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Electron shuttling catalytic effect of mellitic acid in zero-valent iron induced oxidative degradation

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ABSTRACT

The enhanced oxidation capacity of zero-valent iron (ZVI) using mellitic acid (MA) as an electron shuttle catalyst was investigated using 4-chlorophenol (4-CP) as a model pollutant. In the presence of MA, enhanced electron transfer from ZVI surface to molecular oxygen resulted in higher production of hydrogen peroxide (H_2O_2), which subsequently increased the effective concentration of hydroxyl radical ($HO^\bullet$) generated through the Fenton-type reaction. The possible role of MA as an efficient electron shuttle was supported by cyclic voltammetric estimation of MA reduction potential ($E^0 = -0.184\,V_{NHE}$) and corroborated with photocurrent measurements in the ZVI suspension. Control experiments using Fe(II) ions instead of ZVI demonstrated that the presence of MA in the Fe(II)/H_2O_2 homogeneous system had no significant effect on the 4-CP oxidation efficiency. This indicates that the formation of a Fe(II)-MA complex does not contribute to the 4-CP oxidation pathway. The primary role of MA in the ZVI/O_2 system seems to mediate the electron transfer from the ZVI surface to dioxygen. It implies that organic species containing multiple carboxylic ligands (species like MA or its structural analogues) may function as an electron shuttle in the ZVI/O_2 catalytic system.

1. Introduction

The generation of reactive oxygen species (ROS) by soluble iron species (Fe(II) in particular) in aerobic conditions is kinetically unfavorable for electron transfer from the Fe(II)-aquo complex to molecular oxygen [1]. However, by addition of organic acid ligands capable of iron complexation, the reduction potential of the Fe(II)/Fe(III) redox cycle is lowered, which allows efficient oxygen reduction to form hydrogen peroxide (H_2O_2) [2]. The higher reactivity of the Fe(II)-ligand complex towards H_2O_2 decomposition compared to the Fe(II)-aquo species [3–5] also enhances the Fenton reaction and increases the effective hydroxyl radical ($HO^\bullet$) concentration for oxidation of aqueous organics [6–9]. The ligands are also capable of reducing Fe(III) (formed during the Fenton reaction) back to Fe(II) [5,7]. Thus, the dual role of organic ligand as Fe(II) complexing agent and Fe(III) reductant prevents catalyst loss through precipitation and extends the scope of the Fenton reaction to neutral pH applications [10,11].

Compared to the homogeneous Fenton process, the zero-valent iron (ZVI) system generates both Fe(II) and H_2O_2 *in situ* during the iron corrosion process in the presence of molecular oxygen [12–17]. However, the addition of organic ligands like ethylenediamine tetraacetic acid (EDTA), oxalate or nitrilotriacetic acid in the ZVI system exhibits the same effect as observed in the Fe(II)/H_2O_2 homogeneous system. Cheng et al. reported increased oxidative removal of pesticides by the ZVI/O_2 system in the presence of EDTA [14–16] and attributed this enhancement to complexation of *in situ* generated Fe(II) by EDTA, which resulted in higher H_2O_2 formation by Fe(II) complex-mediated oxygen reduction. Keenan and Sedlak demonstrated that the presence of organic ligands in the ZVI system exhibited enhanced oxidation efficiency over a wide pH range, with the highest value obtained at neutral pH [13]. This enhancement of Fenton reaction was explained in terms of ligand-mediated (1) increase in oxygen reduction efficiency through Fe(II) complexation, and (2) retardation in iron precipitation due to higher solubility of the Fe(II)-ligand complex. Thus, the complexation of Fe(II) with the organic ligand has always been highlighted as a primary factor responsible for the enhanced oxidation in ZVI/ligand/O_2 system.

On the other hand, we demonstrated that natural organic matter (NOM), containing multiple groups capable of iron complexation, can enhance the ZVI-mediated oxidation of organic pollutants through an electron shuttling effect without any contribution from the Fe(II)-complexation pathway [18,19]. Both fulvic and humic

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acids mediated electron transfer from the ZVI surface to O_2, which resulted in enhanced H_2O_2 production and Fe(II) dissolution. This subsequently increased the effective $HO^•$ concentration for oxidation of organic pollutants. Although the quinine moieties of NOM were identified as the reactive sites responsible for the electron transfer action using benzoquinone as a proxy substrate [18,19], the effect of aromatic carboxyl groups present in the NOM matrix on the electron shuttling pathway has not been investigated so far. Although large variabilities in composition and functional group distribution makes NOM chemistry highly complex, the carboxylate groups play an important role because of their higher abundance, low pK_a values, and metal complexation properties [5]. They dissociate much more easily than phenolic groups, which facilitates their participation in NOM-mediated redox transformations.

In this study, to understand the electron transfer capacity of carboxylic ligands in ZVI-mediated oxidation, mellitic acid (benzenehexacarboxylic acid or MA) was chosen as a simplified analogue of NOM [20–22]. Using 4-chlorophenol (4-CP) as a model pollutant, this study reports the enhanced oxidation capacity of the ZVI/O_2 system in the presence of MA as a model electron shuttle. MA-mediated electron transfer between ZVI and O_2 increased the formation of H_2O_2 for enhanced $HO^•$ generation through the Fenton-type reaction.

2. Materials and methods

2.1. Chemicals

Chemicals that were used as received in this study include: 4-chlorophenol (4-CP, Sigma), mellitic acid (MA, Aldrich), 2,9-dimethyl-1,10-phenanthroline (DMP, Aldrich), copper(II) sulfate (Kanto Chemicals), iron(II) perchlorate (Aldrich), lithium perchlorate (Aldrich), benzoic acid (Aldrich), 4-hydroxybenzoic acid (*p*-HBA, Aldrich), hydrogen peroxide (H_2O_2, Junsei), sodium chloride (Samchun), hydrochloric acid (Samchun), sulfuric acid (Junsei), methanol (J.T. Baker), sodium phosphate ($NaHPO_4$, Aldrich) and disodium phosphate (Na_2HPO_4, Aldrich). Iron powder (electrolytic iron, 100 mesh) purchased from Fischer Scientific contains >99% iron content with a surface area of 0.3 m^2/g and a grain size of 0.15 mm [23]. For all experiments, it was pre-treated with 1 M HCl for 5 min to remove surface oxide layer and the treated iron powder was then suspended in water (typical concentration 0.2 g/L). This aqueous slurry was then washed with degassed water (nitrogen purged for 1 h) three times before use. Aqueous stock solutions of MA were freshly prepared every week and stored in a refrigerator. All solutions were prepared in distilled water (18 MΩ cm) prepared by a Barnstead purification system.

2.2. Experimental procedure

The reactions were carried out in 120-mL glass bottles that were continuously stirred on a rotary shaker (228 rpm). Using unbuffered solutions, all experiments were carried out under open air condition to allow dissolved O_2 equilibration in the reaction solution and also to prevent its depletion during the reaction. Using stock solutions of 4-CP (2 mM) and MA (5 mM), aliquots were diluted to make the final concentration of 0.1 mM for both 4-CP and MA. The initial pH of the suspension was then adjusted to 2.5 with 1 M $HClO_4$. Sample aliquots (1 mL) were withdrawn from the reactor at regular intervals, filtered through a 0.45-μm PTFE filter (Millipore) and injected into a 2-mL GC vial. All experiments were carried out in triplicates for a given condition.

2.3. Analysis

Quantitative analysis of 4-CP and MA was done using high performance liquid chromatography (HPLC, Agilent 1100) utilizing an Agilent Zorbax 300SB C-18 column along with a diode-array detector. The eluent solution consisted of (a) 0.1% phosphoric acid and acetonitrile (70:30 v/v) for 4-CP and (b) 0.1% phosphoric acid and methanol (95:5 v/v) for MA. Chloride ion production from 4-CP degradation was quantified using ion chromatography (Dionex DX-120) equipped with a Dionex IonPac AS-14 column and a conductivity detector. The eluent composition was 3.5 mM Na_2CO_3 and 1 mM $NaHCO_3$. The pH change during the course of the reaction was monitored by pH meter (Orion, model 720A) equipped with Orion 8102BN electrode.

Cyclic voltammetry (CV) analysis of MA was recorded using a Reference 600 potentiostat (Gamry Instruments) in 0.91 M $LiClO_4$ at pH 2 using a scan rate of 150 mV/s and initial potential fixed at 0 V (*vs.* Ag/AgCl). The current was collected using a Pt electrode (working electrode), a graphite rod (counter electrode) and a Ag/AgCl electrode (reference electrode) immersed in 1 M NaCl adjusted to pH 2.5 in the presence of 0.2 g/L ZVI. Nitrogen gas (>99.9%) was continuously purged through the suspension. For potentiostatic current measurements, the potential of +0.4 V (*vs.* Ag/AgCl) was applied to Pt working electrode using a potentiostat (EG&G Priceton Applied Research, Model 263A). The zero-valent iron suspension was magnetically stirred throughout the entire current measurement.

H_2O_2 concentrations were measured spectrophotometrically (absorbance measurement at 454 nm) using the 2,9-dimethyl-1,10-phenanthroline (DMP) method [24]. Briefly, DMP (1 g in 100 mL ethanol), copper(II) sulfate (0.01 M), and phosphate buffer (0.1 M, pH 7) solutions were added to a 10-mL volumetric flask and mixed together. 2 mL of the filtered sample aliquot was subsequently added to the reagent mixture, and the remaining volume was filled to 10 mL with distilled water. The absorbance at 454 nm was then measured immediately. Blank samples were prepared in the same manner except for replacing sample aliquot by distilled water. Hydroxyl radical ($HO^•$) production was determined using the oxidative conversion of benzoic acid (BA) to *p*-hydroxybenzoic acid (*p*-HBA) as a probe reaction [25]. Cumulative OH radical yield [26,27] was then calculated by estimation of *p*-HBA generation in ZVI slurry containing 10 mM BA in the presence or absence of MA. The quantitative estimation of *p*-HBA was determined by HPLC using 0.1% phosphoric acid and acetonitrile (85:15 v/v) as eluent, flow rate of 1.0 mL/min and 255 nm as detection wavelength.

3. Results and discussion

3.1. Effect of MA on ZVI-induced oxidation

To evaluate the electron transfer capacity of MA, the degradation of 4-CP by ZVI was carried out in the presence and absence of MA. As shown in Fig. 1, 4-CP degradation in air-equilibrated ZVI aqueous suspension was enhanced in the presence of MA. 4-CP degradation was not observed in the absence of ZVI, indicating that there was no direct reaction between 4-CP and MA. Further, the complete absence of 4-CP degradation in anaerobic conditions (N_2-spurged solution) also confirmed that 4-CP was not removed by direct reduction using ZVI. The concurrent generation of chloride ions, which confirms the OH radical-mediated oxidative decomposition of 4-CP [28], was also enhanced when MA was present in the ZVI suspension (Fig. 1). Finally, when methanol (20 mM) was added as a $HO^•$ scavenger, 4-CP oxidation was completely inhibited, which corroborates the primary role of $HO^•$ in 4-CP oxidation using the ZVI/MA system. All these results indicate that the enhanced

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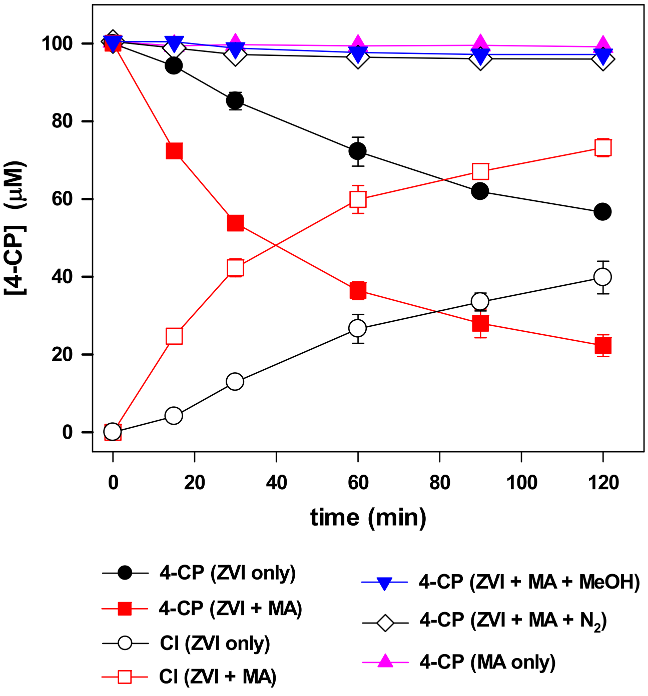

Fig. 1. Degradation of 4-CP with a ZVI aqueous suspension containing MA under different reaction conditions. Methanol was added as OH radical scavenger and nitrogen purging was used to achieve anaerobic conditions. Experimental conditions were: [ZVI] = 0.2 g/L, $[4\text{-CP}]_0$ = 100 μM, [MA] = 100 μM, [methanol] = 20 mM and pH_i = 2.5.

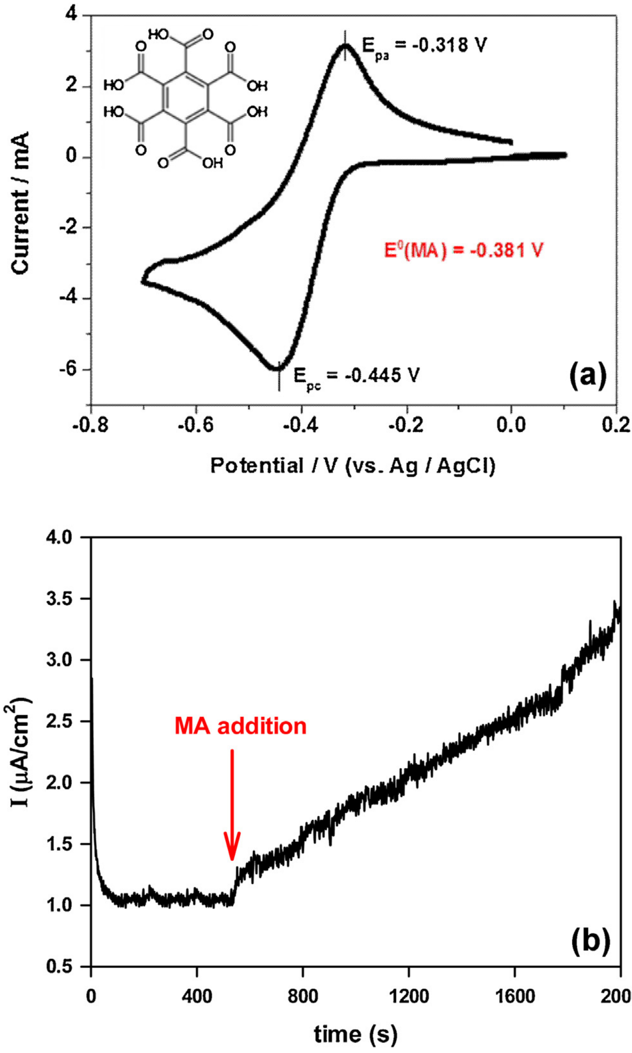

Fig. 2. (a) Cyclic voltammetry analysis of MA aqueous solution in the presence of ZVI. Experimental conditions were: [ZVI] = 0.2 g/L, [MA] = 1 mM, scan rate = 150 mV/s, initial potential = 0.0 V and electrolyte was 0.91 M $LiClO_4$ at pH 2. (b) Photocurrent measurements in the ZVI aqueous suspension in the presence of MA. Photocurrent was collected on a Pt electrode immersed in ZVI suspension and MA was added into the solution after 10 min. Experimental conditions were: [ZVI] = 0.2 g/L, $[MA]_0$ = 100 μM, initial potential = +0.4 V and pH_i = 2.5. NaCl electrolyte solution (1 M) was deoxygenated by continuous N_2-purging during the course of the experiment.

$HO^{\bullet}$ production in the ZVI/MA system using molecular oxygen as a precursor must be responsible for enhanced 4-CP oxidation.

Since carboxylate ligands form strong complexes with Fe(II) and react more rapidly with H_2O_2 than the Fe(II)-aquo species [5,29], Fe(II) generated from ZVI corrosion can complex with MA and initiate O_2 reduction to form H_2O_2 and subsequently $HO^{\bullet}$ through Fenton reaction (Eqs. (1)–(3)) [14].

$$[\text{Fe(II)-MA}] + O_2 \rightarrow [\text{Fe(III)-MA}] + O_2^{\bullet -} \quad (1)$$

$$[\text{Fe(II)-MA}] + O_2^{\bullet -} + 2H^+ \rightarrow [\text{Fe(III)-MA}] + H_2O_2 \quad (2)$$

$$[\text{Fe(II)-MA}] + H_2O_2 \rightarrow [\text{Fe(III)-MA}] + HO^{\bullet} + HO^- \quad (3)$$

To investigate whether this complexation-mediated generation of $HO^{\bullet}$ can occur in the presence of MA, the oxidation of 4-CP was tested in the solution of 2.5 mM Fe(II) and 100 μM MA in aerobic conditions. Unlike other Fe(II)-carboxylate complexes reported in the literature [5,14,29], the oxidation of 4-CP was not observed in the presence of Fe(II) and MA. Although this observation does not clarify the presence or absence of a Fe(II)-MA complex, it simply implies that the Fe(II)-MA complex, if formed, is not capable of oxygen reduction for oxidant generation. Since the oxygen activation pathway through Fe(II)-ligand complexation is more dominant at pH > 5 [13], the use of acidic condition (pH = 2.5) in the present system may explain the absence of the Fe(II)-MA complexation pathway for 4-CP oxidation.

To ascertain whether 4-CP oxidation occurs *via* a heterogeneous pathway which involves the electron transfer from ZVI surface to dioxygen mediated by MA acting as electron shuttle, cyclic voltammetry was done to estimate the reduction potential of MA, which was determined to be $-0.184\,V_{NHE}$ (see Fig. 2(a)). Thus, taking into account the redox potentials for ZVI corrosion $[E^0(Fe^{2+}/Fe^0) = -0.44\,V_{NHE}]$ and oxygen reduction $[E^0(O_2/H_2O_2) = +0.695\,V_{NHE}]$ [17], H_2O_2 production using MA-mediated electron shuttling between ZVI and O_2 is thermodynamically feasible. To obtain a more direct evidence of the electron shuttling effect, current measurements were performed using an inert Pt electrode immersed in the ZVI slurry containing 1 M NaCl electrolyte adjusted to pH 2.5 (Fig. 2(b)). In the absence of MA, the low background current (~1 μA/cm^2) is attributed to the electron release from ZVI oxidation accompanied by Fe(II) dissolution (Eq. (4)). However, when MA was added in the ZVI suspension after 10 min, a sudden increase in current was observed, which indicates that MA acts as an electron shuttle (electron transfer catalyst) between Fe^0 and the Pt working electrode (Eqs. (5)–(6)).

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad (4)$$

$$MA + e^- \rightarrow MA_{red} \quad (5)$$

$$MA_{red} \rightarrow MA + Pt(e^-) \quad (6)$$

Since the solution was continuously purged with N_2 to prevent competitive electron scavenging by dioxygen, the observed increase in current upon adding MA provided a good evidence for MA-mediated electron transfer from the ZVI surface to the Pt electrode.

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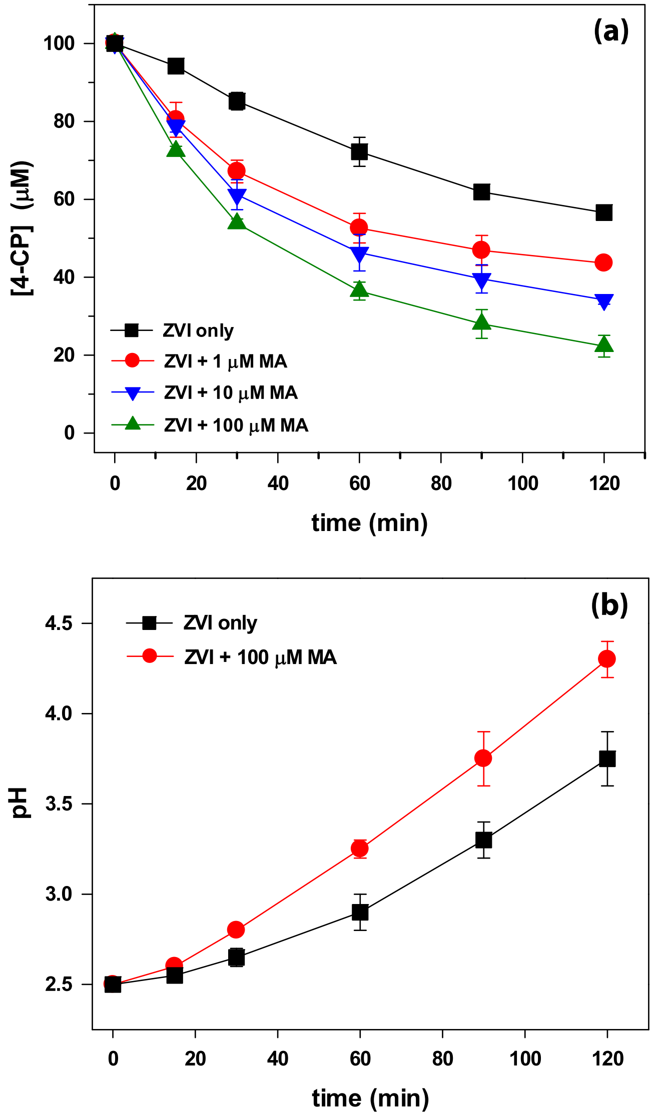

Fig. 3. (a) Effect of MA concentration and (b) Variation of solution pH during 4-CP degradation with ZVI. Experimental conditions were: [ZVI] = 0.2 g/L, $[\text{4-CP}]_0$ = 100 μM, $[\text{MA}]_0$ = 100 μM and pH_i = 2.5

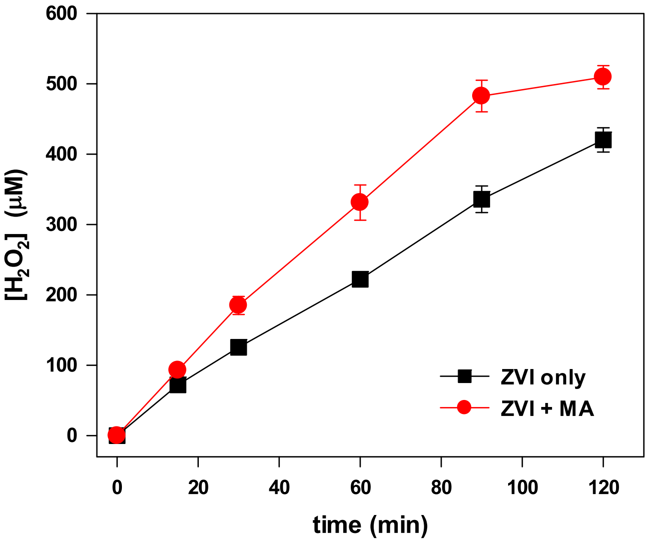

Fig. 4. Time profiles of H_2O_2 generation in ZVI suspension in the presence or absence of MA. 4-CP was not added in the solution. Experimental conditions were: [ZVI] = 0.2 g/L, $[\text{MA}]_0$ = 100 μM and pH_i = 2.5.

The effect of MA concentration on 4-CP oxidation in the ZVI/O_2 system is shown in Fig. 3(a). When MA concentration increased from 1 μM to 100 μM, 4-CP oxidation rate was also enhanced. Although the increase in MA concentration may lead to higher coverage of active sites on the ZVI surface, the observed increase in 4-CP oxidation efficiently indicates that surface blocking by MA does not have any negative impact on the electron transfer mechanism. At the same time, the presence of MA in the ZVI/O_2 system led to a larger pH change (increase in pH) (Fig. 3(b)) during the course of the reaction. This rapid rise in pH can be ascribed to enhanced H_2O_2 generation ($O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$) when more Fe(II) ions are dissoluted from ZVI corrosion (Eq. (4)) in the presence of MA acting as an electron acceptor (Eq. (5)).

However, the complexation of MA on goethite surface (majority oxide surface of acid-washed ZVI [30]) may also contribute an alternative mechanism for the higher pH rise in the ZVI/MA system. During the complexation of MA on the goethite surface, the release of hydroxide ions is directly responsible for the increase in solution pH [20]. This pH increase then contributes to increased passivation of ZVI surface through precipitation of iron hydroxides. However, direct $HO^\bullet$ generation through the ligand-mediated Fenton reaction is marginally affected by this pH rise because the increase in solubility of Fe(II) by ligand complexation reduces the pH-dependence of the Fenton reaction [10,11,13]. It has been also suggested that ligands which form bidentate-mono-nuclear complexes with adjacent hydroxyl groups often enhance dissolution of the metal surface oxides [31]. While there is no direct experimental evidence to confirm the exact structure of the MA-oxide complex, the observed enhancement of 4-CP degradation in the ZVI/MA system indicates that the pH rise does not have a direct influence on the $HO^\bullet$ generation mechanism.

3.2. Oxidative degradation mechanism in ZVI/MA system

The oxidation of 4-CP in the ZVI suspension containing MA as an electron shuttle is initiated by the corrosion of ZVI in aerobic conditions with concurrent reduction of oxygen to H_2O_2 through electron transfer mediated by MA (Eqs. (7)–(8)).

$$Fe^0 + MA \rightarrow Fe^{2+} + MA_{red} \tag{7}$$

$$MA_{red} + O_2 + 2H^+ \rightarrow MA + H_2O_2 \tag{8}$$

Due to the strong tendency of MA to form surface complexes with goethite (dominant iron oxide phase on acid-washed ZVI) under acidic conditions [20,22], electron transfer is facilitated from Fe^0 pits on the iron particle to MA trapped on the nearby goethite sites. The strong electrostatic interaction between the negatively charged MA carboxyl groups and positively charged ZVI surface at acidic pH also facilitates efficient electron transfer from Fe^0 to MA and subsequently from MA to dioxygen. The complexation of *in situ* generated Fe(II) with MA then may promote the Fenton reaction for subsequent OH radical production (Eq. (9)).

$$Fe(II)-MA + H_2O_2 \rightarrow Fe(III)-MA + HO^\bullet + OH^- \tag{9}$$

To confirm whether the increase in oxygen reduction efficiency can be ascribed to MA-mediated electron transfer, the concentrations of H_2O_2 generated using ZVI were estimated in the presence and absence of MA. As seen in Fig. 4, the concentration of H_2O_2 is higher in the presence of MA. Thus, in the presence of MA, both H_2O_2 formation and its subsequent decomposition are enhanced in the initial reaction time, leading to an increase in 4-CP oxidation within the first 1 h (Fig. 1). The observed increase in solution pH within the same time period (Fig. 3(b)) confirms the higher con-

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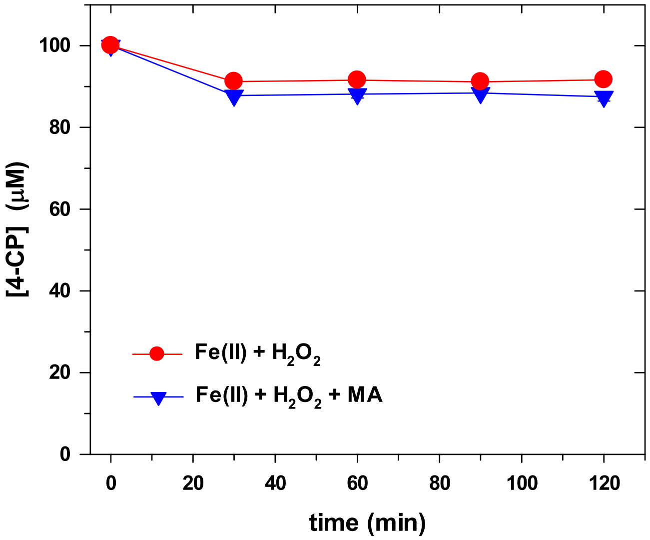

Fig. 5. 4-CP oxidation using Fe(II)-mediated homogeneous Fenton reaction in the presence and absence of MA. Experimental conditions were: $[Fe(II)] = 2.5$ mM, $[H_2O_2] = 300$ μM, $[MA]_0 = 100$ μM and $pH_i = 2.5$.

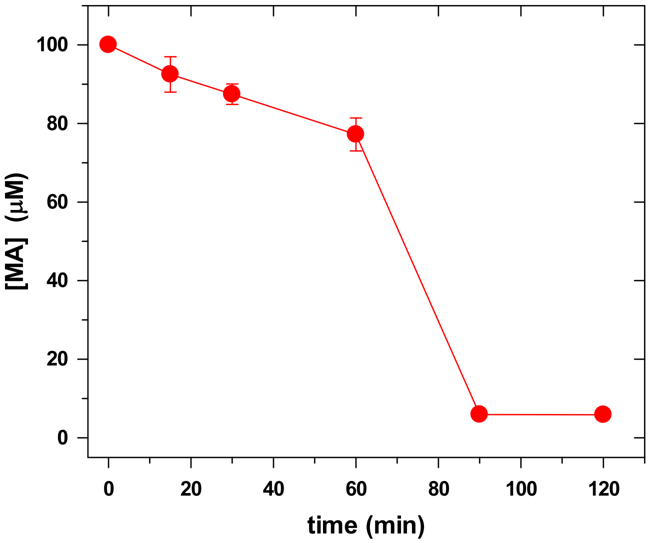

Fig. 6. Time-dependent variation of MA concentration during 4-CP oxidation in the ZVI aqueous suspension. Experimental conditions were: $[ZVI] = 0.2$ g/L, $[MA]_0 = 100$ μM, $[4\text{-}CP] = 100$ μM and $pH_i = 2.5$.

sumption of H^+ during the MA-mediated reduction of O_2 to form H_2O_2 (Eq. (8)). The similar phenomenon was also observed in our previous study, wherein the oxidation capacity of ZVI increased in the presence of NOM [19].

Since the Fenton reaction has been enhanced in the presence of organic ligands due to higher reactivity of Fe(II)-ligand complex with H_2O_2 compared to the uncomplexed Fe(II) ions in previous studies [3–5], the effect of MA acting as a complexing agent on 4-CP oxidation was investigated using Fe(II) ions and H_2O_2 in the presence and absence of MA. As shown in Fig. 5, the presence of MA in the Fe(II)/H_2O_2 homogeneous system had no significant effect on the 4-CP oxidation efficiency. This indicates that the formation of a Fe(II)-MA complex, if possible, does not contribute to the 4-CP oxidation pathway. Thus, the primary role of MA in the ZVI/O_2 system is to efficiently transfer electrons from the ZVI surface to dioxygen, without any synergetic enhancement of the Fe(II)-mediated decomposition of H_2O_2 to $HO^•$.

To estimate the stability of MA in the ZVI-mediated 4-CP oxidation process, the concentration of MA was also monitored simultaneously during the 4-CP degradation reaction (Fig. 6). The MA concentration slowly decreased initially, but was rapidly removed after 1 h. During the initial reaction period, the decrease of 4-CP (Fig. 1) was much more rapid compared to the decline in MA concentration. Although this suggests that 4-CP is a more efficient scavenger of $HO^•$ than MA, the degradation of MA by $HO^•$ is also possible and may result in the generation of secondary pollutants. Detailed intermediate analysis and toxicity assays will be required to confirm by-product toxicity but this is beyond the scope of the present study. However, the rapid removal of MA after 1 h cannot be simply attributed to degradation by $HO^•$ since residual 4-CP (Fig. 1) should still be more reactive towards $HO^•$. It appears that MA was possibly removed from the solution as an insoluble complex with various iron corrosion products which could not be fully characterized in this study. Taking into account the observed increase in pH during 4-CP oxidation (Fig. 3(b)), it is evident that pH increased beyond 3.5 after 90 min. Since the solubility of Fe(III) ions formed during the Fenton reaction decreases significantly at $pH > 3$ [32], the formation of insoluble complexes or precipitates containing MA probably explains the rapid removal of MA. Subsequently, the complete inhibition of MA-mediated electron shuttling after 90 min stops further production of H_2O_2 (Fig. 4). Incidentally, the electron shuttling role of MA can be retarded in the presence of competitive electron acceptors (*e.g.*, Cr(VI), NO_3^-) or other pollutants competing for $HO^•$. Detailed effects of secondary pollutants, intermediates, and complex mixture will be required to understand the overall environmental implications in further studies.

4. Conclusion

The present study demonstrates that mellitic acid, a NOM analogue with multiple carboxylic groups, acts as an efficient electron shuttling catalyst to enhance the oxidizing capacity of ZVI. In the presence of MA, the increase in electron transfer efficiency from ZVI to dioxygen resulted in higher production of both H_2O_2 and $HO^•$ for enhanced oxidation of 4-CP. Cyclic voltammetry and photocurrent measurements support that MA can act as a good electron shuttle with providing the facile dioxygen reduction and H_2O_2 generation. However, it should be noted that this study intends not to propose the use of MA in real ZVI processes, but mainly to demonstrate a possible role of the carboxylate moieties in NOMs in affecting the ZVI redox chemistry.

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References

[1] D.W. King, Environ. Sci. Technol. 32 (1998) 2997–3003.
[2] K.L. Straub, M. Benz, B. Schink, FEMS Microbiol. Ecol. 34 (2001) 181–186.
[3] J.D. Rush, B.H.J. Bielski, J. Phys. Chem. 89 (1985) 5062–5066.
[4] D.L. Sedlak, J. Hoigne, Atmos. Environ. 27A (1993) 2173–2185.
[5] B.M. Voelker, B. Sulzberger, Environ. Sci. Technol. 30 (1996) 1106–1114.
[6] D.F. Laine, S.D. McAllister, I.F. Cheng, J. Electroanal. Chem. 608 (2007) 111–116.
[7] M.D. Paciolla, S. Kolla, S.A. Jansen, Adv. Environ. Res. 7 (2002) 169–178.
[8] S. Piche, F. Larachi, Chem. Eng. Sci. 61 (2006) 3452–3462.
[9] A.L. Rose, T.D. Waite, Environ. Sci. Technol. 37 (2003) 4877–4886.
[10] L. Emmenegger, D.W. King, L. Sigg, B. Sulzberger, Environ. Sci. Technol. 32 (1998) 2990–2996.
[11] J.M. Santana-Casiano, M. Gonzalez-Davila, M.J. Rodriguez, F.J. Millero, Mar. Chem. 70 (2000) 211–222.
[12] O. Gyliene, T. Vengris, A. Stoncius, O. Nivinskiene, J. Hazard. Mater. 159 (2008) 446–451.
[13] C.R. Keenan, D.L. Sedlak, Environ. Sci. Technol. 42 (2008) 6936–6941.

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[14] D.F. Laine, A. Blumenfeld, I.F. Cheng, Ind. Eng. Chem. Res. 47 (2008) 6502–6508.
[15] C. Noradoun, M.D. Engelmann, M. McLaughlin, R. Hutcheson, K. Breen, A. Paszczynski, I.F. Cheng, Ind. Eng. Chem. Res. 42 (2003) 5024–5030.
[16] C.E. Noradoun, I.F. Cheng, Environ. Sci. Technol. 39 (2005) 7158–7163.
[17] R.L. David, CRC Handbook of Chemistry and Physics, seventy seventh ed., CRC Press, New York, 1996.
[18] S.-H. Kang, W. Choi, Environ. Sci. Technol. 43 (2009) 3966–3967.
[19] S.-H. Kang, W. Choi, Environ. Sci. Technol. 43 (2009) 878–883.
[20] M.J. Angrove, J.D. Wells, B.B. Johnson, J. Colloid. Interf. Sci. 296 (2006) 30–40.
[21] D.E. Glammar, D.A. Dzombak, J. Solution Chem. 27 (1998) 89–105.
[22] B.B. Johnson, S. Sjoeberg, P. Persson, Langmuir 20 (2004) 823–828.
[23] T.L. Johnson, M.M. Scherer, P.G. Tratnyek, Environ. Sci. Technol. 30 (1996) 2634–2640.
[24] K. Kosaka, H. Yamada, S. Matsui, S. Echigo, K. Shishida, Environ. Sci. Technol. 32 (1998) 3821–3824.
[25] S.H. Joo, A.J. Feitz, D.L. Sedlak, T.D. Waite, Environ. Sci. Technol. 39 (2005) 1263–1268.
[26] K. Mopper, X. Zhou, Science 250 (1990) 661–664.
[27] X. Zhou, K. Mopper, Mar. Chem. 30 (1990) 71–88.
[28] T. Zhou, Y. Li, J. Ji, F. Wong, X. Lu, Sep. Purif. Technol. 62 (2008) 551–558.
[29] A.J. Feitz, S.H. Joo, J. Guan, Q. Sun, D.L. Sedlak, D.T. Waite, Colloid. Surface. A 265 (2005) 88–94.
[30] C.-C. Liu, D.-H. Tseng, C.-Y. Wang, J. Hazard. Mater. B 136 (2006) 706–713.
[31] W. Stumm, Chemistry of the Solid-Water Interface, John Wiley & Sons, New York, 1992.
[32] A.D. Bokare, W. Choi, Environ. Sci. Technol. 43 (2009) 7130–7135.

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