

以元素鐵配合二氧化碳曝氣
進行五氯酚脫氯研究

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Dechlorination of Pentachlorophenol by Zero-valent Iron Combined with Carbon Dioxide Bubbling

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ABSTRACT

This study describes major findings on PCP removal by $\text{Fe}^0/\text{H}_2\text{O}$ and $\text{Fe}^0/\text{CO}_2/\text{H}_2\text{O}_2$. The bubbling of CO_2 was proved to be an effective and efficient way to obtain acidic solution, which was advantageous for Fe^0 to release electrons into the reaction system. At a neutral pH, the PCP mostly with ionized form tends to be adsorbed onto iron particles surface. With an acidic pH, the PCP mostly with molecular form appears to attach adhesively on the surface of reactor wall and tubing of the reaction system. In addition, water molecules compete for Fe^0 -released electrons more strongly than the PCP, leading to the rising of pH and absence of Cl^- . However, PCP can be dechlorinated through the pathways of Fenton-like and Fenton reaction, the later of which was created by adding H_2O_2 at a later stage into the Fe^0/CO_2 system.

Keywords: Carbon dioxide, dechlorination, pentachlorophenol, zero-valent iron

INTRODUCTION

This study was motivated due to the requirement and urgency of PCP-contaminated groundwater remediation here in Taiwan. On top of this, such remediation information is also rare to find to the present date. Hence, effort was made to provide an innovative Fe^0 -based technology for resolving the above issue of concern.

Basically, the media contaminated by PCP include two phases such as soil and groundwater. PCP-contaminated soil can be treated directly by plasma process (Sharma et al., 2000) and microwave process (Park et al., 2000). Indirectly, the PCP may also be extracted from contaminated soil by using solvent (Khodadoust et al., 1999a; Khodadoust et al., 1999b; Khodadoust et al., 1999c) for subsequent physicochemical or biological treatment. Regarding aqueous PCP treatment, a physical carbon adsorption method was reported by different researchers (Jianlong et al., 2000; Lambert et al., 1997; Durkin et al., 1996). With chemical treatment, Kim and Carraway (2000) have

ever reported the dechlorination of PCP by using zero-valent iron and modified iron metal. There were other reports of PCP degradation by pulse and γ radiation (Fang et al., 1998), and ultrasound (Gondrexon et al., 1999). Ozone was also used as chemical oxidizer for degrading PCP (Kim and Moon, 2000; Kuo and Huang, 1998). Among the advanced oxidation processes (AOPs), PCP was treated by Fenton/photo-Fenton (Oturán et al., 2001; McKinzi and Dichristina, 1999; Engwall et al., 1999; Watts et al., 1999; Spencer et al., 1994), $\text{H}_2\text{O}_2/\text{UV}$ (Ho and Bolton, 1998), photocatalysis (Wilcoxon, 2000; Higarashi and Jardim, 2000; Villasenor et al., 1998; Jardim et al., 1997; Alberici and Jardim, 1994). In addition, several groups of researchers focused on biological degradation of PCP (D'Angelo and Reddy, 2000; Magar et al., 1999; Knoke et al., 1999; Karamanev et al., 1999; Khodadoust et al., 1997; Wilson et al., 1997; Bhattacharya et al., 1996; Cole et al., 1996).

In this study, zero-valent iron was chosen as a main element to initiate PCP dechlorination through reductive reaction pathway. In addition, Fenton process appears to be promising for treating PCP, according to the above literature report. Thus, adding H_2O_2 into Fe^0 solution at a later reaction stage realizes the idea of creating redox environment for PCP dechlorination. To accelerate PCP degradation rate, CO_2 bubbling was used as a way to reduce the solution pH, which is critical and advantageous for Fe^0 to form electrons and Fe^{2+} .

EXPERIMENTAL

Material and Reagents

Zero-valent iron (10 μm , 99.5%) was purchased from Merck and was used in the experiment without any pretreatment. The target compound PCP (98%) was obtained from Aldrich. As shown in Figure 1, the solubility of PCP varies with pH significantly (Arcand et al., 1995). At pH = 9.5, a quantity of as much as 10 g PCP can be dissolved into aqueous solution. The PCP stock solution of 2000 mg/L was prepared by dissolving 0.2 g PCP into 100 mL of pH-adjusted RO water, where pH ranged from 9.5 to 10.5. In preparing the working solution of PCP, the stock solution was diluted by 200 times to obtain a concentration of 10 mg/L, the pH of which was around 6.8-7.2. To extract the PCP from either aqueous or solid phase, the organic solvent ethyl acetate (99.8%, Merck) was employed, with additional concentrated HCl (37%, Merck) addition for the solid phase extraction. In analyzing PCP, the n-hexadecane of (99%, Merck) was used as an internal standard.

Reaction Systems

The work of this study was carried out in two different phases, including PCP removal in the two systems of (i) $\text{Fe}^0/\text{H}_2\text{O}$ and (ii) $\text{Fe}^0/\text{CO}_2/\text{H}_2\text{O}_2$. In the first system, working solution of 35 mL was filled into each of a set of vials with 250 mL volume capacity. After adding 1 g of Fe^0 into each vial, these sample-filled vials were put in a shaker (125 rpm, Hipoint SB-9D) and taken out at different

time intervals to investigate the potential of PCP dechlorination. In the second system, the PCP was treated in a CO₂-bubbled reactor with H₂O₂ addition at a later reaction period. To ensure homogeneous mixing of iron powder, the aqueous mixture was recirculated continuously from the upper to the bottom portion of the reactor at a rate of 830 mL/min (see Figure 2).

PCP Extraction and Analysis

In carrying out the first reaction system, two vials were taken out from the shaker at a designated time point for instrumental analyses, one for aqueous phase and another for solid phase. Basically, the PCP extraction in this study follows the procedure established by Kim and Carraway (2000). Allowing the iron powder to settle down in the vial, a certain amount of the supernatant was withdrawn from the vial, extracted by ethyl acetate, and analyzed by GC/FID (HP 4890) for PCP concentration in aqueous phase. In the case of overall PCP extraction from both aqueous and solid phases, concentrated HCl was added together with ethyl acetate. In the second reaction system, the treated samples were withdrawn from the reactor without pre-filtration for the overall extraction of PCP from both phases, while the withdrawn samples were pre-filtered by 0.2 μm filter paper for quantification of PCP in aqueous phase alone. Figure 3 shows a standard calibration curve of PCP mass injected into GC/FID under various peak area ratios of PCP versus hexadecane. Based on this calibration curve, the PCP was quantified in aqueous phase or both phases.

In addition, other water quality parameters monitored include pH, ORP, DO, Cl⁻, Fe²⁺, and H₂O₂. The pH, ORP and DO were monitored continuously by pH (Suntex, TX1), ORP (Suntex, TX2), and DO (WTW-340) meters, respectively, while the chloride was by ion chromatography (Dionex, DX-120). The stock H₂O₂ solution was quantified by using a potassium permanganate titration method (Vogel, 1978). The residual H₂O₂ concentration in the reaction solution was determined by using the potassium titanium (IV) oxalate method (Sellers, 1980). Under an acidic condition, the H₂O₂ reacts with Ti⁴⁺ to form a yellowish complex. Through the measurement of light absorption at 400 nm, the absorbance can be converted into equivalent H₂O₂ by reading the H₂O₂ value from a pre-determined linear calibration curve. Similarly, ferrous ion is able to form a colored complex with 1,10-phenanthroline (Standard Method), therefore, its concentration can be determined through the measurement of light absorption at 510 nm, which is equivalent to a certain ferrous quantity.

RESULTS AND DISCUSSION

Potential of PCP Adsorption onto Fe⁰

As mentioned earlier, PCP solubility depends on pH remarkably; the lower the pH, the higher the possibility for the PCP to precipitate out of aqueous phase. On the other hand, as the pH decreases, Fe⁰ tends to dissolve into Fe²⁺, with releasing of two electrons. Hence, it is desired to understand

how PCP will distribute between aqueous and solid phases due to solution acidity. As shown in Figure 4, it was demonstrated from Conditions 1 and 2 that PCP of approximately 8% was adsorbed onto Fe⁰, while the adsorption was not observed at all with the presence of concentrated HCl or H₂SO₄. Such a result appears to be in agreement with the literature report (Arcand et al., 1995). In other words, it is required to increase solution acidity to achieve overall PCP extraction from both aqueous and solid phases. In addition, it is also true that the adsorption onto Fe⁰ surface is negligible under acidic condition.

Kinetics of PCP Removal by Fe⁰

Under neutral pH, the PCP was treated with the presence of 1 g Fe⁰/35 mL. Figure 5 shows that the pH remained rather unchanged and the ORP dropped down gradually from +170 to +90 mV, prior to H₂O₂ addition. As the H₂O₂ was added, both the pH and ORP increased. Regarding the kinetics of PCP removal, aqueous PCP disappeared significantly over the period of 15 days, however, the overall PCP was seen to fluctuate along the initial level as reaction time went on. Obviously, most of PCP was transferred from aqueous to solid phase after 15 day shaking of reaction mixture. This is to say that adsorption of PCP by Fe⁰ dominates in such a reaction system. With followup addition of H₂O₂ at time of 16th day, Cl⁻ of approximately 10 mg/L was built up after one day reaction. The reason behind such a phenomenon might be due to the occurrence of Fenton-like reaction, which initiates dechlorination of PCP.

Reaction System with CO₂ Bubbling

The intention of CO₂ bubbling is to create an acidic environment for faster Fe⁰ corrosion, and this in turn might accelerate the reduction of PCP. If H₂O₂ addition is followed at a later reaction period, Fenton oxidation of PCP can be initiated. With such a scenario, the first task is to find out how efficient the pH can be reduced as various bubbling rates of CO₂ are applied. Without PCP and Fe⁰, Figure 6 shows that pH dropped down sharply from neutral pH to around 4-4.5 within less than 10 min. In addition, as the bubbling rate increased from 100 to 400 mL/min, the drop rate of pH is slightly enhanced. As for the ORP profile, there occurred a peak value at a certain time for each bubbling rate. The reason is connected to a slight increase of pH along with the reaction time (See 6A); ORP is found to increase with decreasing pH. Since CO₂ was bubbled into reactor continuously, the DO is anticipated to be stripped out of the aqueous system, as illustrated in Figure 6 (C). As shown in Figure 7, with the presence of Fe⁰ (1-4 g/L), the pH was seen to bounce back after its initial rapid drop; the higher dosage of Fe⁰ led to a faster rate of pH increase. In contrast, the ORP followed the opposite way of pH profile in this reaction system. Since there're no other electron acceptors but H⁺ and H₂O, the solution pH was reduced according to the following reactions.



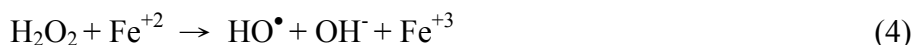


Kinetics of PCP Removal by Fe⁰/CO₂/H₂O₂

In the presence of PCP, experiments were performed to investigate the removal kinetics of PCP in the system of CO₂ bubbling alone. The results were presented in Figure 8. It is peculiar to find that the overall PCP in the reaction system decreased with time significantly even though no apparent degradation reactions are expected. Moreover, the aqueous PCP profile was slightly lower than the overall PCP profile, indicating possible precipitation of PCP due to lower solubility under acidic condition. It appears that PCP adsorbed onto reactor wall and inner surface of recirculation tubing might be responsible for PCP disappearance, especially at a pH as low as 3.5.

As shown in Figure 9, the PCP profile with Fe⁰ is slightly different from the one without the presence of Fe⁰; the former case has a slower rate of PCP disappearance, regardless of liquid or mixed phases. With Fe⁰, the pH profile shows the pattern of sharp dropping down from the initial to a minimum value, which is then followed by rapid bouncing back to a pH level less than the initial one. Figure 7(A) illustrates such a pattern in pH variation. Since the pH was elevated, the PCP tended to remain in the aqueous phase, as described earlier. Such pH-dependent characteristics might explain the reason behind the mentioned difference. Another point to be addressed is considerable accumulation of Fe²⁺ in the reaction mixture, which was as much as 1700 mg/L at time of 180 min. At such a high Fe²⁺ concentration, the solution presented quite a reduced state, which has an ORP of around -600 mV (see Figure 6(B)). Similar to the one presented in Figure 8, the disappearance of PCP is speculated to be all due to its adsorption onto reactor wall and inner surface of tubing since dechlorination product of Cl⁻ was not detectable.

As described above, considerable amount of Fe²⁺ has been accumulated as the reaction carried on. Hence, it motivates the addition of H₂O₂ to initiate Fenton degradation of PCP. Figure 10 shows the experimental results with addition of 154 mg/L of H₂O₂ at time of 90 min. At the time of H₂O₂ addition, two aspects need to be addressed. First, the extracted PCP from aqueous or mixed phases decreased sharply within 5 min period since Fenton reaction has been initiated after H₂O₂ addition (Reaction 4). Such a reaction was evidenced by complete consumption of H₂O₂ and decrease of Fe²⁺ accumulation, and the consequent release of 2 mg/L of Cl⁻ (Reaction 5). Second, the pH dropped by around one unit possibly due to the occurrence of Reactions (6) and (7), while the ORP was seen to rise by around 150 mV. It seems that a larger degree of PCP dechlorination can be achieved by manipulating H₂O₂ dosage and dosing timing.





CONCLUSIONS

Based on the findings in this study, several aspects are concluded for the redox removal of PCP by the two systems of $\text{Fe}^0/\text{H}_2\text{O}$ and $\text{Fe}^0/\text{CO}_2/\text{H}_2\text{O}_2$. First, character of PCP adsorption onto solid phase needs to be taken into account seriously under any range of pH. For example, PCP can be easily adsorbed onto iron particle at a neutral pH, where the PCP exists mostly in an ionized form. On the other hand, as the pH fell into acidic range, its molecular form is water-unlike and is easily expelled to attach on the wall and tubing surface in the reaction system. This renders a fatal problem of differentiating redox degradation of PCP from unexpected adsorption removal of PCP. Future research needs to address this issue of major concern. Second, with the bubbling of CO_2 , acidic environment can be easily created to initiate the Fe^0 -based reaction system. In view of reduction reaction, the released electrons from Fe^0 appear to be consumed mainly by H_2O , rather than by PCP, as evidenced from the rising of pH and absence of Cl^- occurrence. However, it was possible to dechlorinate PCP through the pathways of Fenton-like and Fenton oxidation, if sufficient amount of H_2O_2 is added at a later stage into the systems of $\text{Fe}^0/\text{H}_2\text{O}$ and Fe^0/CO_2 , respectively. Future research should also focus on the intermediates of PCP degradation by the system of $\text{Fe}^0/\text{CO}_2/\text{H}_2\text{O}_2$.

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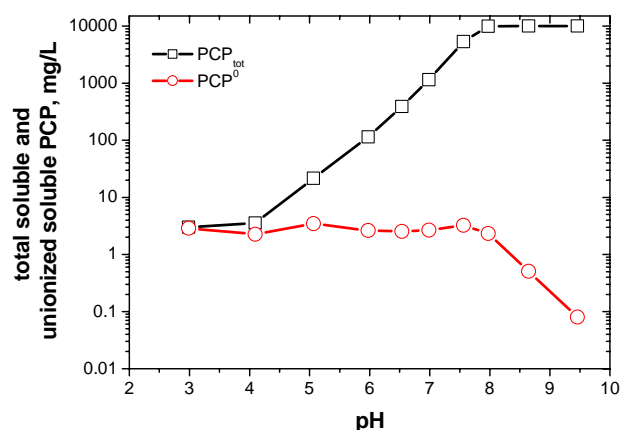


Figure 1. Total soluble and unionized soluble PCP under various pH conditions in “pure” water. Note that measured data were taken from Arcand et al. (1995).

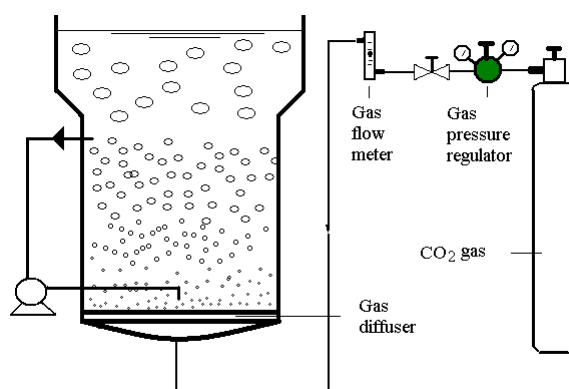


Figure 2. Reactor configuration for the system of Fe⁰/CO₂.

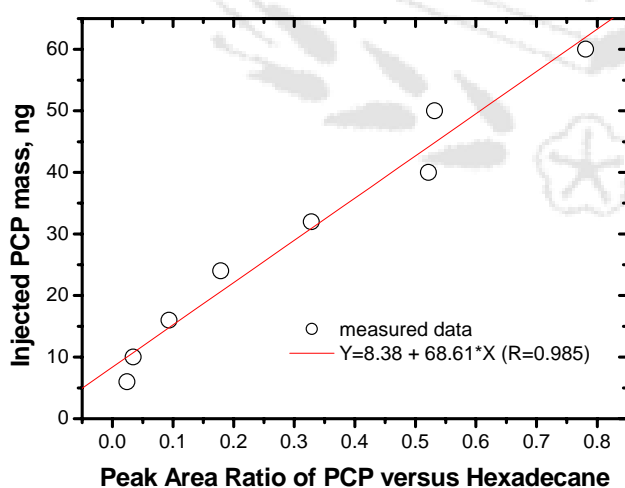


Figure 3. PCP quantification by GC/FID with n-hexadecane as an internal standard. The injection volume of standard solution was 2 μ L and the n-hexadecane was fixed at 7.7 mg/L.

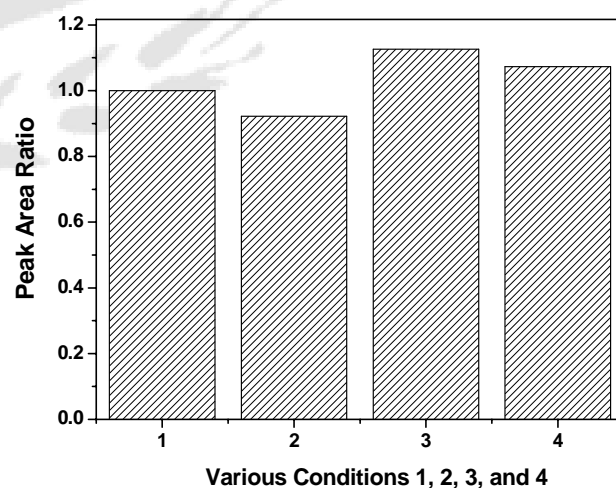


Figure 4. Potential of PCP adsorption onto Fe⁰ under various conditions. Condition 1: 25 mL water sample with unknown PCP concentration and 10 mL ethyl acetate; Condition 2: in the presence of 1 g Fe⁰; Condition 3: in the presence of 1 g Fe⁰ and 2 mL HCl (37%); Condition 4: in the presence of 1 g Fe⁰ and 1 mL H₂SO₄ (96%).

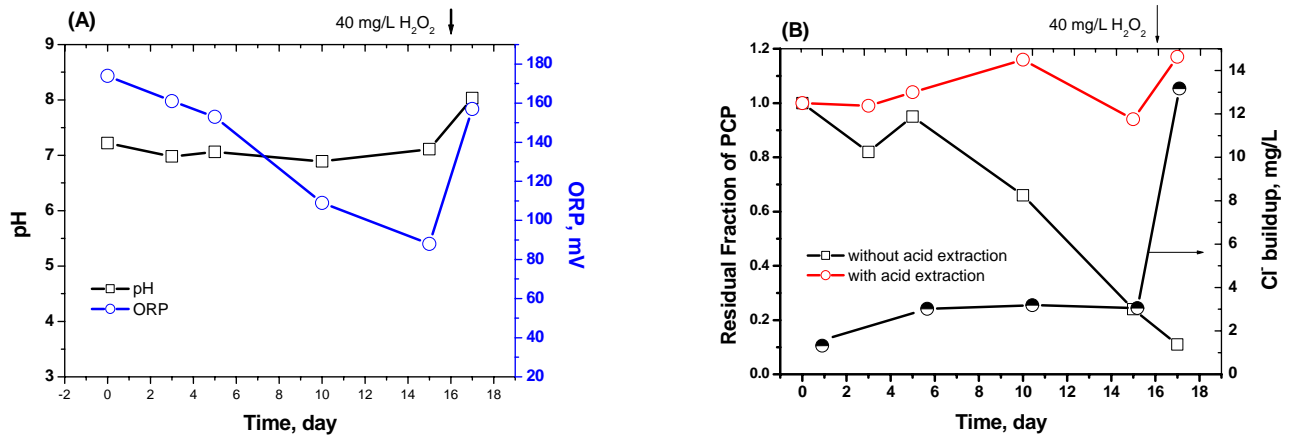


Figure 5. Profiles of (A) pH and ORP; (B) residual soluble PCP and Cl⁻ buildup in the presence of Fe⁰ and the followup addition of H₂O₂. F⁰ dosage = 1 g/35 mL; initial PCP = 10 mg/L.

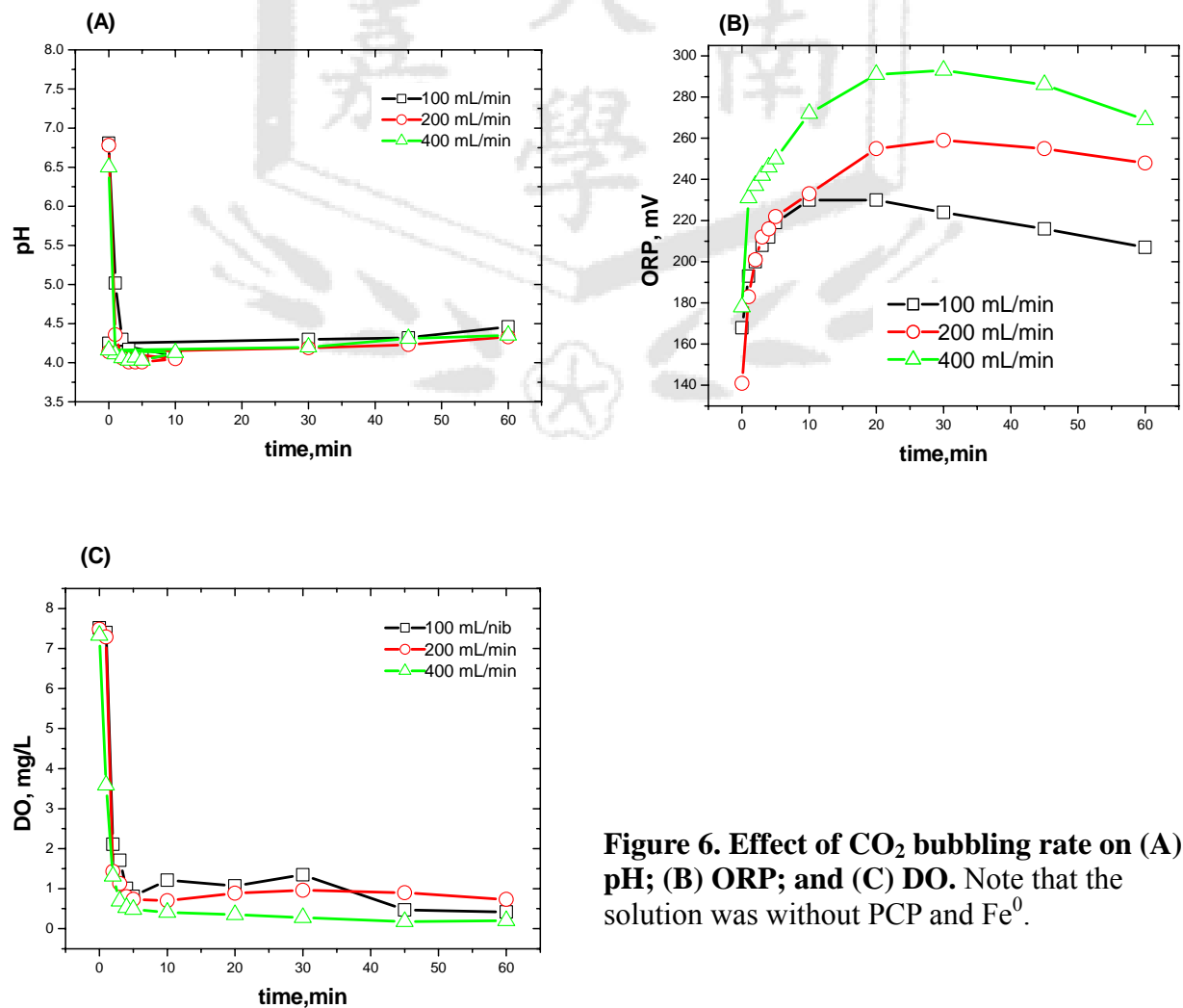


Figure 6. Effect of CO₂ bubbling rate on (A) pH; (B) ORP; and (C) DO. Note that the solution was without PCP and Fe⁰.

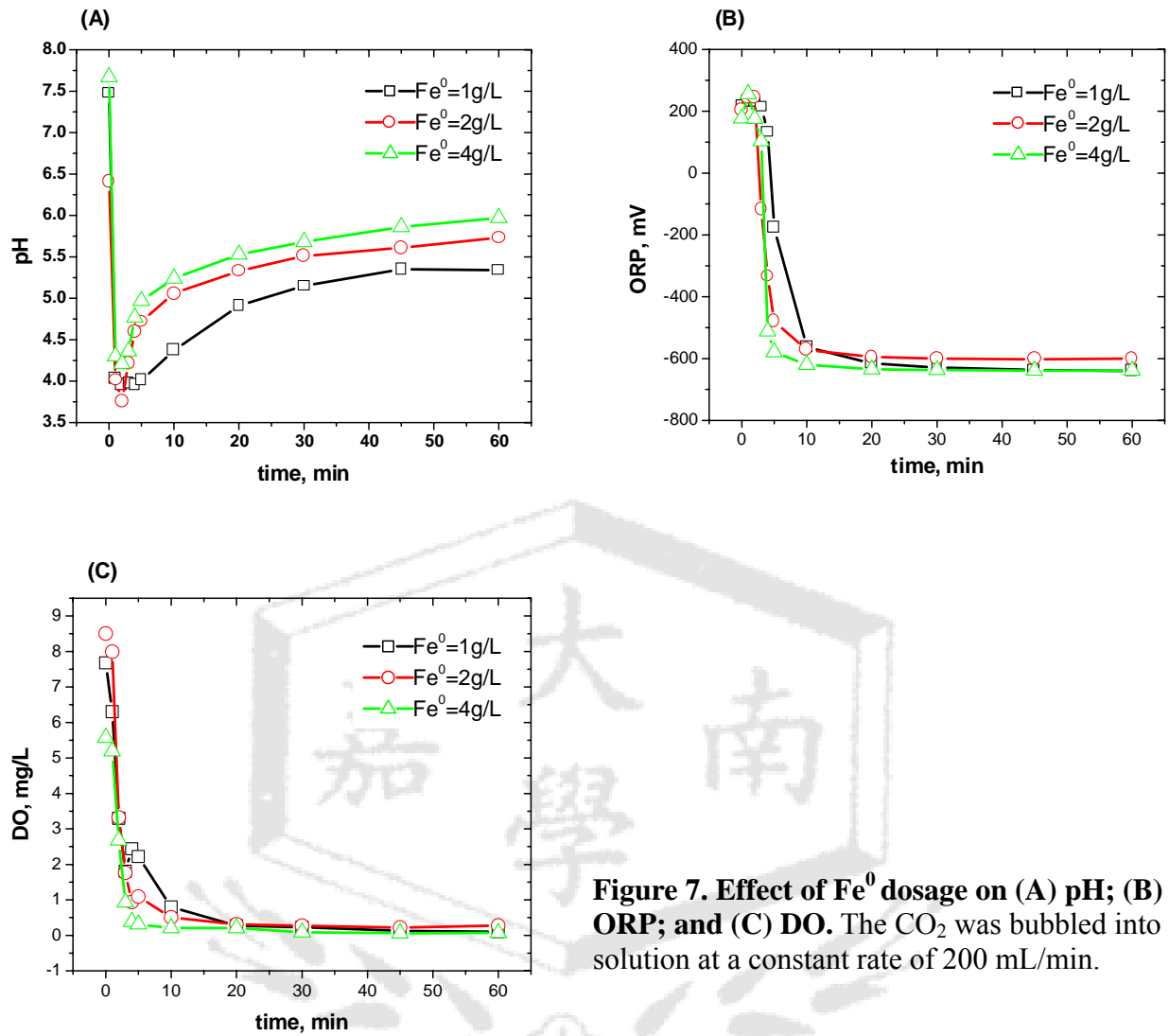


Figure 7. Effect of Fe^0 dosage on (A) pH; (B) ORP; and (C) DO. The CO_2 was bubbled into solution at a constant rate of 200 mL/min.

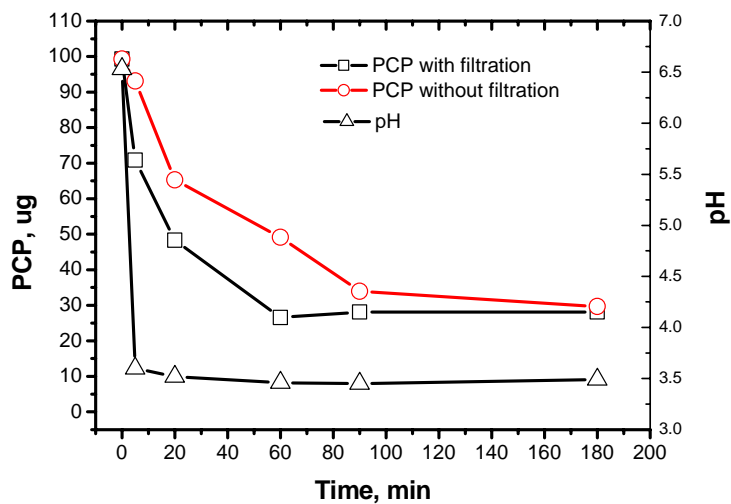


Figure 8. Effect of CO_2 bubbling on measured PCP mass in aqueous and mixed phases. The Fe^0 was not applied in this reaction system.

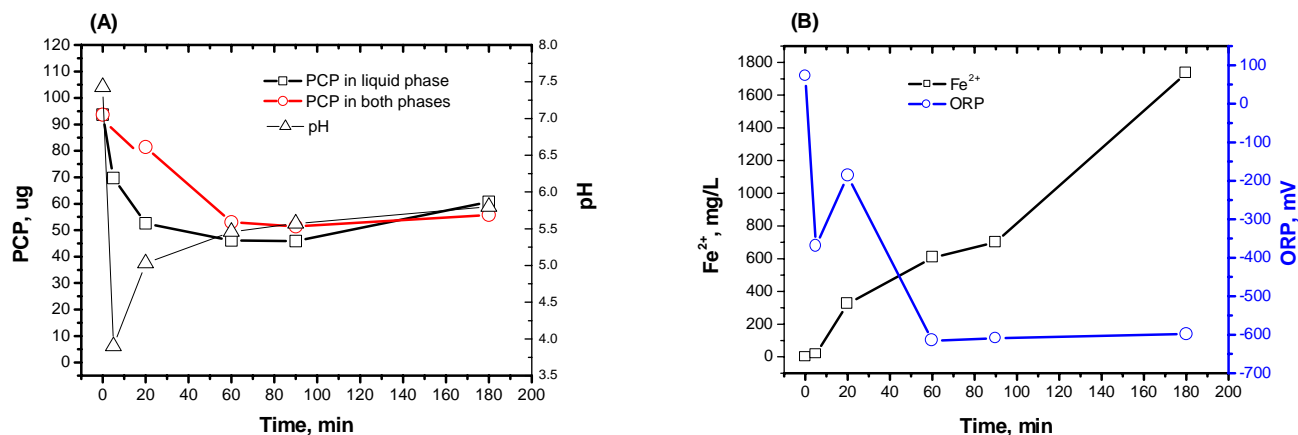


Figure 9. Profiles of (A) measured PCP and pH; and (B) Fe²⁺ and ORP in the absence of H₂O₂. CO₂ bubbling rate = 200 mL/min; Fe⁰ = 2g/L; initial PCP = 10 mg/L. Note that the chloride ion is not detectable in the treated solution.

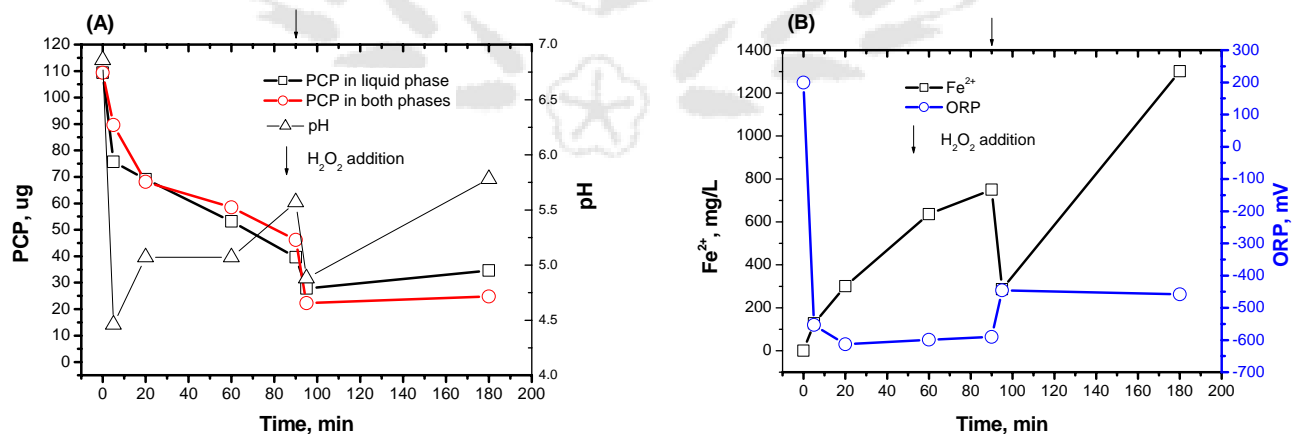


Figure 10. Profiles of (A) measured PCP and pH; and (B) Fe²⁺ and ORP in the presence of H₂O₂. CO₂ bubbling rate = 200 mL/min; Fe⁰ = 2g/L; initial PCP = 10 mg/L. H₂O₂ of 154 mg/L was added twice at 90 min. After 5 min of Fenton reaction, the added H₂O₂ was consumed completely, and 2 mg/L of Cl⁻ was detected.