



## Degradation of trichloroethylene by Fe(II) chelated with cross-linked chitosan in a modified Fenton reaction

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### ABSTRACT

Degradation of trichloroethylene (TCE) by a modified Fenton reaction was investigated in aqueous solution. Fenton reaction can be significantly enhanced in the presence of Fe(II) chelated by cross-linked chitosan (CS) with glutaraldehyde (GLA) at neutral pH. A remarkable oxidative degradation of TCE ( $1.838 \text{ h}^{-1}$ ) was observed in the modified Fenton system with Fe(II)-CS/GLA (10 mM and  $2 \text{ g L}^{-1}$ , respectively) and  $\text{H}_2\text{O}_2$  (318 mM), while no significant degradation ( $0.005 \text{ h}^{-1}$ ) was observed in the classic Fenton reaction system with Fe(II) (10 mM) and  $\text{H}_2\text{O}_2$  (318 mM) at pH 7 in 5 h. The kinetic rate constants for the degradation of TCE in the modified Fenton system was dependent on the initial suspension pH, Fe(II) loading, CS/GLA dosage, and concentration of  $\text{H}_2\text{O}_2$ . We observed the formation of surface Fe(II)-CS/GLA complex using microscopic analyses and identified Fe oxidation (Fe(II) to Fe(III)) coupled with  $\text{H}_2\text{O}_2$  reduction on the Fe(II)-CS/GLA surfaces during the modified Fenton reaction.

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### 1. Introduction

The release of chlorinated organic compounds is a significant public health and environmental concern due to their harmful characteristics such as high carcinogenicity, toxicity, and flammability. Trichloroethylene (TCE) is one of the most well known chlorinated organic compounds frequently and ubiquitously found in soil and groundwater systems [1]. Under the Safe Drinking Water Act, its maximum contaminant level has been set at  $5 \mu\text{g L}^{-1}$  by United States Environmental Protection Agency.

Fast degradation kinetics of TCE by chemical oxidation over other alternative reactions has been reported [1–3]. Fenton process among the chemical oxidation processes has attracted attention due to its low environmental impacts and high reactivity for the removal of organic contaminants. Hydroxyl radical ( $\text{OH}^\bullet$ , oxidation potential: 2.8 V) produced from the Fenton process is a stronger oxidant than hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 1.8 V) and ozone ( $\text{O}_3$ , 2.1 V) oxidizing target organic compounds with higher degradation rates. Classic Fenton system requiring aqueous Fe(II) for the formation of  $\text{OH}^\bullet$  has been properly operated at the pH range of 2–4 by avoiding the formation of  $\text{Fe}(\text{OH})_3(\text{s})$  [4]. Maintaining the low pH in Fenton process is very important to achieve optimal removal of contaminants in water and wastewater treatment systems. However, this may encounter a potential difficulty due to buffer capacity of natural soil, when the process is applied to contaminated soil and

groundwater systems [5]. To overcome the difficulty and enhance removal efficiency at neutral environment easily found in the natural systems, researchers have made extraordinary efforts to develop novel treatment technologies by modifying the classic Fenton process. It has been known that the reactivity of classic Fenton can be significantly enhanced by irradiation of near-UV and visible light, resulting in the regeneration of Fe(II) and more production of  $\text{OH}^\bullet$  during the modified UV-vis Fenton reactions [4–7]. Chelate based-Fenton reactions in which Fe(II) and Fe(III) combined with metal chelating agents can minimize non-specific loss of soluble iron by avoiding its precipitation have been reported to significantly enhance the degradation of organic contaminants even at neutral pH [4,8,9]. Citrate and 2-hydroxyethyliminodiacetic acid have been used as chelating agents for the degradation of TCE [9] and toluene [10], respectively. Recently, chitosan (CS) has attracted researchers' attention as a natural chelating agent of chemical catalysts. A CS-supported palladium catalyst has been efficiently used for the degradation of chlorophenol [11], nitrophenol [12], and nitrotoluene [13]. It has been reported that Cu(II)-CS complex has played a significant role of heterogeneous catalyst for degradations of textile dyes [14] and hydroquinone [15].

CS can be obtained from full or partial deacetylation of chitin, one of the most abundant biopolymers in natural environment. Due to its unique properties such as biocompatibility, biodegradability, hydrophilicity, non-toxicity, and chemical inertness, it has been used in a variety of industries, e.g., pharmaceutical, environmental, and biotechnological industries [16,17]. Raw CS can be easily dissolved in most mineral acids and oxidized by  $\text{OH}^\bullet$  in the Fenton process [18]. The stability and inertness of CS against  $\text{OH}^\bullet$  can be

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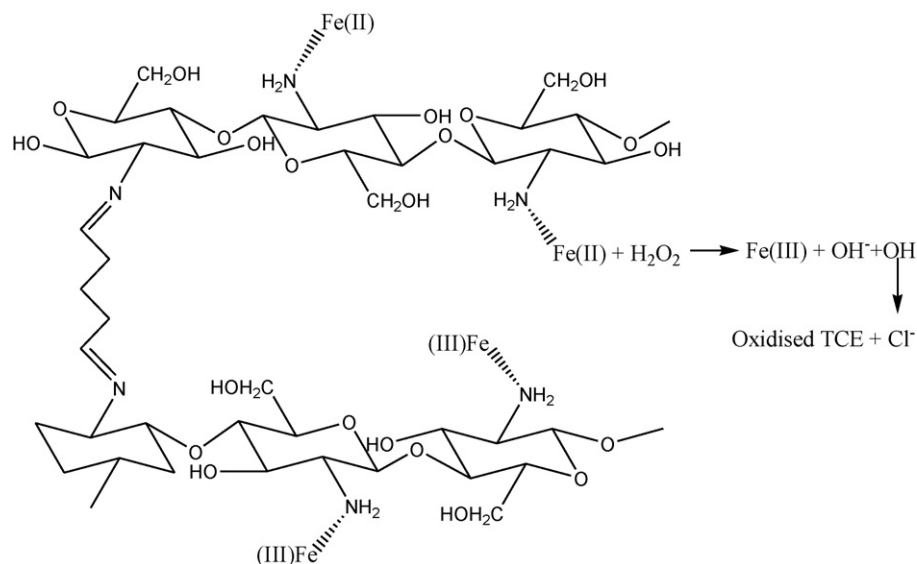


Fig. 1. Initiation of oxidative degradation of TCE by Fe(II)-CS/GLA in the modified Fenton reaction.

obtained by a chemical cross-linking process. Glutaraldehyde (GLA) has been used as a cross-linking agent to stabilize CS by forming imine ( $-\text{C}=\text{N}-$ ) group via Schiff base reaction between an amine group of CS and an aldehyde group of GLA. Although the cross-linking process decreases the availability of amine group for Fe(II) sorption [19,20], it can improve resistance of cross-linked CS with GLA (CS/GLA) to chemical degradations [17,20]. The amine group from CS structure can provide multiple binding sites to form complexes with Fe(II), which can avoid the precipitation of  $\text{Fe}(\text{OH})_3(\text{s})$  even at neutral pH during the modified Fenton reaction. Fig. 1 shows a chemical structure of Fe(II)-CS/GLA and initiation of the modified Fenton reaction. There have been many experimental reports about CS as a support material for environmental catalysts. However, a catalytic role of Fe(II)-CS/GLA for oxidative degradation of chlorinated organics in the modified Fenton reaction has not been studied significantly.

The objective of this study was to characterize the oxidative degradation of TCE by modified Fenton reaction with Fe(II)-CS/GLA. Batch kinetic experiments were conducted to investigate the effect of initial suspension pH, Fe(II) loading, CS dosage, and concentration of  $\text{H}_2\text{O}_2$  on the degradation kinetics of TCE and to determine an optimal operation condition. TCE and Fe(II)-CS/GLA were chosen as a representative contaminant and a reactant for the modified Fenton system, respectively. Spectroscopic and microscopic analyses on the surface of Fe(II)-CS/GLA were conducted to explore the modified Fenton reaction mechanism during the oxidative degradation of TCE.

## 2. Experimental

### 2.1. Chemicals

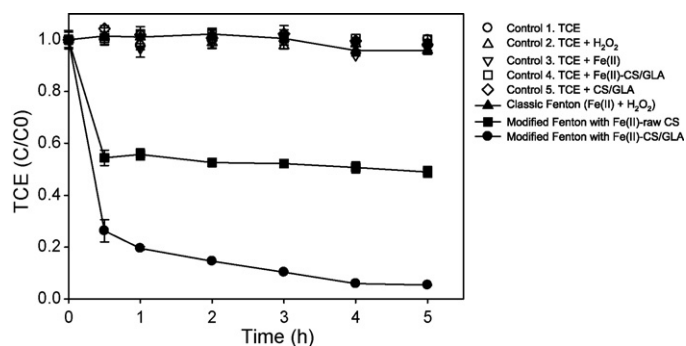
Please refer to chemicals in the [supporting information](#).

### 2.2. Experimental procedures

Batch kinetic experiments were conducted to characterize the oxidative degradation of TCE by Fe(II)-CS/GLA using an amber borosilicate glass vial (nominal volume: 20 mL, Kimble) with an open-top cap with a three-layered septum system [21]. Fe(II)-CS/GLA suspension was freshly prepared for each experimental run with a great caution. An exact amount of Fe(II) was dissolved in ultra-pure deionized water (DIW, 18 M $\Omega$  cm) resulting

in 10 mM Fe(II) solution. An exact amount of CS/GLA was added to the solution for a chelation between Fe(II) and CS/GLA ( $2 \text{ g L}^{-1}$ ) and the suspension was mixed at 100 rpm for 1 h at room temperature. The initial pH of Fe(II)-CS/GLA suspension was adjusted at 7 by the addition of 5 M NaOH. An exact amount of the suspension (23.3 mL) was transferred to the vials right before an initiation of modified Fenton reaction to avoid a potential iron flocculation and/or precipitation with dissolved oxygen. The reaction was initiated by spiking 100  $\mu\text{L}$  TCE stock solution and adding an exact amount of 600  $\mu\text{L}$   $\text{H}_2\text{O}_2$  into the vials, resulting in 0.1 and 318 mM, respectively. The vials were capped immediately, mounted on a tumbler, and mixed at 7 rpm and room temperature in the dark room to avoid photoreactions [6,7,22]. To compare the reactivity of classic Fenton and to investigate effectiveness of cross-linking step, batch kinetic samples (i.e.,  $\text{Fe(II)} + \text{TCE} + \text{H}_2\text{O}_2$  and  $\text{Fe(II)-raw CS} + \text{TCE} + \text{H}_2\text{O}_2$ ) were also prepared by following the procedure described above. No headspace was allowed for all samples and controls during the reaction time. Five types of controls (DIW + TCE, DIW + TCE +  $\text{H}_2\text{O}_2$ , DIW + Fe(II) + TCE, DIW + CS/GLA + TCE, and DIW + Fe(II)-CS/GLA + TCE) were prepared to check any possible losses of TCE due to sorption, volatilization, homogeneous oxidative degradation, and reductive dechlorination during the reaction time in each experiment. The degradation kinetics of TCE was monitored by measuring its aqueous concentration at each sampling time. All controls and samples were prepared in duplicate.

Batch kinetic experiments were also carried out to investigate the effect of environmental parameters (initial suspension pH, Fe(II) loading, dosage of CS/GLA, and concentration of  $\text{H}_2\text{O}_2$ ) on the TCE degradation kinetics. For a parametric study where initial suspension pH was an environmental parameter, the initial pH of Fe(II)-CS/GLA suspension was adjusted by 5 M NaOH and its effect was investigated in the pH range of 5–7. Fe(II) loading and CS/GLA dosage were 10 mM and  $2 \text{ g L}^{-1}$ , respectively. The reaction was initiated by subsequent spiking of stock TCE and  $\text{H}_2\text{O}_2$ , resulting in 0.1 and 318 mM, respectively. The effect of Fe(II) loading on the TCE degradation kinetics was identified at four different levels (1, 3, 5, and 10 mM). The initial pH of Fe(II)-CS/GLA suspension was set at pH 7 and the experiment was conducted at the same concentrations of CS/GLA, TCE and  $\text{H}_2\text{O}_2$ . To investigate the effect of CS/GLA dosage and  $\text{H}_2\text{O}_2$  concentration on the degradation kinetics, we used five different dosages of CS/GLA (0.4, 1, 2, 4, and  $10 \text{ g L}^{-1}$ ) and five different concentrations of  $\text{H}_2\text{O}_2$  (27, 53, 159, 318, and 530 mM)



**Fig. 2.** Degradation of TCE under different experimental conditions (5 types of controls, classic Fenton reaction, modified Fenton reactions with Fe(II)-raw CS and Fe(II)-CS/GLA). The controlled experimental factors are:  $[TCE]_0 = 0.1$  mM,  $[Fe(II)]_0 = 10$  mM,  $[H_2O_2]_0 = 318$  mM,  $[raw\ CS\ and\ CS/GLA] = 2$  g L<sup>-1</sup>, and initial suspension pH 7.

under the same experimental conditions previously. All batch samples and controls were prepared in duplicate and their preparations followed the same experimental procedure described above.

### 2.3. Analytical procedures

Please refer to analytical procedures in the [supporting information](#).

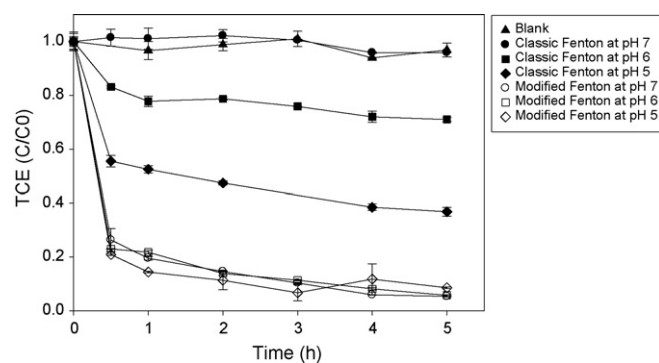
### 2.4. Data handling

Please refer to data handling in the [supporting information](#).

## 3. Results and discussion

### 3.1. Enhanced degradation of TCE by Fe(II)-CS/GLA in the modified Fenton reaction

Fig. 2 shows TCE degradation kinetics by Fe(II)-CS/GLA in the modified Fenton system at pH 7. Control tests were conducted to check potential losses of TCE during the modified Fenton reaction. TCE recoveries of all control samples were more than 98%, indicating no significant TCE losses due to sorption and volatilization in a batch reactor, oxidation by H<sub>2</sub>O<sub>2</sub>, reductions by aqueous Fe(II) and Fe(II)-CS/GLA, and sorption by CS/GLA during the reaction. Oxidative degradation of TCE by H<sub>2</sub>O<sub>2</sub> was reported [23], however no significant TCE removal has been observed in the tests due to different experimental conditions. Reductive dechlorination of chlorinated organics is typically known as a heterogeneous surface reaction [24,25], however we have found no significant reductive degradation of TCE by Fe(II)-CS/GLA. On the contrary, we have observed 95% of TCE degradation by the Fe(II)-CS/GLA in the modified Fenton system in 5 h. This implies that TCE can be significantly degraded by OH<sup>•</sup> generated by the modified Fenton reaction (Fe(II)-CS/GLA + H<sub>2</sub>O<sub>2</sub>). A specific evidence for the initiation of modified Fenton reaction on the surface of Fe(II)-CS/GLA in the surface analysis section can explain the reaction mechanism clearly. Mild TCE degradation (50%) by Fe(II)-raw CS has been observed in the modified system, while no significant degradation has been done in the classic Fenton system. Fe(II)-CS/GLA enhanced the oxidative degradation of TCE by increasing the stability of chelated Fe(II) at pH 7 so that the generation of OH<sup>•</sup> can occur easily. However, aqueous Fe(II) in the classic Fenton system formed an iron precipitation (Fe(OH)<sub>3(s)</sub>) at pH 7, which hinders OH<sup>•</sup> generation [4]. Kinetic rate constant ( $k_2$ ) for the Fe(II)-raw CS was 0.712 h<sup>-1</sup>, which is 2.6 times smaller than that with Fe(II)-CS/GLA. This is due to the decrease of raw CS during the reaction. The raw CS structure may



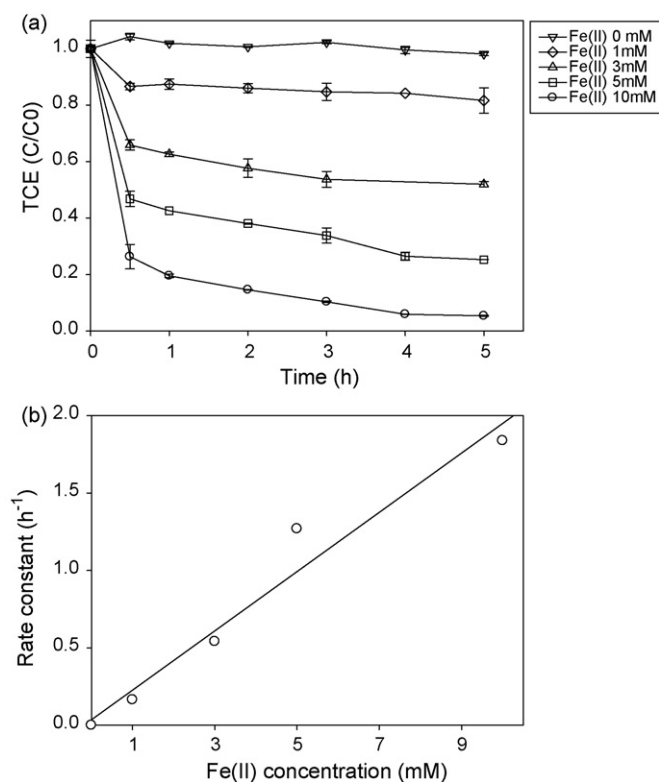
**Fig. 3.** Effect of initial suspension pH on the oxidative degradation of TCE in the modified Fenton reaction. Experimental boundary conditions:  $[TCE]_0 = 0.1$  mM,  $[Fe(II)]_0 = 10$  mM,  $[H_2O_2]_0 = 318$  mM, and  $[CS/GLA] = 2$  g L<sup>-1</sup>.

be attacked by OH<sup>•</sup> generated during the reaction which can be associated at the β-D-(1 → 4) glucosidic linkages [18]. Some metal chelating reagents such as gallic acid and L-ascorbic acid have been reported to be easily oxidized by OH<sup>•</sup> during the oxidative degradation [8,26]. The result indicates that the cross-linking by GLA can enhance the oxidative degradation of TCE by improving the chemical resistance of CS against OH<sup>•</sup>. TCE may be transformed to CO<sub>2</sub> and chloride as major transformation products via oxidative degradation by OH<sup>•</sup> and less amounts of organic acids (formic acid, glyoxylic acid, and dichloroacetic acid) and photoproducts (dichloroacetyl chloride and phosgene) may also be produced during the degradation of TCE [27,28]. No measurements for the transformation products in a modified Fenton reaction were carried out in this study.

### 3.2. Effect of initial suspension pH, [Fe(II)]<sub>0</sub>, CS/GLA dosages, and [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> on the degradation kinetics of TCE

Fig. 3 shows the effect of initial suspension pH on TCE degradation kinetics. As the suspension pH increased from 5 to 7, the degradation of TCE by classic Fenton reaction showed significant decrease in  $k_2$  value. The kinetic rate constant at pH 7 (0.005 h<sup>-1</sup>) was 235.8 times smaller than that at pH 5 (1.179 h<sup>-1</sup>), while no significant decrease was observed in the modified Fenton reaction (from 2.174 to 1.838 h<sup>-1</sup>). This indicates that, as it is well known, the degradation of TCE in the classic Fenton reaction was significantly influenced by the initial suspension pH [4]. The effect of initial suspension pH has been reported to be an important parameter in the classic Fenton system controlling Fe(II) concentration and OH<sup>•</sup> production rate [4,29]. As the pH increased to 7, H<sub>2</sub>O<sub>2</sub> was decomposed to oxygen and water and Fe(II) was precipitated to Fe(OH)<sub>3(s)</sub> resulting in the decrease of OH<sup>•</sup> [4,30,31]. In contrast, the removal of TCE at the neutral pH was more than 93% in the modified Fenton reaction with Fe(II)-CS/GLA. The pH change did not significantly affect the degradation of TCE in the system. This is due to a consistent catalytic role of Fe(II)-CS/GLA for the oxidative degradation of TCE under the different pHs. The Fe(II)-CS/GLA chelating structure can avoid the aqueous iron precipitation to Fe(OH)<sub>3(s)</sub> at neutral pH. This indicates that the modified Fenton reaction can improve the weak point of the classic Fenton system at high pH condition. The slight decrease of  $k_2$  value in the modified Fenton system as the pH increased may be caused by self-decomposition of H<sub>2</sub>O<sub>2</sub> and/or increase of hydroxide ions leading to the decrease of OH<sup>•</sup> (i.e., Fe<sup>2+</sup> + H<sub>2</sub>O<sub>2</sub> → Fe<sup>3+</sup> + OH<sup>-</sup> + OH<sup>•</sup>) [4,32,33].

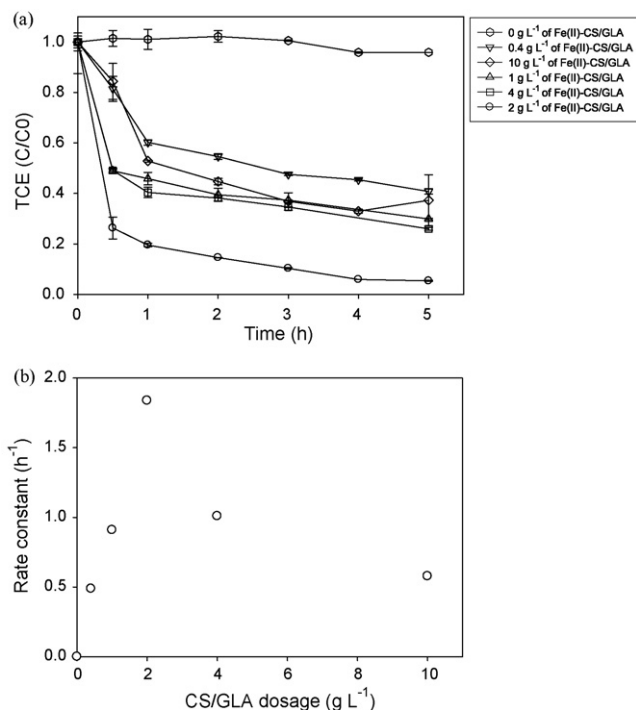
Fig. 4(b) shows the variation of kinetic rate constants for the degradation of TCE at different Fe(II) contents in Fe(II)-CS/GLA. As the content of Fe(II) increased, the kinetic rate constant



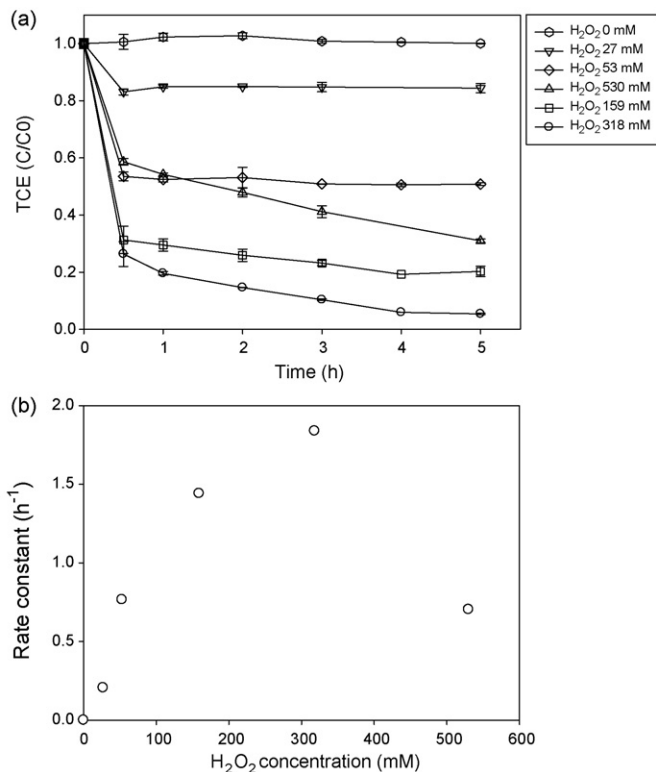
**Fig. 4.** Effect of Fe(II) loading on the oxidative degradation of TCE in the modified Fenton reaction (a). The variation of kinetic rate constants with respect to Fe(II) loading (b). Experimental boundary conditions:  $[TCE]_0 = 0.1$  mM,  $[H_2O_2]_0 = 318$  mM, and  $[CS/GLA] = 2$  g L<sup>-1</sup> at initial suspension pH 7.

increased linearly.  $k_2$  value in the presence of 10 mM Fe(II)-CS/GLA (1.838 h<sup>-1</sup>) was 11.1 times greater than that at 1 mM Fe(II)-CS/GLA. This is because the Fe(II) content is directly related to the production of OH<sup>\*</sup>. As the concentration of aqueous Fe(II) solution to synthesize Fe(II)-CS/GLA increased, the Fe(II) content in Fe(II)-CS/GLA increased. In the previous Fe(II) adsorption isotherm test on the surface of CS/GLA, its content has been reported to increase (0–40 mg g<sup>-1</sup>), as the concentration of aqueous Fe(II) increased (0–600 mg L<sup>-1</sup>) [19]. The result leads to produce more OH<sup>\*</sup> under the experimental condition so that the increased Fe(II) can enhance the degradation kinetics of TCE in the modified Fenton system. This tendency is very similar to that reported for oxidative degradation of alachlor by a modified Fenton reaction with Fe(II)-citrate [32].

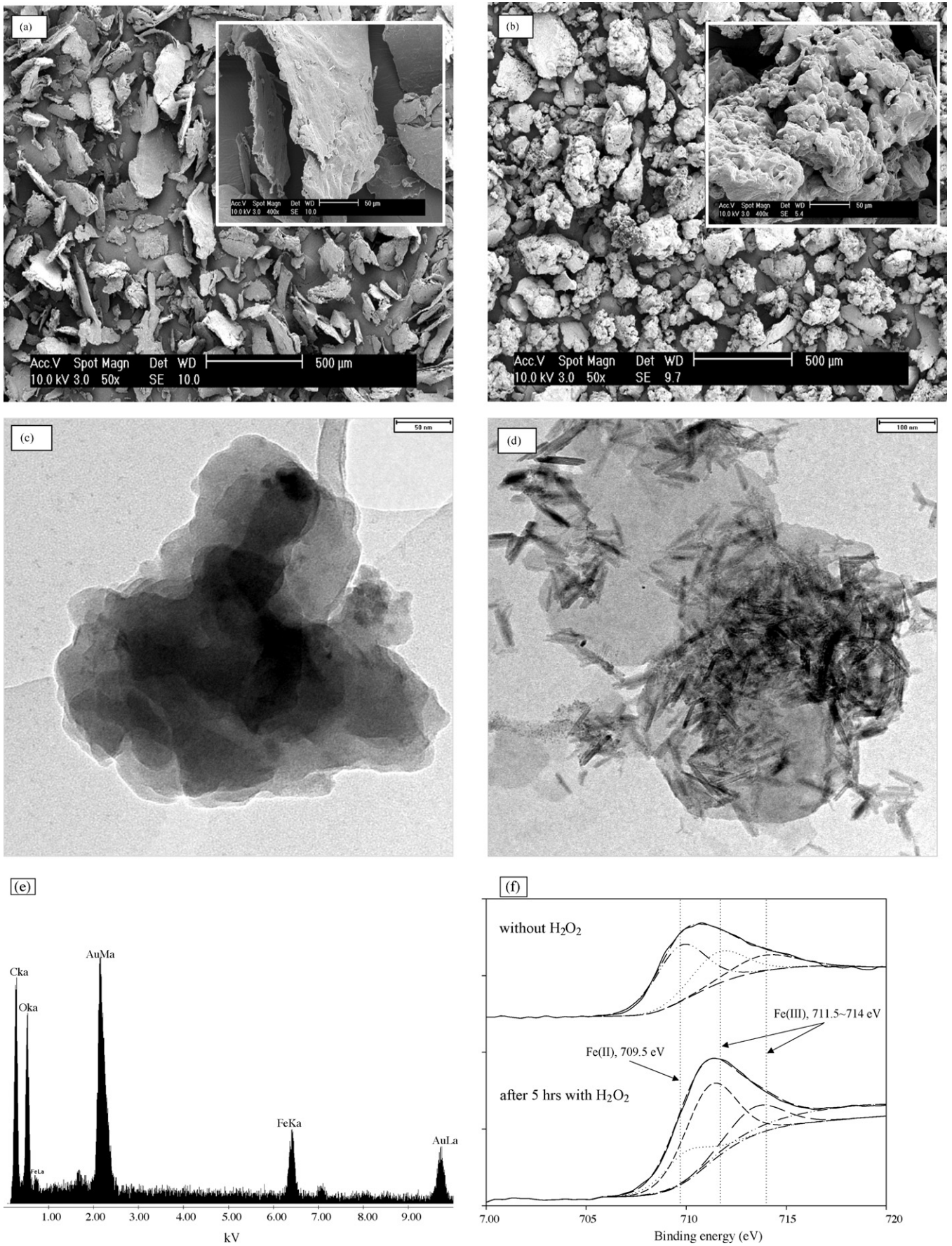
Fig. 5(b) shows the variation of kinetic rate constants for the degradation of TCE at different CS/GLA dosages. The kinetic rate constants linearly increased until the dosage increase to 2 g L<sup>-1</sup>, which may be due to the increase of Fe(II) content in Fe(II)-CS/GLA leading to more production of OH<sup>\*</sup>. Measured Fe(II) concentration adsorbed on the CS/GLA surface was 46 mg L<sup>-1</sup> at 1 g L<sup>-1</sup> of CS/GLA and increased linearly to 92 mg L<sup>-1</sup> as the dosage doubled. However, the kinetic rate constant decreased significantly as the CS/GLA dosage continuously increased to 10 g L<sup>-1</sup>.  $k_2$  values at 4 and 10 g L<sup>-1</sup> CS/GLA decreased by 1.8 and 3.2 times, compared to that at 2 g L<sup>-1</sup> CS/GLA (1.838 h<sup>-1</sup>). This can be explained by self scavenging of OH<sup>\*</sup> by a high content of Fe(II) in the Fenton reaction (i.e.,  $Fe^{2+} + OH^* \rightarrow Fe^{3+} + OH^-$ ) [6,33]. The self scavenging of OH<sup>\*</sup> seemed to start immediately after a maximum  $k_2$  value at 2 g L<sup>-1</sup> and deteriorated reactivity of the modified system by 10 g L<sup>-1</sup>. Calculated molar ratio of  $[H_2O_2]_0/[Fe]_0$  decreased, as the dosage increased under constant  $H_2O_2$  concentration. It was 96.5 and 38.6 at 4 and 10 g L<sup>-1</sup> CS/GLA, respectively, which is in good agreement with an experimental result that a detrimental effect on  $H_2O_2$  decomposi-



**Fig. 5.** Effect of CS/GLA dosage on the oxidative degradation of TCE in the modified Fenton reaction (a). The variation of kinetic rate constants with respect to CS/GLA dosage (b). Experimental boundary conditions:  $[TCE]_0 = 0.1$  mM,  $[Fe(II)]_0 = 10$  mM, and  $[H_2O_2]_0 = 318$  mM at initial suspension pH 7.



**Fig. 6.** Effect of  $H_2O_2$  concentration on the oxidative degradation of TCE in the modified Fenton reaction (a). The variation of kinetic rate constants with respect to  $H_2O_2$  concentration (b). Experimental boundary conditions:  $[TCE]_0 = 0.1$  mM,  $[Fe(II)]_0 = 10$  mM, and  $[CS/GLA] = 2$  g L<sup>-1</sup> at initial suspension pH 7.



**Fig. 7.** SEM images of raw CS (a) and Fe(II)-CS/GLA (b). TEM images of CS/GLA (c) and Fe(II)-CS/GLA (d). SEM/EDX analysis of Fe(II)-CS/GLA (e). XPS spectra for the narrow scan of Fe 2p<sub>3/2</sub> on the surfaces of Fe(II)-CS/GLA with and without H<sub>2</sub>O<sub>2</sub> after reaction time (5 h) (f).

tion leading to OH• formation occurred at the ratio lower than 100 and higher than 250 [34].

Fig. 6(a) shows the effect of H<sub>2</sub>O<sub>2</sub> concentration on the TCE degradation kinetics. A maximum kinetic rate constant (1.838 h<sup>-1</sup>) was observed at 318 mM H<sub>2</sub>O<sub>2</sub>, which is 9 times greater than that at 27 mM H<sub>2</sub>O<sub>2</sub>. This is due to the increase of OH• produced from the decomposition of increased H<sub>2</sub>O<sub>2</sub> in the modified Fenton system. However, the kinetic rate constant started to decrease after reaching its maximum value. The molar ratio of [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>/[Fe]<sub>0</sub> increased, as H<sub>2</sub>O<sub>2</sub> concentration increased continuously. It was 192 at the maximum kinetic rate constant and 324 at highest H<sub>2</sub>O<sub>2</sub> concentration, which is also in good agreement with the experimental results described above [34]. The results can be explained by a subsequent OH• scavenging mechanism, i.e., H<sub>2</sub>O<sub>2</sub>, known as a strong OH• scavenger at high concentration [4,29], can consume OH• rapidly resulting in the formation of less reactive HO<sub>2</sub>• (H<sub>2</sub>O<sub>2</sub> + OH• → HO<sub>2</sub>• + H<sub>2</sub>O) for the oxidative degradation of TCE. HO<sub>2</sub>• can also scavenge OH• (HO<sub>2</sub>• + OH• → H<sub>2</sub>O + O<sub>2</sub>), therefore OH• scavenging by HO<sub>2</sub>• competes with the TCE degradation in the modified Fenton system leading to the significant decrease of kinetic rate constant at 530 mM H<sub>2</sub>O<sub>2</sub>.

### 3.3. Surface analyses to identify the reaction mechanism on the surface of Fe(II)-CS/GLA

Fig. 7(a) and (b) show the SEM images of raw CS and Fe(II)-CS/GLA. A simple flake shape of raw CS particles changed to porous and harsh spherical shape after cross-linking and chelation treatments. Fig. 7(c) and (d) are TEM images of CS/GLA and Fe(II)-CS/GLA showing an evidence for the aggregation and crystal growth (black sticks shape) of iron on the surfaces. SEM/EDX analysis on the surface of Fe(II)-CS/GLA (Fig. 7(e)) shows that the main chemical components on the surfaces are O, C, and Fe. Fe peak was shown at Fe(II)-CS/GLA sample, while no peak was detected at CS/GLA sample (figure is not shown). This indicates that iron is properly chelated with amine group in CS/GLA structure via Fe(II)-chelation treatment [19].

XPS analysis was conducted to investigate the redox state of Fe on the surfaces of CS/GLA with and without H<sub>2</sub>O<sub>2</sub> at the end of reaction time (5 h). Fig. 7(f) shows the narrow region spectra for Fe 2p<sub>3/2</sub> which were composed of three identical peaks at 709.5, 711.5, and 714 eV, respectively. The binding energy for Fe(II)-O and Fe(III)-O has been reported to be in the range of 709–709.5 and 711–714 eV, respectively [35,36]. Area percentage of each peak is summarized in Fig. 7(f). Fe on the CS/GLA surfaces without H<sub>2</sub>O<sub>2</sub> was composed of 34.87% Fe(II) and 65.13% Fe(III), while its composition changed to 26.85% Fe(II) and 73.15% Fe(III) after the reaction with H<sub>2</sub>O<sub>2</sub>. Because no reductive dechlorination of TCE by Fe(II)-CS/GLA was observed in the control tests, the oxidation of Fe(II) to Fe(III) on the surface of CS/GLA can be associated with a coupled reduction of H<sub>2</sub>O<sub>2</sub> to OH•. This supports the initiation of the modified Fenton reaction on the Fe(II)-CS/GLA with H<sub>2</sub>O<sub>2</sub>. The content of Fe(III) in Fe(II)-CS/GLA without H<sub>2</sub>O<sub>2</sub> was relatively high, which may be due to the surface oxidation of Fe(II) during sample preparation and/or Fe(II) oxidation by dissolved oxygen during the reaction time.

## 4. Conclusion

An experimental study was conducted to characterize the oxidative degradation of TCE by Fe(II)-CS/GLA and to investigate the effect of environmental factors on the degradation kinetics in modified Fenton system. Significant amount of TCE (95%) was degraded in the modified Fenton reaction, while no degradation was observed in classic Fenton reaction at neutral pH. The neutral pH deteriorating reactivity of the classic Fenton reaction did not

significantly affect the degradation of TCE in the modified Fenton reaction by avoiding iron precipitation due to the stable Fe(II)-CS/GLA structure. The oxidative degradation of TCE was enhanced by the increase of Fe(II) content directly proportional to the production of OH•. However, under an excessive Fe(II) content by the increase of CS/GLA dosage, kinetic rate constant for the oxidative degradation of TCE significantly decreased due to self scavenging of OH•. Similar tendency on the degradation kinetics of TCE by the Fe(II) content was observed when the effect of H<sub>2</sub>O<sub>2</sub> concentration was investigated. The results can be used to estimate optimal amounts of Fe(II)-CS/GLA and H<sub>2</sub>O<sub>2</sub> to enhance the oxidative degradation of TCE in the modified Fenton system. Based on the results of surface analyses, we can propose a reaction mechanism for the oxidative degradation of TCE by Fe(II)-CS/GLA in the modified Fenton system; (1) Fe(II) is properly chelated with amine group of CS/GLA, which forms a stable chemical structure to avoid iron precipitation during the modified Fenton reaction at neutral pH, (2) electrons produced from the oxidation of Fe(II)-CS/GLA to Fe(III)-CS/GLA can be associated with a coupled reduction of H<sub>2</sub>O<sub>2</sub> to OH• leading to the initiation of oxidative degradation of TCE. (3) Fe(III)-CS/GLA is reduced to Fe(II)-CS/GLA by H<sub>2</sub>O<sub>2</sub> so that a catalytic role of Fe(II)-CS/GLA could be continued during the modified Fenton reaction. The results obtained from this study can provide basic understanding to develop novel remediation alternatives and apply Fe(II)-CS/GLA to the classic Fenton reaction which does not work well for the remediation of soil and groundwater contaminated with chlorinated organics at neutral pH.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.01.062.

## References

- [1] K. Kim, M.D. Gurol, Reaction of nonaqueous phase TCE with permanganate, *Environ. Sci. Technol.* 39 (2005) 9303–9308.
- [2] G. Chen, G.E. Hoag, P. Chedda, F. Nadim, B.A. Woody, G.M. Dobbs, The mechanism and applicability of in situ oxidation of trichloroethylene with Fenton's reagent, *J. Hazard. Mater.* 87 (2001) 171–186.
- [3] S.J. Masten, S.H.R. Davies, Efficacy of in-situ ozonation for the remediation of PAH contaminated soils, *J. Contam. Hydrol.* 28 (1997) 327–335.
- [4] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, *Crit. Rev. Environ. Sci. Technol.* 36 (2006) 1–84.
- [5] G.C.C. Yang, C.Y. Liu, Remediation of TCE contaminated soils by in situ EK-Fenton process, *J. Hazard. Mater.* 85 (2001) 317–331.
- [6] R.G. Zepp, B.C. Faust, J. Hoigne, Hydroxyl radical formation in aqueous reactions (pH 3–8) of iron(II) with hydrogen-peroxide—the photo Fenton reaction, *Environ. Sci. Technol.* 26 (1992) 313–319.
- [7] J.J. Pignatello, Dark and photoassisted Fe<sup>3+</sup>-catalyzed degradation of chlorophenoxy herbicides by hydrogen-peroxide, *Environ. Sci. Technol.* 26 (1992) 944–951.
- [8] Y.F. Sun, J.J. Pignatello, Chemical treatment of pesticide wastes—evaluation of Fe(III) chelates for catalytic hydrogen-peroxide oxidation of 2,4-D at circum neutral pH, *J. Agric. Food. Chem.* 40 (1992) 322–327.
- [9] S. Lewis, A. Lynch, L. Bachas, S. Hampson, L. Ormsbee, D. Bhattacharyya, Chelate-modified fenton reaction for the degradation of trichloroethylene in aqueous and two-phase systems, *Environ. Eng. Sci.* 26 (2009) 849–859.
- [10] N. Kang, I. Hua, Enhanced chemical oxidation of aromatic hydrocarbons in soil systems, *Chemosphere* 61 (2005) 909–922.
- [11] T. Vincent, S. Spinelli, E. Guibal, Chitosan-supported palladium catalyst. II. Chlorophenol dehalogenation, *Ind. Eng. Chem. Res.* 42 (2003) 5968–5976.
- [12] T. Vincent, E. Guibal, Chitosan-supported palladium catalyst. 5. Nitrophenol degradation using palladium supported on hollow chitosan fibers, *Environ. Sci. Technol.* 38 (2004) 4233–4240.

- [13] F.P. Blondet, T. Vincent, E. Guibal, Hydrogenation of nitrotoluene using palladium supported on chitosan hollow fiber: catalyst characterization and influence of operative parameters studied by experimental design methodology, *Int. J. Biol. Macromol.* 43 (2008) 69–78.
- [14] R. Sulakova, R. Hrdina, G.M.B. Soares, Oxidation of azo textile soluble dyes with hydrogen peroxide in the presence of Cu(II)-chitosan heterogeneous catalysts, *Dyes Pigm.* 73 (2007) 19–24.
- [15] E. Guibal, T. Vincent, E. Touraud, S. Colombo, A. Ferguson, Oxidation of hydroquinone to p-benzoquinone catalyzed by Cu(II) supported on chitosan flakes, *J. Appl. Polym. Sci.* 100 (2006) 3034–3043.
- [16] D.J. Macquarrie, J.J.E. Hardy, Applications of functionalized chitosan in catalysis, *Ind. Eng. Chem. Res.* 44 (2005) 8499–8520.
- [17] P. Chassary, T. Vincent, J.S. Marcano, L.E. Macaskie, E. Guibal, Palladium and platinum recovery from bicomponent mixtures using chitosan derivatives, *Hydrometallurgy* 76 (2005) 131–147.
- [18] Q.Z. Huang, S.M. Wang, J.F. Huang, L.H. Zhuo, Y.C. Guo, Study on the heterogeneous degradation of chitosan with hydrogen peroxide under the catalysis of phosphotungstic acid, *Carbohydr. Polym.* 68 (2007) 761–765.
- [19] W.S.W. Ngah, S. Ab Ghani, A. Kamari, Adsorption behaviour of Fe(II) and Fe(III) ions in aqueous solution on chitosan and cross-linked chitosan beads, *Bioresour. Technol.* 96 (2005) 443–450.
- [20] T.Y. Hsien, G.L. Rorrer, Heterogeneous cross-linking of chitosan gel beads: kinetics, modeling, and influence on cadmium ion adsorption capacity, *Ind. Eng. Chem. Res.* 36 (1997) 3631–3638.
- [21] W. Lee, B. Batchelor, Reductive capacity of natural reductants, *Environ. Sci. Technol.* 37 (2003) 535–541.
- [22] C. Chevaldonnet, H. Cardy, A. Dargelos, Ab initio CI calculations on the PE and VUV spectra of hydrogen peroxide, *Chem. Phys.* 102 (1986) 55–61.
- [23] D.D. Gates, R.L. Siegrist, In-situ chemical oxidation of trichloroethylene using hydrogen peroxide, *J. Environ. Eng. ASCE* 121 (1995) 639–644.
- [24] R.A. Maithreepala, R.A. Doong, Reductive dechlorination of carbon tetrachloride in aqueous solutions containing ferrous and copper ions, *Environ. Sci. Technol.* 24 (2004) 6676–6684.
- [25] M. Elsner, R.P. Schwarzenbach, S.B. Haderlein, Reactivity of Fe(II)-bearing minerals toward reductive transformation of organic contaminants, *Environ. Sci. Technol.* 38 (2004) 799–807.
- [26] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH/O<sup>-</sup>) in aqueous solution, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886.
- [27] H.T. Pham, K. Suto, C. Inoue, Trichloroethylene transformation in aerobic pyrite suspension: pathways and kinetic modeling, *Environ. Sci. Technol.* 43 (2009) 6744–6749.
- [28] K.H. Wang, J.M. Jehng, Y.H. Hsieh, C.Y. Chang, The reaction pathway for the heterogeneous photocatalysis of trichloroethylene in gas phase, *J. Hazard. Mater.* 90 (2002) 63–75.
- [29] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, *J. Hazard. Mater.* 98 (2003) 33–50.
- [30] S. Papic, D. Vujevic, N. Koprivanac, D. Sinko, Decolourization and mineralization of commercial reactive dyes by using homogeneous and heterogeneous Fenton and UV/Fenton processes, *J. Hazard. Mater.* 164 (2009) 1137–1145.
- [31] W.G. Kuo, Decolorizing dye wastewater with Fenton's reagent, *Water Res.* 26 (1992) 881–886.
- [32] H. Katsumata, S. Kaneco, T. Suzuki, K. Ohta, Y. Yobiko, Photo-Fenton degradation of alachlor in the presence of citrate solution, *J. Photochem. Photobiol. A* 180 (2006) 38–45.
- [33] J.M. Joseph, H. Destailats, H.M. Hung, M.R. Hoffmann, The sonochemical degradation of azobenzene and related azo dyes: rate enhancements via Fenton's reactions, *J. Phys. Chem. A* 104 (2000) 301–307.
- [34] J. De Laat, H. Gallard, Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: mechanism and kinetic modeling, *Environ. Sci. Technol.* 33 (1999) 2726–2732.
- [35] M. Mullet, S. Boursiquot, M. Abdelmoula, J.M. Genin, J.J. Ehrhardt, Surface chemistry and structural properties of mackinawite prepared by reaction of sulfide ions with metallic iron, *Geochim. Cosmochim. Acta* 66 (2002) 829–836.
- [36] J.E. Thomas, C.F. Jones, W.M. Skinner, R.S.C. Smart, The role of surface sulfur species in the inhibition of pyrrhotite dissolution in acid conditions, *Geochim. Cosmochim. Acta* 62 (1998) 1555–1565.