL) of filtered sample was injected into the HPLC with a reverse-phase C18 column (250 mm \times 4.6 mm id, 5 μm). Mobile phase was consisted of 90% CH_3CN with DIW and the flow rate was 1.0 mL min^{-1} . Peaks were measured at 254 nm and identified by the retention time.

Colorimetric analyses to measure the concentrations of Fe species (Fe(II) and Fe(III)) and H_2O_2 in aqueous phase were performed by UV/Visible spectrophotometer (Agilent 8453). Aqueous samples were withdrawn by a syringe at each sampling time and filtered by 0.2 μm membrane filter (Whatman). To measure Fe(II) concentration, an aliquot of filtrate (1 mL) was introduced into the 15 mL test tube containing 1 mL of acid quench solution and 1 mL of

ferrozine solution. Analysis was conducted by shaking the tube for 2-3 sec, transferring whole aqueous mixture into a standard 1 cm quartz cuvette, and measuring the absorbance at 562 nm (ferrozine method) (Stookey 1970). Total aqueous Fe concentration can be measured using reductant solution instead of acid quench solution with the same analytical procedure with Fe(II) measurement described above. Fe(III) concentration can be calculated by subtracting the concentration of aqueous Fe(II) from total Fe. To measure H₂O₂ concentration, an aliquot of filtrate (100 µL) was introduced into the 15 mL test tube containing 2.8 mL of DIW and 0.1 mL of Ti(SO₄)₂ solution (2.9%, diluted in 1.2% H₂SO₄ solution). Analysis was conducted by shaking the tube for 2-3 sec, transferring whole aqueous mixture into a standard 1 cm quartz cuvette, and measuring the absorbance at 405 nm (titanium sulfate method) (Eisenberg 1943).

Ammonium (NH₄⁺) as a CPC transformation product was analyzed by Nessler method (UV/Visible Spectrophotometer with Humas analysis kit). Total organic carbon (TOC) was analyzed by TOC Combustion Analyzer, Apollo 9000.

Gas chromatograph/mass spectrometry (GC/MS) analysis, HP 5890II GC with a 5971 mass selective detector was operated on the scan mode. The separation was carried out on an HP-5 column (Agilent Technologies, Inc.: 30 m × 0.32 mm × 0.25 µm). The initial temperature was set at 45 °C and was held for 1 min. The oven was heated to 280 °C with a heating rate of 24 °C/min, and then the temperature was ramped to 310 °C with a rate of 5 °C/min with maintaining the temperature for 1 min. The solvent delay time was set for 9 min while the temperature of the transfer line was set at 170 °C. Mass spectra were recorded at 3 scans/s under electron impact of 70 eV at the mass range of 50 ~ 550 amu.

3. RESULTS AND DISCUSSION

3.1. Enhanced Degradation of Pyrene in CPC Solution by Pyrite Fenton Reaction

Fig. 1 shows the oxidative degradation kinetics of pyrene in the presence and absence of CPC in pyrite Fenton system at initial pH 7, which was characterized by measuring residual pyrene after the reaction. Reactions in control sample without pyrite (Control 1 and 2) showed no significant degradation of pyrene. The results from control samples without pyrite showed there was no significant loss such as volatilization in a batch reactor, photodegradation by sunlight or oxidation by hydrogen peroxide (98% pyrene recovery). When pyrite was added to pyrene solution, there was adsorption on the pyrite surface and pore in the presence and absence of CPC (15% and 61%), respectively. Relatively high portion for sorption of pyrene on pyrite surface in the absence of CPC was resulted from high hydrophobic property ($\log K_{ow} = 4.88$). However, the sorption effect on pyrene degradation in pyrite Fenton system was not significant because pyrene was not detected from extraction by acetonitrile after finishing Fenton reaction (data not shown). Classic Fenton reaction at initial pH 3 showed the limited degradation of pyrene (35%). Low reactivity and early termination of classic Fenton reaction was not only due to the quenching effect consuming OH• by aqueous Fe(II) (i.e., $Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH^-$) at high iron concentrations (Teel et al. 2001, Li et al. 2005, Duesterberg and Waite 2006) but also resulted from the little remnant H₂O₂ concentration after 10 min (Fig. 2). Pyrene with CPC in pyrite Fenton system was degraded to 96% in 180 min. The degradation pattern of pyrene with CPC showed pseudo-1st-order reaction kinetics (0.0194 min⁻¹). Pyrene without CPC in pyrite Fenton system abruptly decreased to 87% in 2 min, followed by slow decrease of pyrene. Then, it was fully degraded in 180 min. Compared to the degradation of pyrene with CPC, degradation of pyrene without CPC showed 2nd-order kinetics. Mild degradation kinetics of pyrene with CPC in pyrite Fenton system was resulted from the competitive consumption of OH• by CPC as well as pyrene. However, degradation of pyrene without CPC showed initial rapid kinetics, indicating that there is no competition to consume OH•. Relatively mild but full degradation of

pyrene with CPC in pyrite Fenton system can be attained due to the sustainable Fenton reaction by the longer durability of pyrite as an iron source, resulting partly from the generating reaction of Fe(II) ($\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$) (Mckibben and Barnes 1986, Che et al. 2011a). Intrinsic property of pyrite to lower solution pH to favorable value for Fenton reaction by producing H^+ in the presence of H_2O_2 ($2\text{FeS}_2 + 15\text{H}_2\text{O}_2 \rightarrow 2\text{Fe}^{3+} + 4\text{SO}_4^{2-} + 2\text{H}^+ + 14\text{H}_2\text{O}$) indicates that pyrite Fenton system can occur without pH adjustment process. Furthermore, property on CPC increasing the solubility of pyrene can make the present pyrite Fenton system advantageous for treating wastewater highly contaminated with PAHs (Fig. 1).

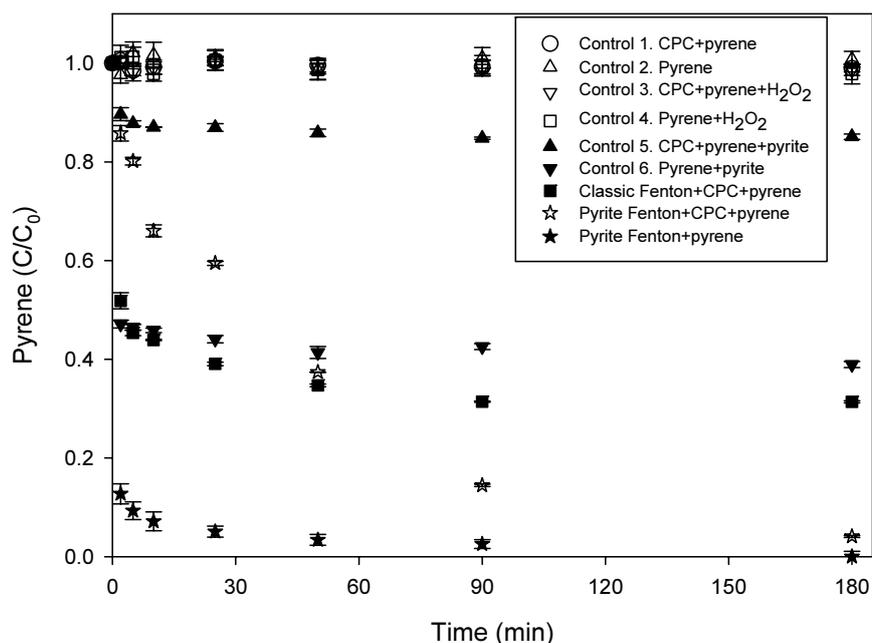
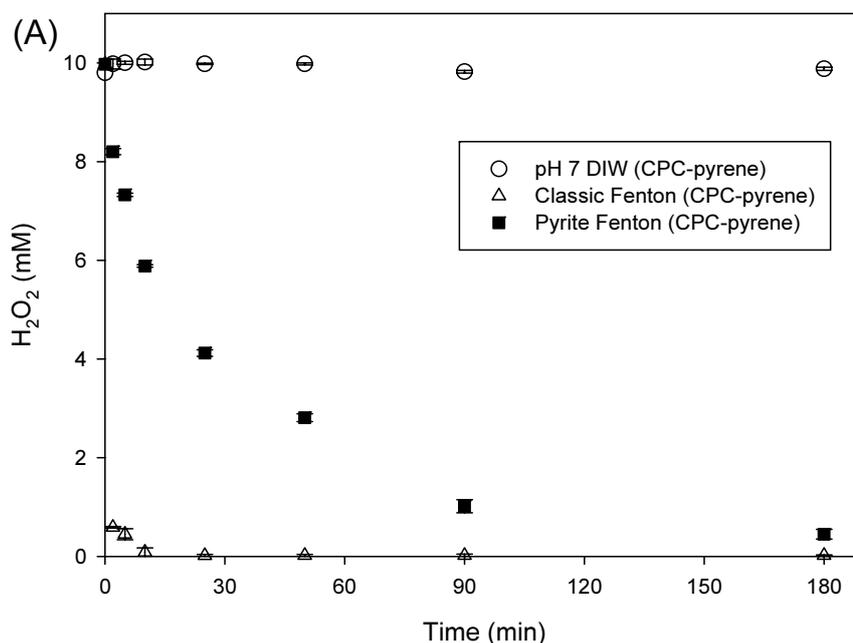


Fig. 1. Comparison of oxidative pyrene degradation in the presence and absence of CPC in pyrite Fenton system. Experimental conditions: $[\text{Pyrite}]_0 = [\text{Fe(II)}]_0 = 25 \text{ mM}$, $[\text{Pyrene}]_{0,\text{CPC}} = 42.03 \text{ }\mu\text{M}$, $[\text{Pyrene}]_0 = 0.213 \text{ }\mu\text{M}$, $[\text{CPC}]_0 = 1.8 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 9.8 \text{ mM}$, initial pH for pyrite Fenton = 7, and initial pH for classic Fenton = 3.

Fig. 2 shows the variation of Fe species and H_2O_2 during pyrite Fenton reaction and classic Fenton reaction. H_2O_2 concentration in control sample did not show any significant loss from the reaction system. H_2O_2 concentration in pyrite Fenton system decreased gradually by following pseudo-1st-order kinetics (0.0287 min^{-1}) while that in classic Fenton system rapidly decreased to 90% in 2 min, followed by 2nd-order kinetics showing subsequent slow decrease of H_2O_2 to 180 min. Cohn et al. reported that surface bound Fe(II) reacted with O_2 to release Fe(III) and consequently H_2O_2 increased in pyrite slurry system under aerobic condition without adding H_2O_2 (Cohn et al. 2006). However, it is difficult to suggest that there was the increase of H_2O_2 resulted from the reaction of surface bound Fe(II) with O_2 in our single-dose batch system. Fe(II) concentration in pyrite Fenton system was very low till 90 min (0.7113 mM) due to the faster reaction with H_2O_2 than dissolution from pyrite surface. It started to increase after consuming most of initial H_2O_2 as well as pyrene in pyrite Fenton system. During the given reaction time, the Fe(II) concentration did not reach equilibrium concentration. Fe(II) in classic Fenton system decreased abruptly by half concentration within very short time (i.e., only during initial 2 min). It did not decrease from the time because none of H_2O_2 was remained in classic Fenton system. The oxidative reactivity of pyrite Fenton system was evaluated by monitoring the values from calculating each ratio of the consumed H_2O_2 concentration to the amount of iron

dissolved in the pyrite Fenton system. Molar ratios of consumed H_2O_2 concentration to total dissolved iron concentration with respect to time increased slowly ($0.9 \sim 1.9$) but kept constant from 90 min (around 1.9), indicating that the Fenton reaction by pyrite slurry with H_2O_2 was kept occurring during the given reaction time. For the efficiency evaluation of H_2O_2 conversion to $\text{OH}\cdot$, the molar ratios of the consumed H_2O_2 to the degraded pyrene during pyrite Fenton reaction were calculated. The values, indicating the stoichiometry of the generation of $\text{OH}\cdot$ by the reaction between pyrite and H_2O_2 in the present system, were $165:1 \sim 260:1$, which indicates that generated $\text{OH}\cdot$ was efficiently reacted with pyrene in pyrite Fenton system. Previous study on this value in p-nitrophenol degradation by nano-magnetite Fenton reaction showed high ratio of the value ($1450:1$). This is due probably to the direct production of non-radicals such as O_2 and H_2O by 2 electron transfer reactions ($2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$) instead of the $\text{OH}\cdot$ generation (Sun and Lemley 2011). The rapid degradation of pyrene in CPC solution by pyrite Fenton reaction (Fig. 1) in this research can be explained by the proper amount of $\text{OH}\cdot$ and its efficient use for pyrene degradation. In addition, 5.6 mM of total aqueous iron concentration (22.4% of iron content in pyrite) at 180 min in pyrite Fenton system indicates that remnant 19.4 mM of iron in pyrite can be available more for the Fenton reaction. Based on the observation for H_2O_2 degradation kinetics along with Fe species variation in pyrite Fenton system and classic Fenton system, H_2O_2 reacted slowly but continuously with Fe(II) dissolved from pyrite surface in pyrite Fenton system while it reacted with high concentration of aqueous Fe(II) (25 mM) within very short time in classic Fenton system, resulting from quenching reaction consuming $\text{OH}\cdot$ by excessive Fe(II). This led to deceleration of pyrene degradation kinetics.



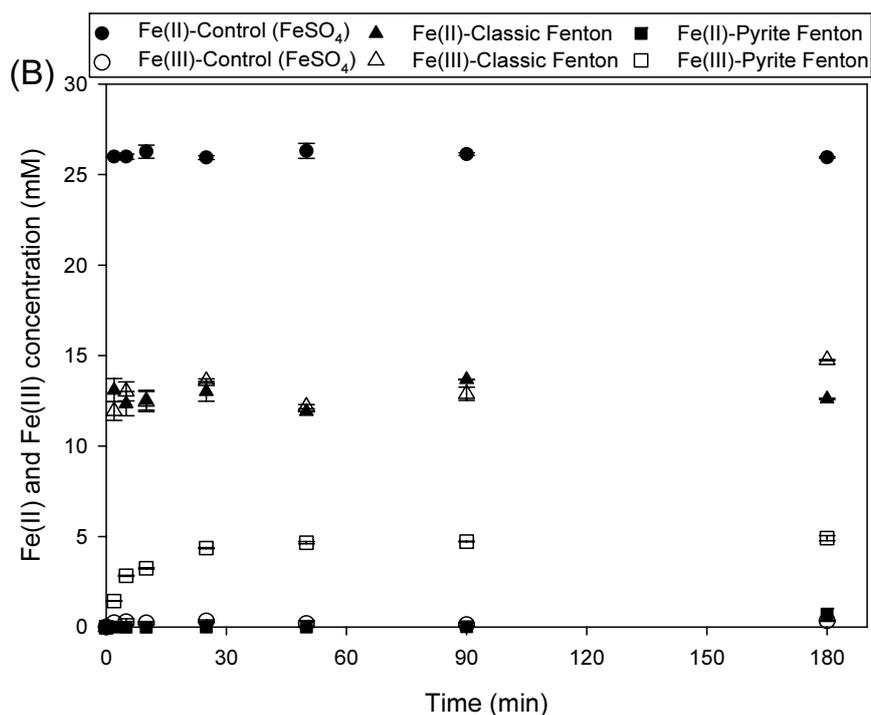


Fig. 2. Variation of (A) H_2O_2 and (B) Fe species during pyrite Fenton reaction and classic Fenton reaction. Experimental condition: $[\text{Pyrite}]_0 = [\text{Fe(II)}]_0 = 25 \text{ mM}$, $[\text{Pyrene}]_{0,\text{CPC}} = 42.03 \text{ }\mu\text{M}$, $[\text{CPC}]_0 = 1.8 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 9.8 \text{ mM}$, initial pH for pyrite Fenton = 7, and initial pH for classic Fenton = 3.

Fig. 3 shows the role of oxidant and reductant produced in pyrite Fenton system in degradation kinetics of pyrene in CPC solution. Pyrite Fenton system has been known to produce reductant ($\text{O}_2^{\bullet-}$) as well as oxidant ($\text{OH}\cdot$) (Che and Lee 2011b). The degradation kinetics of pyrene in CPC solution by pyrite Fenton reaction without adding either t-butanol or chloroform was properly described by the pseudo-1st-order kinetics ($0.0194 \pm 0.0024 \text{ min}^{-1}$, $R^2 = 0.9767$). When t-butanol was added in pyrite Fenton system as $\text{OH}\cdot$ scavenger, the kinetic rate of pyrene degradation significantly was 13 times lower (0.0015 min^{-1}) than that without t-butanol condition. Meanwhile, the degradation kinetic rate of pyrene in CPC solution by pyrite Fenton reaction in the presence of chloroform as $\text{O}_2^{\bullet-}$ scavenger decreased to 22.2% (0.0151 min^{-1}) compared to that without chloroform, however the influence of chloroform was not significant based on the degradation pattern shown in Fig. 3. This result indicates that pyrene in CPC solution was not reductively degraded by $\text{O}_2^{\bullet-}$ in pyrite Fenton system. Significant influence of t-butanol on pyrene degradation in CPC solution clearly shows that pyrene was oxidatively degraded by $\text{OH}\cdot$ in pyrite Fenton system.

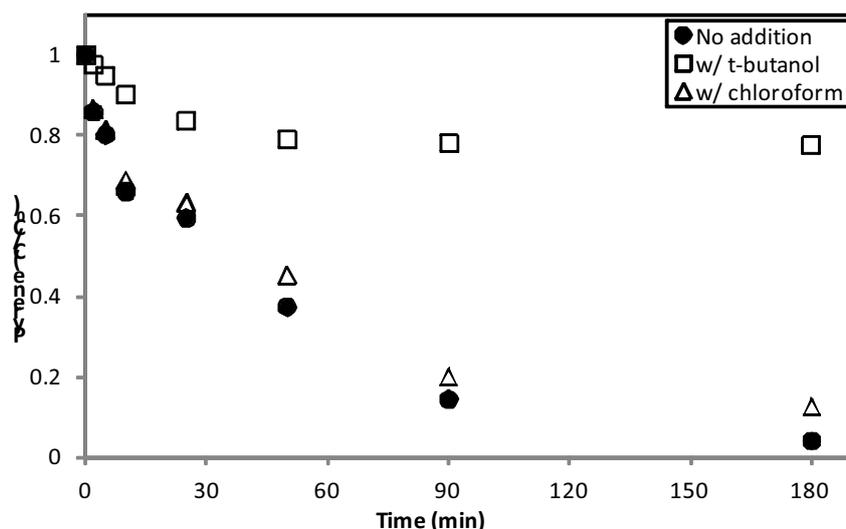


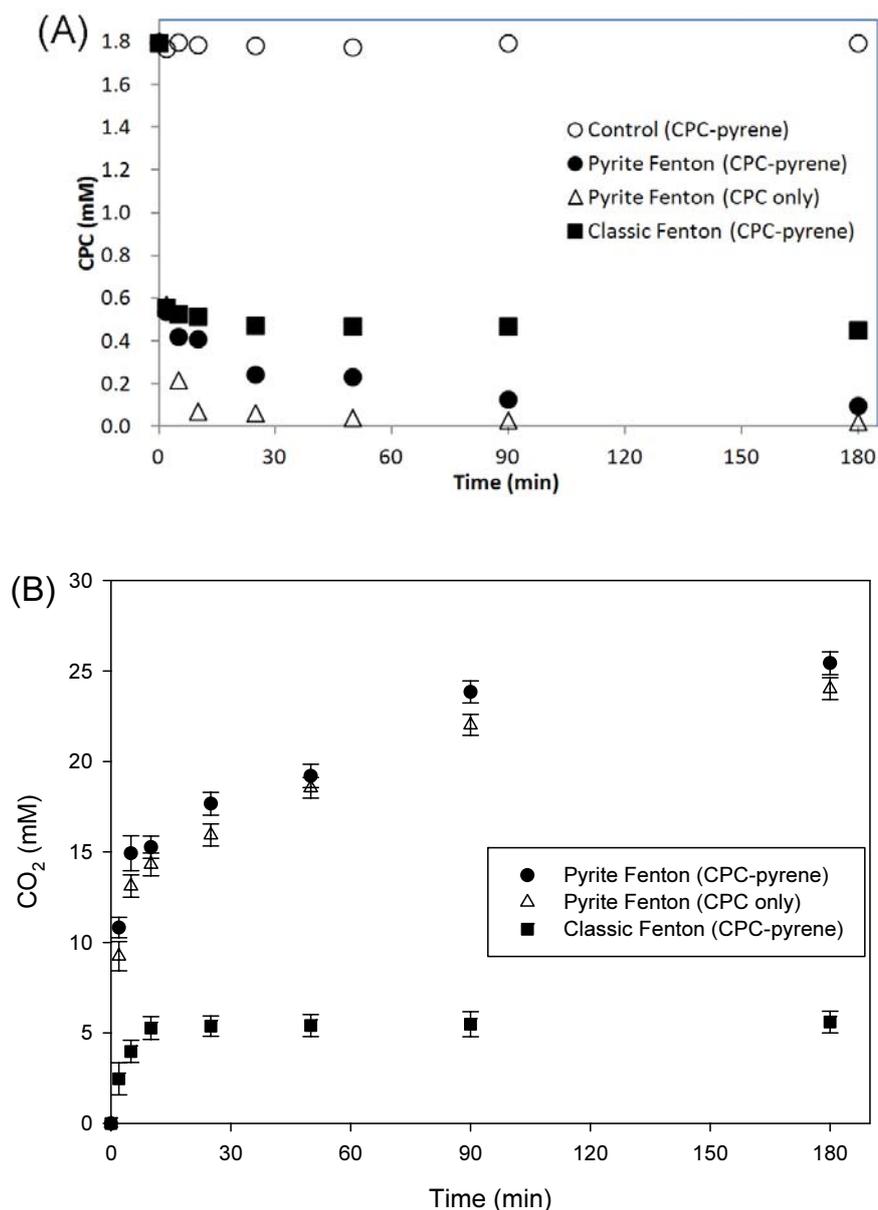
Fig. 3. Effect of t-butanol ($\text{OH}\cdot$ scavenger) and chloroform ($\text{O}_2\cdot^-$ scavenger) on the degradation kinetics of pyrene in CPC solution by pyrite Fenton reaction. Experimental condition: $[\text{Pyrite}]_0 = 25 \text{ mM}$, $[\text{Pyrene}]_{0,\text{CPC}} = 42.03 \text{ }\mu\text{M}$, $[\text{CPC}]_0 = 1.8 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 9.8 \text{ mM}$, $[\text{t-butanol}]_0 = 1 \text{ M}$, $[\text{chloroform}]_0 = 1 \text{ M}$, and initial pH for pyrite Fenton = 7.

3.2. Oxidative Degradation of CPC with Pyrene in Pyrite Fenton System

Fig. 4 shows the oxidative degradation of CPC in the presence and absence of pyrene by pyrite Fenton reaction and CPC by-products in pyrite Fenton system with/without pyrene and in classic Fenton with pyrene. Degradation of CPC in the presence of pyrene by pyrite Fenton reaction (0.4194 min^{-1}) was slower than that of CPC without pyrene in the same system (0.5317 min^{-1}), implying even small amounts of pyrene may affect CPC degradation kinetics by pyrite Fenton reaction due to its intrinsic recalcitrant structure. Classic Fenton system showed typical 2nd-order degradation patterns similar to the case of pyrene degradation result in this study, resulted from the same reason with the inhibited degradation kinetics of pyrene due to the insufficient H_2O_2 as well as the excessive initial aqueous Fe(II) concentration.

CPC was degraded to carbon dioxide (CO_2) and ammonium (NH_4^+) by $\text{OH}\cdot$ in pyrite Fenton system. It has been reported that CPC was oxidatively degraded to CO_2 and ammonia (NH_3) by an oxidant (ferrate(IV)) due to the basic system condition (pH 9.2) (Eng et al. 2006). CO_2 production from the CPC degradation with pyrene by pyrite Fenton reaction increased rapidly by 5 min with a slope of 3 mM/min , followed by slow increase (0.06 mM/min) to 25 mM at 180 min. In the absence of pyrene, CO_2 in CPC degradation in the same reaction condition increased by 10 min (1.2 mM/min), increased to 20 mM at 180 min (0.05 mM/min). Relatively large amount of CO_2 production in the presence of pyrene was attributed to the mineralization of pyrene to CO_2 . However, CO_2 which was produced from classic Fenton system increased to 10 min, and then kept constant at 5.4 mM to 180 min. Rapid increase of CO_2 followed by constant production amount is the same pattern of classic Fenton reaction for the degradation of pyrene as well as CPC due to the intrinsic limitation of the reaction (i.e., early loss of reactivity). Conversion to NH_4^+ from CPC occurred more rapidly in classic Fenton than in pyrite Fenton reaction till 25 min, however the amount of NH_4^+ in pyrite Fenton system exceeded that in classic Fenton system from that reaction time. This pattern reveals the characteristics of Fenton systems, resulted from slow but continuous reactivity in pyrite Fenton system and early termination of reactivity in classic Fenton system. On the other hand, the order of CPC degradation in Fenton reaction has been reported that there was hydrophobic aliphatic chain first, followed by the opening of pyridinium ring and formation of NH_4^+ (Eng et al. 2006). Relatively

strong reactivity at initial time in classic Fenton reaction may degrade the alkyl chain in CPC, followed by transformation of nitrogen moiety in pyridinium ring to NH_4^+ from the early reaction time. Characteristics of weak reactivity in initial stage compared to classic Fenton reaction but producing $\text{OH}\cdot$ sustainably in pyrite Fenton reaction probably made this system to overwhelm after 25 min of reaction time for the transformation of nitrogen to NH_4^+ as the reactivity in classic Fenton system became to be phased out. TOC from CPC degradation was not fully removed at the end of the reaction time, indicating that carboxylic acids (provided in section for pyrene transformation products study) and remnant CPC are contributing as TOC concentration in aqueous phase (data not shown). These results support that even potential toxic surfactants in the presence with PAHs can be adequately treated in pyrite Fenton system.



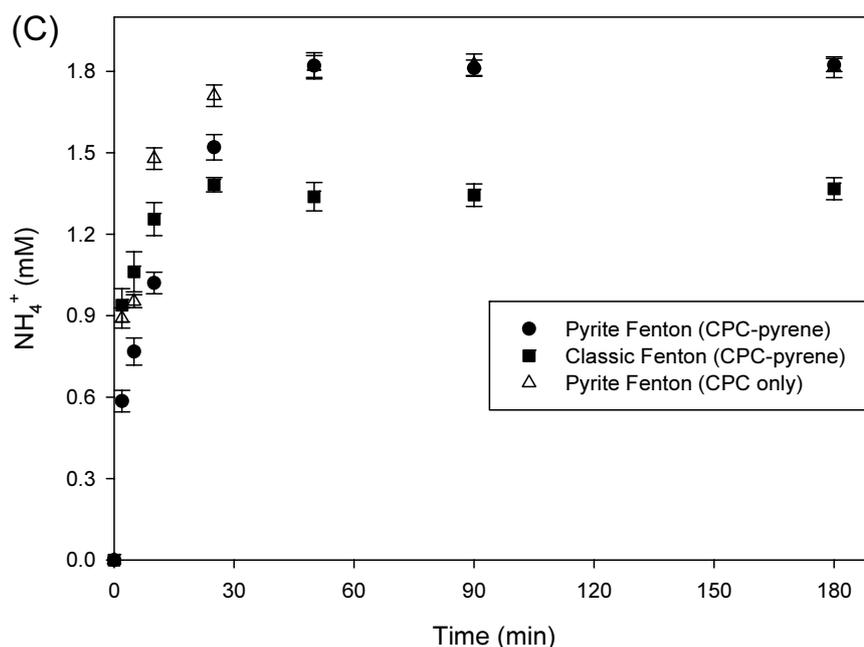
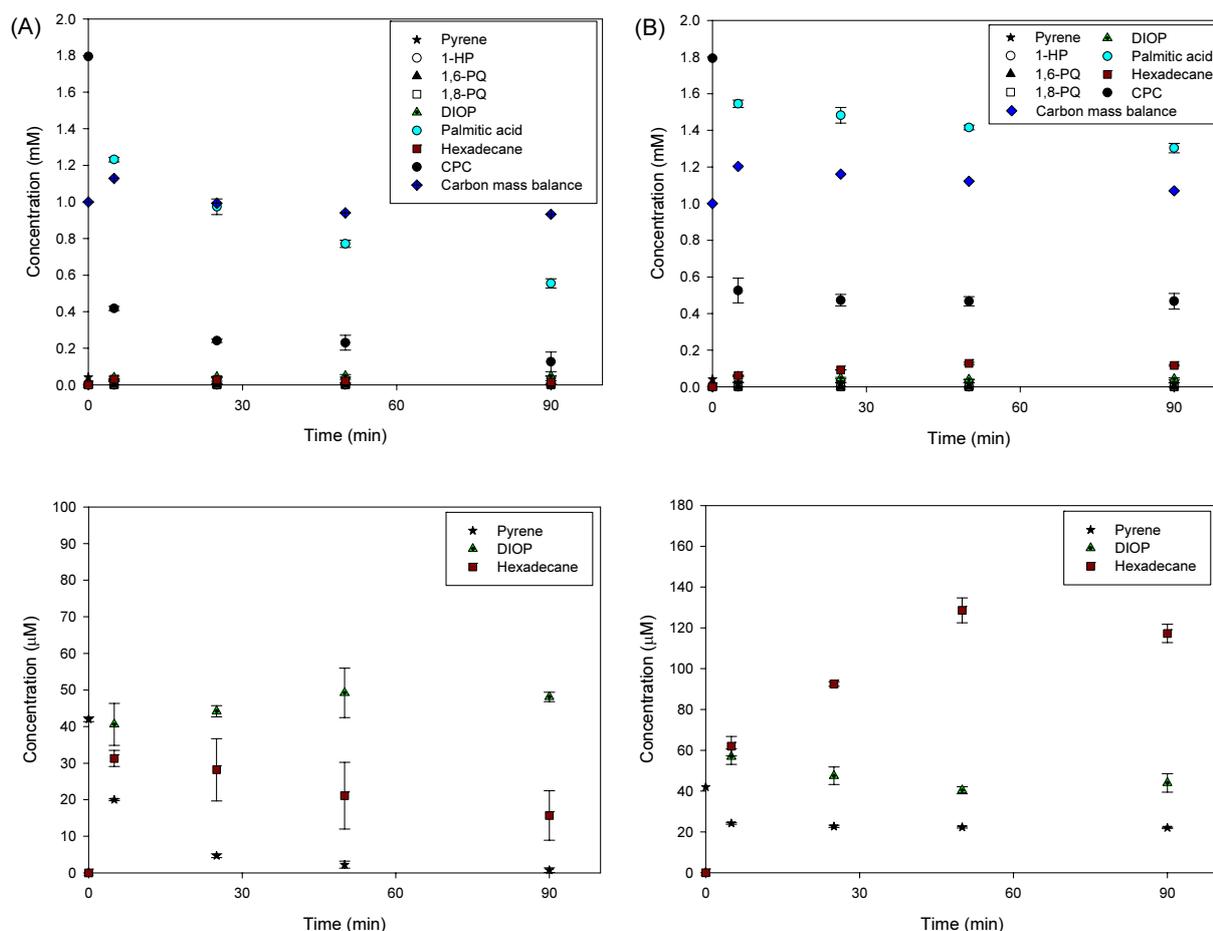


Fig. 4. Oxidative degradation of (A) CPC and variation of (B) CO_2 and (C) NH_4^+ in pyrite Fenton system with/without pyrene and in classic Fenton with pyrene. Experimental condition: $[\text{Pyrite}]_0 = [\text{Fe(II)}]_0 = 25 \text{ mM}$, $[\text{Pyrene}]_{0,\text{CPC}} = 42.03 \text{ }\mu\text{M}$, $[\text{CPC}]_0 = 1.8 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 9.8 \text{ mM}$, initial pH for pyrite Fenton = 7, and initial pH for classic Fenton = 3.

3.3. Degradation Pathway of Pyrene in CPC Solution by Fenton Reactions

Oxidative products occurred during the degradation of pyrene in CPC solution by pyrite Fenton reaction were identified to propose the reaction mechanism along with the pathway to mineralization. Fig. 5 presents the distribution of pyrene by-products in CPC solution by pyrite Fenton reaction and classic Fenton reaction (1-hydroxypyrene (1-HP), 1,6-&1,8-pyrenequinone (1,6-&1,8-PQ), diisooctyl phthalate (DIOP), palmitic acid, and hexadecane). These by-products were chosen based on preliminary experiments and other literatures focused on oxidative degradation of pyrene. HPLC analysis showed that oxy-pyrenes such as 1-HP, 1,6-PQ, and 1,8-PQ were existed as intermediates in both pyrite Fenton and classic Fenton system (Fig. 5(A)(Bottom) and Fig. 5(B)(Bottom)), while GC/MS analysis presented that carboxylic acids such as DIOP, palmitic acid, and aliphatic hydrocarbons such as hexadecane were transformed from pyrene, 1-HP, 1,6-PQ, or 1,8-PQ (Figs. 5(A)(Top) and (Middle) and Figs. 5(B)(Top) and (Middle)). Oxy-pyrenes have been reported to possess more toxicity than parent pyrene, indicating that incomplete degradation should cause environmentally adverse effects (Lundstedt et al. 2007). Fig. 5(A)(Bottom) showed that 1-HP increased to $0.28 \text{ }\mu\text{M}$ until 50 min, then it started to decrease to $0.09 \text{ }\mu\text{M}$ at 90 min as an intermediate. Both 1,6-PQ and 1,8-PQ were not detected till 90 min in pyrite Fenton system, except for $0.0254 \text{ }\mu\text{M}$ of 1,6-PQ at 50 min. Although Fig. 5(B)(Bottom) showed that the overall concentration of 1-HP in classic Fenton system was higher than that in pyrite Fenton system and that the concentration of 1-HP increased to $0.64 \text{ }\mu\text{M}$ until 25 min, the concentration of 1-HP started to decrease from 50 min as an intermediate. In contrast, 1,6- and 1,8-PQ, which were not detected until 25 min, and started to increase from 50 min. This is due to the loss of reactivity in classic Fenton system in this study. As the intermediates identified and quantified using GC/MS, DIOP in Fig. 5(A)(Middle) and Fig. 5(B)(Middle) keep its concentration constant relatively although overall concentrations

of DIOP in classic Fenton system were higher than that in pyrite Fenton system (i.e., 41 ~ 49 μM in pyrite Fenton system and 40 ~ 57 μM in classic Fenton system, respectively). The concentration of palmitic acid as an intermediate between DIOP and hexadecane showed that the decrease pattern in pyrite Fenton system with 1.23 mM at 5 min and a slope of 0.008 mM/min was steeper than that in classic Fenton system with 1.54 mM at 5 min and a slope of 0.003 mM/min (Fig. 5(A)(Top) and Fig. 5(B)(Top)). Hexadecane in pyrite Fenton system showed the decrease from 31.3 mM at 5 min to 15.7 mM at 90 min, while it in classic Fenton system increased to 128.6 mM at 50 min and started to decrease a little bit (117.3 mM) at 90 min (Fig. 5(A)(Middle) and Fig. 5(B)(Middle)). Carbon mass balance in pyrite Fenton system was in the range of 93 ~ 113% while that in classic Fenton system was in the range of 107~120%, indicating that there may be an overestimate in classic Fenton system. A series of these results indicated that Fenton reaction producing $\text{OH}\cdot$ in present research was capable of degrading pyrene via ring opening, as evidenced by intermediates such as carboxylic acids, and further oxidation by $\text{OH}\cdot$ (and other oxygenated radicals such as $\text{O}_2\cdot^-$ as discussed in the section describing the effect of t-butanol and chloroform on the degradation kinetics of pyrene) to other fragments and byproducts (hexadecane and CO_2) if the intermediates were to remain exposed to $\text{OH}\cdot$. Based on the distribution and amount of each transformation product, it can be concluded that pyrite Fenton system can be considered as the promising technology to treat wastewater containing PAHs as well as surfactants from soil washing process. From this result, pyrene was shown to be transformed via oxy-pyrene intermediates to carboxylic acids, and further destructed to aliphatic hydrocarbons and finally mineralized to CO_2 .



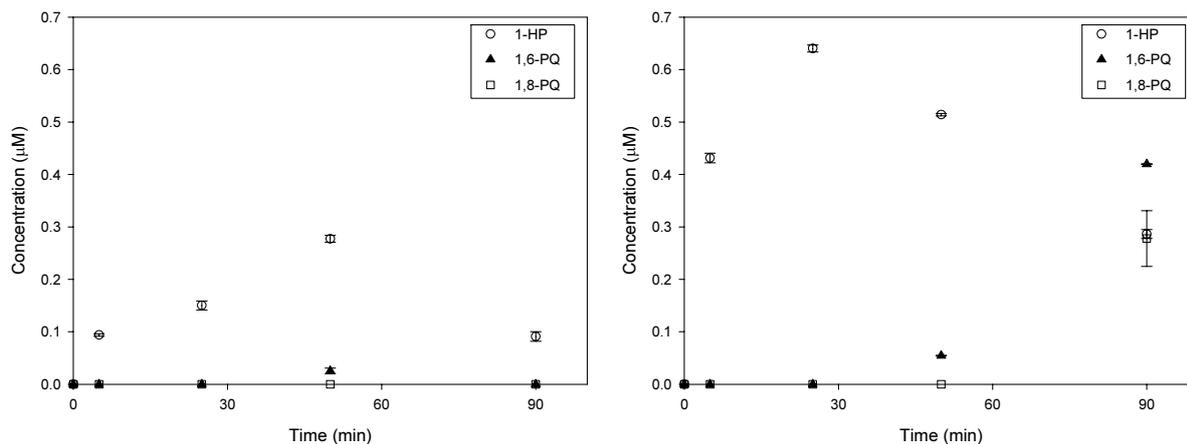


Fig. 5. Measured concentrations of pyrene by-products in CPC solution by (A) pyrite Fenton reaction and (B) classic Fenton reaction. Experimental condition: $[\text{Pyrite}]_0 = [\text{Fe(II)}]_0 = 25 \text{ mM}$, $[\text{Pyrene}]_{0,\text{CPC}} = 42.03 \text{ }\mu\text{M}$, $[\text{CPC}]_0 = 1.8 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 9.8 \text{ mM}$, initial pH for pyrite Fenton = 7, and initial pH for classic Fenton = 3.

4. CONCLUSIONS

This research has demonstrated the complete degradation of pyrene in CPC solution by pyrite Fenton reaction at initial pH 7. Enhanced degradation of pyrene in the pyrite Fenton system compared to that in classic Fenton system was attributed to intrinsic property of pyrite to make system pH favorable for Fenton reaction (i.e., pH 3-4) induced by pyrite oxidation by H_2O_2 in suspension and sustainable Fenton reaction resulted from Fe(II) generation from Fe(III) on pyrite surface. Sufficient Fe(II) in pyrite as an iron source and efficient conversion of $\text{OH}\cdot$ from H_2O_2 in this pyrite Fenton system were the key factors to complete degradation of CPC as well as pyrene without accumulating toxic transformation products. CPC was transformed to CO_2 and NH_4^+ . Transformation study showed pyrite Fenton system can treat pyrene more effectively than classic Fenton system. Pyrene can be transformed via oxy-pyrene intermediates to carboxylic acids, and further destructed to aliphatic hydrocarbons and finally mineralized to CO_2 . Therefore, pyrite Fenton system can cope with fatal limitations of classic Fenton reaction showing relatively slow and incomplete oxidation of pyrene with accumulating toxic products. Moreover, abundance of pyrite in nature and simple process (i.e., addition of H_2O_2 to pyrite slurry in ambient conditions without controlling pH condition) can make this pyrite Fenton system more feasible. The experimental results obtained from this research can provide basic knowledge to understand the degradation mechanism of pyrene in CPC by pyrite Fenton reaction and to design the effective heterogeneous oxidation process for remediation of wastewater contaminated by both PAHs and surfactants.

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