Degradation of carbon tetrachloride in modified Fenton reaction

Youngmin Lee, Sungjun Bae, and Woojin Lee[†]

Department of Civil and Environmental Engineering, Korea Advanced Institute of Science and Technology,
373-1, Guseong-dong, Yuseong-gu, Daejeon 305-701, Korea

Abstract−We showed that the dechlorination of carbon tetrachloride (CT) can be significantly enhanced at near-neutral pH by modified Fenton reaction in the presence of Fe(II) chelated by cross-linked chitosan (CS) with glutaraldehyde (GLA). CT dechlorination was verified by monitoring the release of chloride and detection of intermediates such as trichloromethane and dichloromethane in the modified Fenton system with Fe(II) chelated by cross-linked CS with GLA (Fe(II)-CS/GLA). Measured chlorine mass balance of each sample was greater than 91% of total chlorine mass corresponding to initial CT concentration throughout the reaction. Addition of hydroxyl radical scavenger (2-propanol) enhanced the CT degradation in 5 h at near-neutral pH (removal efficiency from 57.2% to 92.4%), while the addition significantly inhibited trichloroethylene (TCE) degradation at the same condition (74.7% to 19.9%). This implies that, in contrast to the dechlorination of TCE, that of CT did not follow an oxidative dechlorination pathway but a reductive dechlorination pathway in the modified Fenton system with Fe(II)-CS/GLA. Dechlorination kinetics of CT in the modified Fenton system was affected by the concentrations of H_2O_2, Fe(II), and CT. The formation of surface Fe(II)-CS/GLA complex and its valence change from Fe(II) to Fe(III) observed during the modified Fenton reaction gave a clue to identify the proposed reaction mechanism properly.

Key words: Modified Fenton Reaction, Cross-linked Chitosan, Fe(II) Chelation, Redox Degradation, Carbon Tetrachloride

INTRODUCTION

The Fenton process, producing a powerful and nonselective oxidant (OH•), has attracted attention among the advanced oxidation processes due to its low harmful environmental impacts and high reactivity for the removal of organic contaminants. In water and wastewater treatment, maintaining low solution pH in the Fenton process is important to achieve successful contaminant removal, because the classic Fenton requiring aqueous Fe(II) for the formation of OH• has been properly operated at the pH range of 2-4 by avoiding the formation of $Fe(OH)_{3(S)}$ [1]. However, it has been reported that OH• is less reactive with highly halogenated and nitro-substituted organic compounds, i.e., perhalogenated alkanes (carbon tetra chloride (CT) and hexachloroethane) and 1,3,5-trinitrobenzene [2,3]. There have been efforts to overcome the difficulty by modifying the classic Fenton process and developing novel remediation technologies so that the removal of highly chlorinated organic compounds can be enhanced at neutral soil environment easily found in a natural system. Modification options for the classic Fenton system have been developed by use of chelating agents [4-6], alternative catalysts such as Fe(III) promoting a superoxide-driven reaction [7], iron oxide and oxyhydroxide minerals [8,9], and addition of excess H_2O_2 [10]. The modified reactions by chelating agents have been reported to significantly enhance the degradation of organic contaminants even at neutral pH [5]. Ethylenediaminetetraacetic acid (EDTA) has been used as a representative chelating agent for the degradation of hexachloroethane at pH 6.8 [6]. Chitosan (CS) has been also used for the modification of classic Fenton reaction

and attracted attention as a natural chelating agent due to its unique properties of biocompatibility, hydrophilicity, non-toxicity, and chemical inertness. CS-supported Pd and Cu catalysts have played a significant role of heterogeneous catalysts for degradations of chlorophenol [11], nitrophenol [12], nitrotoluene [13], textile dyes [14], and hydroquinone [15].

The preparation procedure of CS and its characteristics as a biopolymer have been described everywhere [16,17]. Due to its structural vulnerability against mineral acids and OH•, CS has been treated by a cross-linking agent such as glutaraldehyde (GLA) to obtain chemically stable and inert cross-linked CS (CS/GLA) [16]. Amine group from CS/GLA provides multiple binding sites to form complexes with Fe(II) (Fe(II)-CS/GLA) that can avoid the precipitation of aqueous Fe(II) to $Fe(OH)_{3(S)}$ at near-neutral pH during the Fenton reaction [18]. There have been many experimental studies about CS as a support material for environmental catalysts. However, a catalytic role of Fe(II)-CS/GLA for the degradation of perchlorinated compounds in the modified Fenton reaction has not been carried out yet. It has been reported that CT degradation in the Fenton reaction was driven by non-OH• reactants, i.e., $HO_2^•$, $O_2^{•-}$, and HO_2^- and $O_2^{•-}$ may be the main reactant for the CT degradation [4,6,10]. These results suggest that perchlorinated alkanes in the Fenton reaction can be reduced by HO_2^- and $O_2^{•-}$, not oxidized by OH•. However, the reaction mechanism for degradation of perchlorinated alkanes in the modified Fenton reaction is still unclear and no research has been conducted for its identification in the presence of Fe(II)-CS/GLA to date.

The objective of this study was to identify the reaction mechanism for the degradation of perchlorinated alkanes by the modified Fenton reaction with Fe(II)-CS/GLA. CT, one of the most well-known perchlorinated alkanes showing harmful characteristics such

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[†]To whom correspondence should be addressed.
E-mail: woojin_lee@kaist.ac.kr

as high carcinogenicity, toxicity, and flammability, was selected as a representative of perchlorinated alkanes. Batch kinetic experiments were conducted to characterize the dechlorination of CT by Fe(II)-CS/GLA in the modified Fenton system and to investigate the effect of concentrations of H_2O_2, Fe(II), and CT on the dechlorination kinetics of CT.

EXPERIMENTAL SECTION

1. Materials

CT (99.5%, Aldrich) was used as a target compound and trichloromethane (99%, Aldrich) and dichloromethane (99.9%, Merck) were used as potential intermediate products. Trichloroethylene (TCE, 98%, Sigma) was used for the comparison of reaction mechanism between TCE and CT removal. $FeSO_4 \cdot 6H_2O$ (99%, Sigma), H_2O_2 (30 wt%, Junsei), and 2-propanol (99.5%, Junsei) were used for batch kinetic tests. Other experimental materials (CS, GLA and CS/GLA) were prepared by following the previous work [18].

2. Experimental Procedures

To characterize the degradation of CT and to identify its transformation products in the modified Fenton reaction with Fe(II)-CS/GLA, batch reactors were used with a three-layered septum system [19]. Experimental procedures in this study were similar to previous work, except the different pH and target compound [18]. The cross-linked CS beads were prepared by following a well known synthesis method [12,20]. Commercial CS flakes were dissolved in 5% (v/v) CH_3COOH solution for 3 hrs. The CS solution was added into a precipitation bath including 0.5 M NaOH and formed CS gel beads. They were washed with deionized water several times to remove residual NaOH and cross-linked with 0.025 M GLA solution by mixing for 24 hrs at room temperature (25±0.5 °C). The CS/GLA were rinsed with deionized water, air-dried, and ground using a mortar and pestle, sieved (<250 μm), and then stored at room temperature.

To compare reactivity of the modified Fenton reaction with Fe(II)-CS/GLA to that of classic Fenton, a control sample for the classic Fenton reaction (i.e., aqueous Fe(II)+CT+H_2O_2) was prepared. Additionally, four types of controls (deionized water (DIW)+CT, DIW+CT+H_2O_2, DIW+aqueous Fe(II)+CT, and DIW+Fe(II)-CS/GLA+CT) were also prepared to check any possible losses of CT due to sorption, volatilization, homogeneous oxidative degradation, and reductive dechlorination during the reaction in each experimental run. No headspace was allowed for all samples and controls during the reaction.

Batch mechanistic tests to investigate the reaction mechanism in the modified Fenton system with Fe(II)-CS/GLA were conducted by monitoring the degradation of CT and production of its transformation products in aqueous solution at each sampling time. The reaction was initiated by spiking an exact amount of CT stock solution into vials (0.94 mM) at the same experimental conditions described above. 2-propanol was used as an OH• scavenger due to its high reactivity with oxidants (k_{OH}=$3 \times 10^9 M^{-1}s^{-1}$) and low reactivity with reductants (k_e=$1 \times 10^6 M^{-1}s^{-1}$) [2]. To investigate the scavenging effect of 2-propanol on the dechlorination kinetics of CT, batch test samples were prepared by following the procedure described above and the test was initiated by spiking an exact amount of 2-propanol into vials (0.9 M) at the same experimental condi-

tions. TCE, one of the well known chlorinated contaminants easily degraded by OH• via oxidative reaction mechanism [3,21], was also used to investigate the scavenging effect and to compare its reaction mechanism in the modified Fenton reaction to that of CT. A TCE test was initiated by spiking an exact amount of stock TCE solution into the vials (0.1 mM) at the same experimental conditions described above.

Batch kinetic experiments were also carried out to investigate the concentration effect of H_2O_2, Fe(II), and CT on the degradation kinetics of CT. To investigate the effect of H_2O_2 concentration on the degradation kinetics, we used five different concentrations of H_2O_2 (53, 106, 212, 318, and 530 mM). The effect of Fe(II) loading and CT concentration on the CT degradation kinetics were also identified at five different concentrations, i.e., 0.5, 1, 2, 5, and 10 mM for Fe(II) and 0.1, 0.5, 1, 2, and 4 mM for CT, respectively. All samples and controls for the parametric experiments were prepared by following the experimental procedure described above and by adjusting the factors at exact concentrations as specified. The degradation kinetics of CT was monitored to investigate the concentration effect of environmental factors by measuring its aqueous concentration at each sampling time. All batch samples and controls in this study were prepared in duplicate.

3. Analytical Procedures

Concentrations of CT, TCE, tri-, and dichloromethane in aqueous solution were measured using a GC (HP 5890) with an electron capture detector (ECD) and HP-5 column (J&W Co.: 30 m length, 0.32 mm i.d., and 0.25 μm thickness). The temperatures of injector, detector, and oven were 175, 200, and 80 °C, respectively. Vials at each sampling time were centrifuged at 3,000 rpm for 5 min and 100 μL of supernatant was transferred to 2 mL GC-vials containing 1.4 mL extractant (n-hexane with 10 mg L^{-1} 1,2-DBP). GC-vials were mounted on orbital shaker to extract residual CT and TCE for 1 h at 200 rpm and 1 μL of extractant was injected into the GC-ECD injector.

Chloride concentration in aqueous solution at each sampling time was measured by an ion chromatograph (DX-120, DIONEX) with an IonPac AS4A-SC anion column and a conductivity detector. An exact amount of NaOH (2 M) was added to each vial to quench the modified Fenton reaction immediately after the collecting of samples for CT measurement. The vial was centrifuged at 3,000 rpm for 30 min and 100 μL of supernatant was transferred to a conical tube containing 4.9 mL DIW for dilution. The diluted sample was filtered by a membrane filter (0.2 μm pore size, Advantec Co, Japan) and the filtrate was introduced into an IC injector.

RESULTS AND DISCUSSION

1. Enhanced Degradation of CT by Fe(II)-CS/GLA in the Modified Fenton System

CT degradation kinetics were obtained by Fe(II)-CS/GLA in a modified Fenton system at pH 6 (Fig. 1). Potential CT losses were checked by conducting several control tests. CT recoveries of all control samples (CT, CT+Fe(II), CT+Fe(II)-CS/GLA, CT+H_2O_2, and CT+CS/GLA) were more than 90%, indicating no significant losses due to sorption and volatilization in a batch reactor (CT), reductions by aqueous Fe(II) and Fe(II)-CS/GLA (CT+Fe(II) and CT+Fe(II)-CS/GLA), oxidation by H_2O_2 (CT+H_2O_2), and sorption
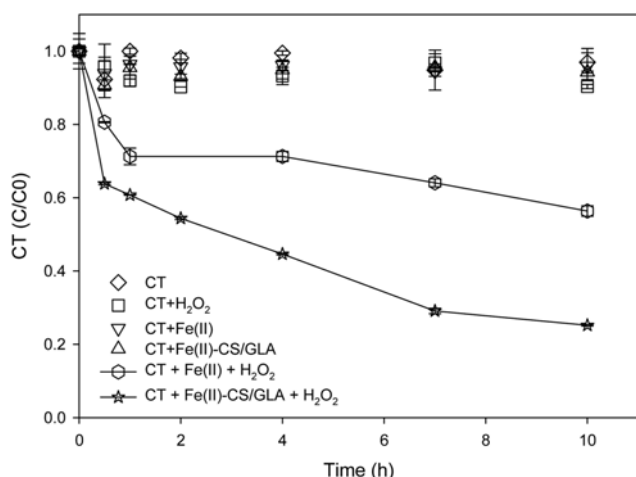
Fig. 1. Degradation of CT under different experimental conditions (Four types of controls, classic Fenton reaction, modified Fenton reactions with Fe(II)-CS/GLA). The controlled experimental factors are: $[CT]_0=0.1$ mM, $[Fe(II)]_0=5$ mM (0.28 g L^{-1}), $[H_2O_2]_0=318$ mM, $[CS/GLA]=2$ g L^{-1}, and initial suspension pH=6.
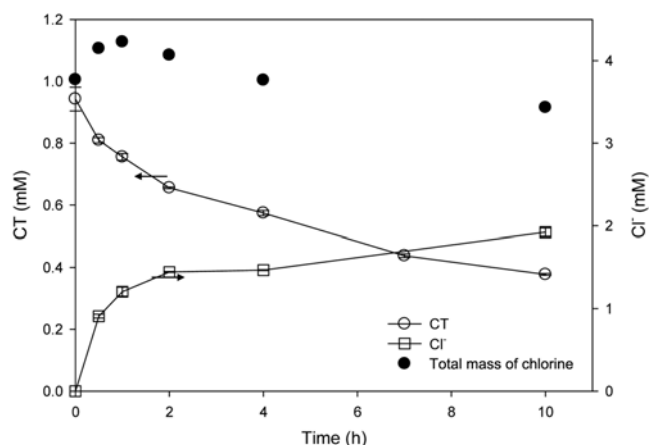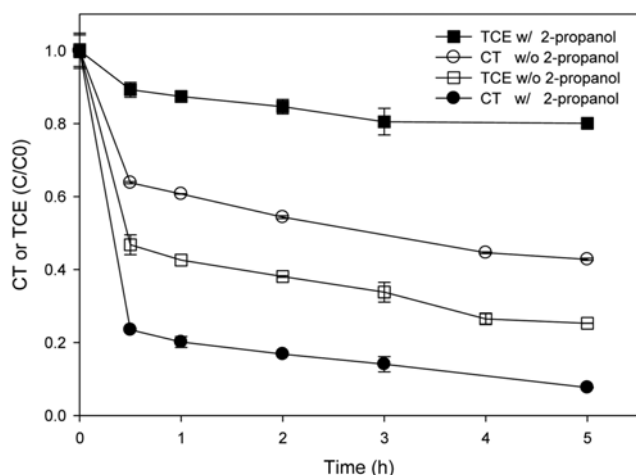

Fig. 2. Formation Cl^- and total chlorine mass balance in the modified Fenton reaction. Experimental conditions: $[CT]_0=0.94$ mM, $[Fe(II)]_0=5$ mM (0.28 g L^{-1}), $[H_2O_2]_0=318$ mM, $[CS/GLA]=2$ g L^{-1}, and initial suspension pH=6.

by CS/GLA (CT+CS/GLA) during the reaction. Reductive dechlorination of chlorinated hydrocarbons has been reported to occur in the presence of Fe(II) species including aqueous Fe(II), soluble Fe(II) complexes, surface-bound Fe(II), and structural Fe(II) in iron bearing soil minerals [22,23]. However, no significant reductive degradation of CT has been observed in the presence of aqueous Fe(II) and Fe(II)-CS/GLA (without H_2O_2) in this study due probably to different experimental conditions. We have observed 74.8% of CT degradation by the Fe(II)-CS/GLA in the modified Fenton system in 10 h, while 43% of CT degradation occurred in the classic Fenton system at pH 6. Aqueous Fe(II) in the classic Fenton system formed iron precipitates $(Fe(OH)_{3(s)})$ at pH 6, which hindered the Fenton chain reaction for the degradation of CT [1,24]. CS/GLA enhanced the degradation of CT by increasing the stability of chelated Fe(II) by avoiding the precipitation of aqueous Fe(II) in the modified Fenton system. Specific evidences by 2-propanol experiment and product study in the next section can explain the CT degradation mechanism by Fe(II)-CS/GLA in the modified Fenton reaction clearly.

2. Identification of Redox Dechlorination Mechanism of CT by Fe(II)-CS/GLA in the Modified Fenton System

The results obtained from SEM/EDX and TEM analysis in previous study showed that iron was properly chelated with amine group in CS/GLA [18]. XPS data in previous study showed that electrons released from the Fe(II)-CS/GLA were used for the reduction of H_2O_2 to OH• and that Fe(III)-CS/GLA can be reduced by H_2O_2 in the modified Fenton reaction [18]. Based on the results of surface analysis in previous study, we can propose a role of Fe(II)-CS/GLA for the degradation of CT in the modified Fenton system; i.e., Fe(II)-CS/GLA avoiding the formation of aqueous iron precipitation at near-neutral pH releases electrons to reduce H_2O_2 to OH• leading to the initiation of the modified Fenton reaction for the degradation of CT. It is oxidized to Fe(III)-CS/GLA simultaneously and can be reduced to Fe(II)-CS/GLA by H_2O_2 again. Therefore, its catalytic role to degrade CT could be continuously carried out

during the reaction.

Aqueous Cl^- concentration was measured at each sampling time to confirm the dechlorination of CT by Fe(II)-CS/GLA in the modified Fenton reaction. Fig. 2 shows the dechlorination of CT, its corresponding formation of Cl^-, and total mass of chlorine during the reaction. No significant CT degradation (3%) and chloride formation (no detection) were observed during control tests under the same experimental conditions (data are not shown in the figure). However, chloride formed rapidly in the modified Fenton system with Fe(II)-CS/GLA at an early stage and total mass balance of chlorine (measured Cl^- concentration+chlorine concentration equivalent to CT concentration) at each sampling time stayed greater than 91% of total chlorine mass of initial CT throughout the experiment. Less chlorinated products such as tri- (CF) and dichloromethanes (DCM) were detected in the near range of detection limit which was not able to quantify its concentrations, while monochloromethane was not detected throughout the experiment. This may be caused due to a rapid reductive transformation of CT by a potential reductant such as $O_2^{\cdot-}$ formed during the modified Fenton reaction. The formation of Cl^- and less chlorinated products confirms that the CT degradation by Fe(II)-CS/GLA in the modified Fenton system mainly followed a reductive dechlorination pathway. Perchlorinated alkanes have been recognized to be easily reduced but hardly oxidized, while less chlorinated organic compounds are hardly reduced but easily oxidized in pyrite Fenton system [25]. This suggests that the products, less chlorinated CF and DCM, can be selectively oxidized by reactive oxidants such as OH• after the reductive dechlorination of CT by Fe(II)-CS/GLA in the modified Fenton system. Because a small amount of reduction products was measured during the reaction, we can hypothesize that the relatively strong oxidative degradation occurred for further transformation of CF and DCM. No analytical measurements to identify and quantify oxidation products such as phosgene, carbon dioxide, and carbonate were conducted in this study [4,26,27].

It has been reported that OH• is a main reactant for oxidative degradation of TCE by Fe(II)-CS/GLA in the modified Fenton system [18]. Based on the transformation products, however, OH• does not

Fig. 3. Degradation of CT and TCE in modified Fenton reactions with and without 2-propanol. Experimental conditions: $[CT]_0$ and $[TCE]_0$=0.1 mM, $[Fe(II)]_0$=5 mM (0.28 g L^{-1}), $[H_2O_2]_0$= 318 mM, [CS/GLA]=2 g L^{-1}, and initial suspension pH=6.

Fig. 4. Effect of H_2O_2 concentration on the degradation of CT in the modified Fenton reaction. Experimental conditions: $[CT]_0$ =0.1 mM, $[Fe(II)]_0$=5 mM (0.28 g L^{-1}), [CS/GLA]=2 g L^{-1}, and initial suspension pH=6.

seem to be a potential reactant for the reductive dechlorination of CT in the same system. To check the role of OH• in the degradation of CT and further understand its reaction mechanism, batch kinetic tests were conducted by adding an excess amount of 2-propanol to scavenge OH• in the modified Fenton system at pH 6. Fig. 3 shows that CT degradation was enhanced from 57.2% to 92.4% by the addition of 2-propanol, while TCE degradation was significantly inhibited from 74.7% to 19.9% by 2-propanol in the modified Fenton system. The enhancement of CT degradation with 2-propanol may be due to the increase of $O_2^{\cdot-}$, which is in good agreement with an experimental result showing a reductive degradation of CT by KO_2 with excess amount of 2-propanol [4,6]. $O_2^{\cdot-}$ is a more reactive reductant in aprotic solvent than in water because its solvation by water decreases its lifetime and reactivity [4]. In the presence of 2-propanol, the main reaction to produce potential reactants in the system is Fe(III)-CS/GLA catalyzed decomposition of H_2O_2 to $HO_2^{\cdot}$ (Fe(III)-CS/GLA+H_2O_2→Fe(II)-CS/GLA+$HO_2^{\cdot}$+H^+), which can be equilibrated with $O_2^{\cdot-}$ ($HO_2^{\cdot}$↔$O_2^{\cdot-}$+H^+, pK_a=4.8). Both $HO_2^{\cdot}$ and $O_2^{\cdot-}$ could be reactive chemical species available for the CT degradation. Although $HO_2^{\cdot}$ is weaker oxidant (oxidation potential: 1.7 V) than OH• (2.8 V), it is unlikely for the reductive dechlorination of CT to occur. On the contrary, $O_2^{\cdot-}$ known as a reductant and nucleophile can play the main role for the reductive dechlorination of CT [2,4,28]. Less degradation efficiency in CT degradation without 2-propanol is likely due to the consumption of $HO_2^{\cdot}$ by OH• in an early stage (OH•+$HO_2^{\cdot}$→H_2O+O_2). This suggests that OH• cannot play the main role in the degradation of CT by Fe(II)-CS/GLA in the modified Fenton system but $O_2^{\cdot-}$ can. The inhibition of TCE degradation by Fe(II)-CS/GLA in the modified Fenton reaction with 2-propanol is due to its OH• scavenging effect, which is very similar to an experimental result showing the degradation of 1-butyl-3-methylimidazolium chloride in the Fenton reaction with 2-propanol [29]. Therefore, the oxidative degradation of TCE can be significantly occurring by OH• produced in the modified Fenton system without 2-propanol. The results indicate that the degradation of chlorinated contaminant in the modified Fenton reaction with Fe(II)-CS/
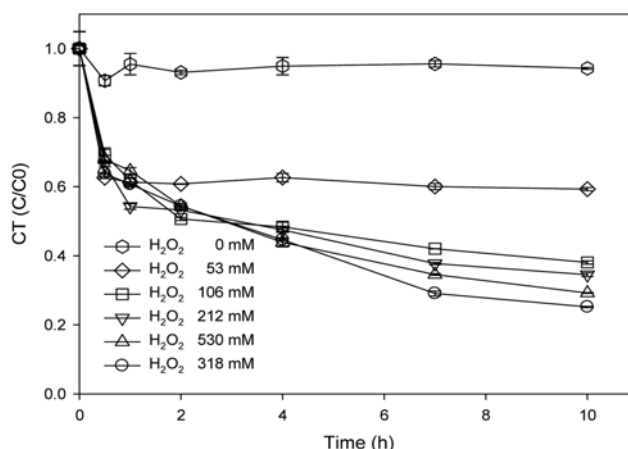
GLA can follow a versatile reaction pathway depending on the contaminant type, i.e., TCE was degraded by OH• via oxidative degradation and CT was mainly done by $O_2^{\cdot-}$ via reductive dechlorination.

3. Effect of Concentrations of H_2O_2, Fe(II), and CT on the Degradation Kinetics of CT

Fig. 4 shows the effect of H_2O_2 concentration on the CT degradation kinetics in the modified Fenton system with Fe(II)-CS/GLA. It has been reported that CT degradation did not occur by $O_2^{\cdot-}$ in deionized water, but it can occur by the classic Fenton reaction with an excess amount of H_2O_2 (>100 mM) [4,6]. We have observed an enhancement of CT degradation by the increase of H_2O_2 in the modified Fenton system with Fe(II)-CS/GLA. This is due to the increase of $O_2^{\cdot-}$ formed from the decomposition of increased H_2O_2 in the modified Fenton system, which can be properly supported by experimental results showing the increase of $O_2^{\cdot-}$ by increasing H_2O_2 concentration in suspensions with metal oxides [30]. Although the maximum removal of CT (74.8%) was observed at 318 mM H_2O_2, the degradation rate of CT with respect to time decreased with the increase of H_2O_2 concentration due to less CT removal in the first two sampling times caused by scavenging of •OH by extra H_2O_2. This indicates a saturation in degradation kinetic rates of CT due to saturation in the formation rate of $O_2^{\cdot-}$ in the modified Fenton system [31]. The formation rate of $O_2^{\cdot-}$ can decrease as the increase of H_2O_2 concentration, which may be due to its subsequent $HO_2^{\cdot}$ scavenging mechanism, i.e., H_2O_2 can consume more $HO_2^{\cdot}$ with respect to time as it increases (H_2O_2+$HO_2^{\cdot}$→H_2O+O_2+OH•), resulting in less formation of $O_2^{\cdot-}$ with respect to time for the reductive dechlorination of CT [24].

Fig. 5 shows degradation profiles of CT by Fe(II)-CS/GLA at different concentrations of Fe(II) added for its chelation on CS/GLA surfaces. CT removal increased as the concentration of Fe(II) increased by 5 mM. This implies that the Fe(II) concentration significantly affected the formation of $O_2^{\cdot-}$ in the modified Fenton reaction. As the concentration of Fe(II) increased, Fe(II) content in Fe(II)-CS/GLA increased. It has been reported that sorbed content of Fe(II) increased from 0 to 40 mg g^{-1} as aqueous concentration of Fe(II) increased from 0 to 600 mg L^{-1} in the previous adsorption isotherm
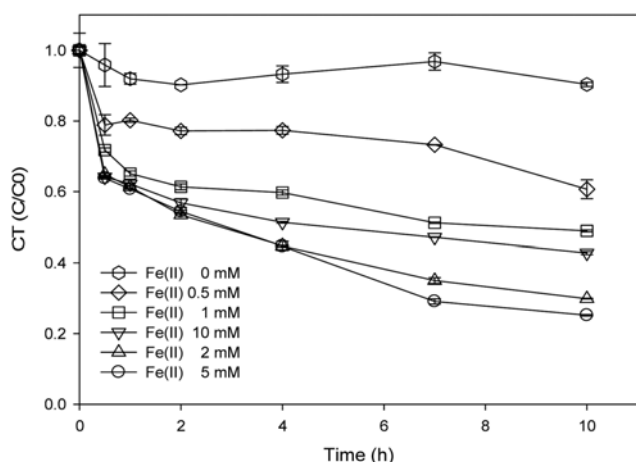
Fig. 5. Effect of Fe(II) concentration on the degradation of CT in the modified Fenton reaction. Experimental conditions: $[CT]_0$=0.1 mM, $[H_2O_2]_0$=318 mM, [CS/GLA]=2 g L^{-1}, and initial suspension pH=6.
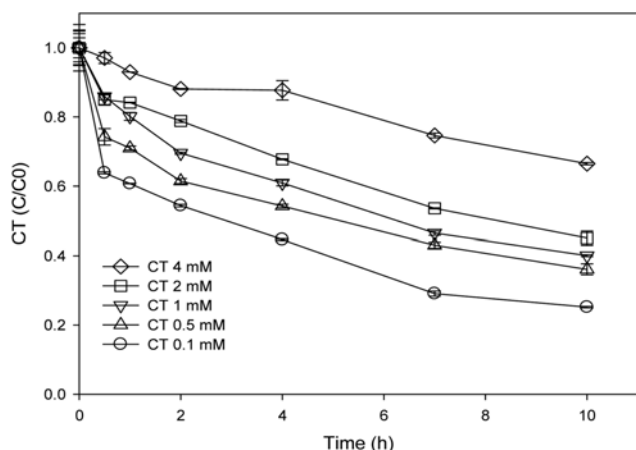

Fig. 6. Effect of CT concentration on its degradation in the modified Fenton reaction. Experimental conditions: $[Fe(II)]_0$= 5 mM (0.28 g L^{-1}), $[H_2O_2]_0$=318 mM, [CS/GLA]=2 g L^{-1}, and initial suspension pH=6.

test on the surface of CS/GLA [20]. This leads to more production of $O_2^{\cdot-}$ and enhancement of CT degradation kinetics in the modified Fenton system. CT removal, however, decreased at 10 mM Fe(II), which may be due to self scavenging of $HO_2^{\cdot}$ at high content of Fe(II)-CS/GLA in the modified Fenton reaction (Fe(II)-CS/GLA+$HO_2^{\cdot}$→ Fe(III)-CS/GLA+O_2+H^+ and/or Fe(III)-CS/GLA+$HO_2^{\cdot}$→Fe(II)-CS/GLA+HO_2^-) [10,24].

Fig. 6 shows the effect of CT concentration on the CT degradation by Fe(II)-CS/GLA. The removal efficiency of CT decreased from 74.8 to 33.5% as the concentration of CT increased from 0.1 to 4 mM. Except 4 mM case, CT concentration decreased quickly at first sampling time (30 min) and then its degradation rate slowed down as the reaction proceeded. This is due to the limited amount of reactant ($O_2^{\cdot-}$) produced in the modified Fenton system at constant concentrations of Fe(II)-CS/GLA and H_2O_2. At lower CT concentration, $O_2^{\cdot-}$ concentration formed during the modified Fenton reaction was high enough to fully degrade CT. This indicates that

CT concentration was a main factor to affect its degradation kinetics (i.e., much more like pseudo-first order kinetics). In contrast, at higher CT concentration, $O_2^{\cdot-}$ formed during the reaction at same experimental conditions was not enough to fully degrade CT. Therefore, both concentrations of CT and $O_2^{\cdot-}$ can influence the degradation kinetics of CT. This suggests that the modified Fenton reaction of CT by Fe(II)-CS/GLA follows a reactant limiting second-order degradation kinetics. Therefore, the degradation of CT decreased as CT concentration increased.

CONCLUSIONS

The experimental results obtained from this study established that the modified Fenton reaction with Fe(II)-CS/GLA can effectively dechlorinate CT at near-neutral pH by avoiding iron precipitation, a difficult problem required to be solved for the enhancement of classic Fenton reaction and its proper application. The dechlorination of CT in the modified Fenton system was influenced by the concentrations of H_2O_2, Fe(II), and CT. The results can be applied to estimate optimal amounts of Fe(II)-CS/GLA and H_2O_2 to enhance the degradation of CT in the modified Fenton system. The degradation of chlorinated contaminant in the modified Fenton reaction with Fe(II)-CS/GLA can follow either an oxidative or reductive degradation pathway depending on the contaminant type. We can estimate its degradation kinetics and predict the different reaction mechanism based on the experimental results. However, further research to identify an effect of contaminant type on the reaction mechanism needs to be conducted for clear understanding of degradations of chlorinated contaminants in the modified Fenton system and their proper applications. The results obtained from the Fe(II)-CS/GLA study can provide basic knowledge to develop novel and versatile remediation alternatives and give a clear scientific solution for the application of Fenton reaction to soil and groundwater contaminated with perchlorinated alkanes at near-neutral pH, which generally does not work well at remediation sites.

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