Influence of Chelating Agents on Fenton-Type Reaction Using Ferrous Ion and Hypochlorous Acid

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ABSTRACT
Iron-based advanced oxidation technologies, such as the Fenton process, are widely used for industrial wastewater treatment. However, wastewater sometimes contains chelating agents such as detergents, stabilizers, and masking agents for metallic ions, which have a potential to inhibit the iron-based advanced oxidation process through the masking of iron. In this research, we investigated the influence of chelating agents on Fenton-type reaction using ferrous ion (Fe^{2+}) and hypochlorous acid (HOCl). Chelating agents tested were oxalic acid, ethylenediaminetetraacetic acid (EDTA) and 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP). Hydroxyl radicals generated were determined by 1,4-dioxane degradation. When HOCl was reacted with Fe^{2+} at pH 6.0, oxalic acid and EDTA strongly inhibited the 1,4-dioxane degradation. However, the inhibition effect declined at acidic pH because of the protonation of carboxyl groups in the chelating agents. The HEDP differed from the other chelating agents in the inhibition effect. It showed the inhibition effect only under the low dose at pH 6.0. On the contrary, the higher dose and acidic pH enhanced the 1,4-dioxane degradation efficiency. The regeneration of Fe^{2+} from ferric ion (Fe^{3+}) by the degradation of Fe^{3+}-HEDP complex was inferred to be responsible for the enhancement effect.

Keywords: advanced oxidation, chelating agent, Fenton-type reaction, hypochlorous acid

INTRODUCTION

The Fenton process is widely used for treatments of industrial wastewater and landfill leachate (Deng and Englehardt, 2006; Bautista *et al*., 2008), because it requires no noble equipment like an ozonizer and a UV lamp. However, it has a few disadvantages: generation of plenty of iron sludge and handling of hydrogen peroxide (H_2O_2) reagent, which is costly and is a dangerous chemical classified into "division 5.1 oxidizing substance" by United Nations (2011). To resolve the disadvantages, Tomat and Vecchi (1971) firstly proposed the onsite production of Fenton's reagent (ferrous ion (Fe^{2+}) and H_2O_2) by the electrochemical reduction of ferric ion (Fe^{3+}) and oxygen in aqueous acid solution. In the electrochemical Fenton process, Fe^{2+} is repeatedly used for Fenton reaction, because Fe^{3+} produced from Fe^{2+} in Fenton reaction is retransformed into Fe^{2+} electrochemically. Consequently, the electrochemical Fenton process successfully reduces the mass of iron sludge in two ways: a decrease in the initial iron input due to the recycle of iron in the reactor and reuse of redissolved iron sludge as an iron source for the process. Furthermore, the electrochemical Fenton process can obviate the handling of H_2O_2 reagent. However, the reduction of Fe^{3+} competes with the reduction of oxygen at cathodes in the electrochemical Fenton process. Therefore, a new electrochemical Fenton-type process using Fe^{2+} and hypochlorous acid (HOCl) as Fenton-like reagent has been proposed (Kishimoto and Sugimura, 2010). The responsible reactions for the electrochemical Fenton-type process are as follows:

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Bulk reaction: $Fe^{2+} + HOCl \rightarrow Fe^{3+} + \cdot OH + Cl^-$ (1)
Anodic reaction: $2Cl^- \rightarrow Cl_2 + 2e^-$, $Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$ (2)
Cathodic reaction: $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (3)

In this process, the Fenton-type reaction (equation (1), Candeias *et al*., 1994) was used to generate hydroxyl radicals (·OH) instead of the conventional Fenton reaction. Since the electrochemical regeneration of HOCl (equation (2)) is an anodic reaction, the competition of electrode reactions (equations (2) and (3)) can be avoided. Consequently, the new electrochemical Fenton-type process can theoretically generate 1 mol of ·OH from 2 mol of electrons, whereas the conventional electrochemical Fenton process requires 3 mol of electrons for the generation of 1 mol of ·OH as displayed by equations (4) and (5).

Bulk reaction: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$ (4)
Cathodic reaction: $Fe^{3+} + e^- \rightarrow Fe^{2+}$, $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ (5)

The low requirement of electron of the electrochemical Fenton-type process results in low energy consumption compared to the conventional electrochemical Fenton process. This process functions well as an advanced oxidation process. However, industrial wastewater often contains chelating agents such as detergents, stabilizers, and masking agents for metallic ions, which have a potential to inhibit the iron-based advanced oxidation process through masking of iron. Li *et al*. (2007b) demonstrated that chelating agents of citrate and poly(acrylic acid) constrained the Fenton reaction by lowering free Fe^{2+}. However, there are some reports that iron-chelating agents did not constrain the Fenton reaction. For examples, Li *et al*. (2007a) focused on the determination of ·OH by the electron spin resonance during Fenton reaction with ethylenediaminetetraacetic acid (EDTA), and the results showed that EDTA did not affect ·OH generation, but quenched spin-trapping radicals. Rastogi *et al*. (2009) discussed the effects of three chelating agents, citrate, pyrophosphate, and (S, S)-ethylenediamine-N, N'-disuccinic acid (EDDS) on Fenton reaction. Citrate and EDDS enhanced 4-chlorophenol degradation by Fenton reaction, although pyrophosphate inhibited it. However, these reports focused on the chelate-based Fenton process, which functions at neutral pH. Most of the chelating agents contain carboxyl, phosphonic, and/or amino groups as functional groups. Since these functional groups associate with protons at acidic condition, the iron-chelating ability may weaken at acidic condition. However, there is little information on the influence of chelating agents on Fenton reaction at acidic condition. Furthermore, there is no report on the influence of iron-chelating agents on the Fenton-type reaction using Fe^{2+} and HOCl.

Therefore, influences of chelating agents on the Fenton-type reaction were explored to clarify the applicability of the Fenton-type reaction to wastewater containing chelating agents.

Various chelating agents are commercially used all over the world, which are mainly categorized into three types: carboxylic, aminocarboxylic, and phosphonic. A few examples of chelating agents are shown in Fig. 1. Oxalic acid (OA) is a simple carboxylic ligand with two carboxyl groups. It is often produced during advanced oxidation processes as a degradation intermediate of aromatics (Garcia-Segura and

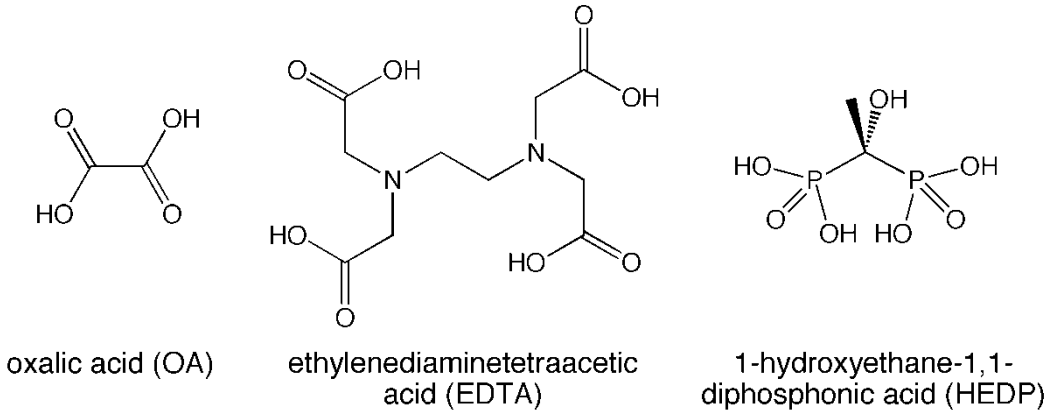

Fig. 1 - Structures of chelating agents.

Brillas, 2011). A typical aminocarboxylic ligand, EDTA, has two tertiary amino groups and four carboxyl groups. It is the most popular aminocarboxylic chelator (Nörtemann, 1999) but it is cytotoxic and weakly genotoxic (The Cosmetic Ingredient Review Expert Panel, 2002). Moreover, it is not degraded by conventional biological and physicochemical methods (Nörtemann, 1999). Thus, it is one of the persistent organic pollutants. A typical phosphonic ligand, 1-Hydroxyethane-1,1-diphosphonic acid (HEDP), has two phosphonic groups. Each phosphonic group can release two protons. As it is more soluble to acid solution than aminocarboxylic chelators like EDTA, it is often used under acidic condition. The worldwide consumption of phosphonates including HEDP grows steadily at 3% annually (Kołodyńska *et al*., 2009). However, no biodegradation of phosphonic chelating agents is observed in the environment (Nowack, 2003). In this research OA, EDTA, and HEDP were used, because it is expected that industrial wastewater often contains EDTA or HEDP and that OA is generated during the electrochemical Fenton-type process of industrial wastewater.

MATERIALS AND METHODS

Materials

Ferrous sulfate heptahydrate and sodium hypochlorite solution (8 – 13.5% of analytical reagent, Nacalai Tesque, Japan) were used as Fenton-like reagent for the Fenton-type reaction. The exact free chlorine concentration of the sodium hypochlorite solution was determined before each experiment by iodometric method (Japanese Standards Association, 1998). For the Fenton treatment, H_2O_2 solution (ca. 30% of analytical reagent, Santoku Chemical Industries, Japan) was used instead of the sodium hypochlorite solution. The H_2O_2 concentration was determined by the colorimetric method proposed by Baga *et al*. (1988).

Chelating agents tested were oxalic acid dihydrate as OA, disodium dihydrogen ethylenediaminetetraacetate dehydrate as EDTA, and HEDP (Tokyo Chemical Industry, Japan).

We used 1,4-dioxane as a ·OH probe, because it is highly reactive with ·OH (Moriaty *et al*., 2003), but unreactive with H_2O_2 and HOCl (Klečka and Gonsior, 1986). The solution pH was adjusted by sodium hydroxide and sulfuric acid. Sodium sulfite was

used as a reductant of excess HOCl in a sample. Ferric chloride hexahydrate was used as a ferric ion (Fe^{3+}) source.

All chemicals except sodium hypochlorite solution, H_2O_2 solution, and HEDP were guaranteed reagent grade supplied by Nacalai Tesque Co. Ltd. (Japan). All chemicals were used without further purification.

Fenton or Fenton-type Experiments

Two solutions were prepared for a series of Fenton-type experiments. Solution A contained 4.0 mM of ferrous sulfate, 40 mM of 1,4-dioxane and adequate concentration of a chelating agent. Solution B was 2 – 20 mM of sodium hypochlorite solution or H_2O_2 solution. The pH of both solutions was set at 2.0 – 6.0 by the addition of 1.0 M of sulfuric acid or 5.0 M of sodium hydroxide. Solutions A and B were prepared every time just before the experimental run.

At the beginning of an experiment, 500 mL of solution A was poured into a glass beaker and was stirred with a mixer (SMT-102, As One, Japan). Then, 500 mL of solution B was added into the beaker, and the experimental run started. The experimental run continued for 30 minutes with mixing (G-value: 388 sec^{-1}). A pH controller (FD-02, TGK, Japan) was installed in the beaker to establish a constant pH.

When the solution was sampled, aliquots of sodium sulfite and sodium hydroxide solution (0.5 M) were added to the sample solution immediately to consume the excess HOCl and to change the solution pH into 12 for the removal of free ferrous and ferric ions. The final concentration of sodium sulfite was set at the same concentration as the initial HOCl. The exact addition rate of sodium hydroxide depended on the experimental condition and was determined by preliminary tests. Then, the solution was filtered with a membrane filter of 0.45-μm pore size (Minisart RC25, Sartorius Stedim Biotech, France). The concentration of 1,4-dioxane in the filtrate was analyzed with a high performance liquid chromatography system (LC-10ADVP, Shimadzu, Japan) with a refractive index detector (RID-10A, Shimadzu, Japan). Measurement conditions were as follows: mobile phase - 1 mM of hydrochloric acid; flow rate - 1.0 mL min^{-1}; column - Cosmosil 5C18-PAQ packed column (250 mm in length, 4.6 mm in inner diameter); oven temperature - 40ºC; and injection volume - 25 μL. The final concentration of 1,4-dioxane was corrected by the dilution rate of the sample solution. We preliminary checked the accuracy of the experimental procedure, and the unbiased standard deviation of 1,4-dioxane removal was estimated to be 0.10 mM.

Absorption Spectrum Analysis

To investigate the interaction between HEDP and Fe^{2+}, the absorption spectra of Fe^{2+}, Fe^{3+}, HEDP, and mixtures of HEDP and Fe^{2+} were measured with a UV-Vis spectrophotometer (UV-2500, Shimadzu, Japan). The final concentrations were 2.0 mM for Fe^{2+} and Fe^{3+} and 1.0 or 10 mM for HEDP.

RESULTS AND DISCUSSION

1,4-dioxane Removal by the Fenton's Reaction and the Fenton-type Reaction

Removal of 1,4-dioxane (R_{dx}) by the Fenton's reaction or the Fenton-type reaction was

investigated at a Fe^{2+} dose ($D_{Fe(II)}$) of 2.0 mM, various H_2O_2 (D_{H2O2}) and HOCl (D_{HOCl}) doses, and pH 2.5. Figure 2 shows the experimental results. When the Fenton process was applied, R_{dx} increased with an increase in D_{H2O2}. The R_{dx} at a D_{H2O2} of 1.0 mM was nearly equal to 1 mM. This means that almost all H_2O_2 produced ·OH and the ·OH attacked 1,4-dioxane. However, the D_{H2O2} over 2 mM resulted in higher R_{dx} than $D_{Fe(II)}$. Since H_2O_2 can reduce Fe^{3+} into Fe^{2+} (Bautista *et al*., 2008), the regeneration of Fe^{2+} by H_2O_2 was thought to lead to a higher R_{dx}.

Contrary to the Fenton's reaction, R_{dx} by the Fenton-type reaction had a ceiling around 2 mM, which was equal to $D_{Fe(II)}$. This means that HOCl cannot reduce Fe^{3+} into Fe^{2+} and a stoichiometric relation between the limiting reactant and R_{dx} is established under this experimental condition.

Influences of Three Chelating Agents on the Fenton-type Reaction

Influences of three chelating agents at a dose of 10 mM are summarized in Fig. 3. Although the Fenton-type reaction without chelating agents showed around 2 mM of R_{dx} at both acidic and neutral pH, each chelating agent changed the R_{dx} value. The Fenton-type reaction was strongly inhibited by OA at pH 6.0, but the inhibition effect was deteriorated at acidic pH. The inhibition rates at pH 2.0, 2.5, and 6.0, which were

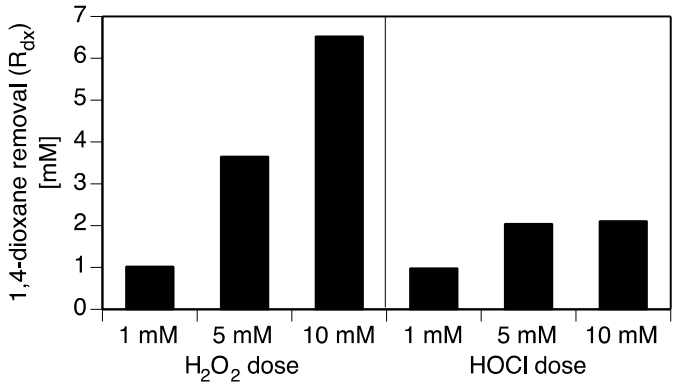

Fig. 2 - Removal of 1,4-dioxane by Fenton reaction and Fenton-type reaction at various H_2O_2 and HOCl doses ($D_{Fe(II)}$: 2.0 mM, pH 2.5).

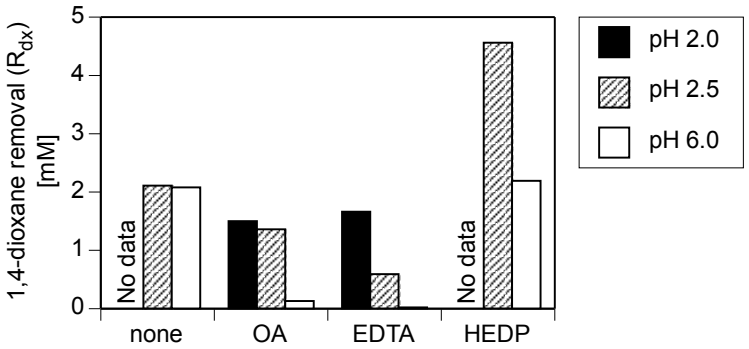

Fig. 3 - Removal of 1,4-dioxane by the Fenton-type reaction with the addition of each chelating agent (10 mM) at various pH ($D_{Fe(II)}$: 2.0 mM, D_{HOCl}: 10 mM).

25, 32, and 94%, respectively, and were evaluated from the following equation.

$$IR = \left(1 - \frac{R_{dx}}{D_{Fe(II)}}\right) \times 100 \quad (6)$$

where, IR is the inhibition rate [%].

The profile of EDTA was similar to that of OA. However, the inhibition effect was more sensitive to pH than that of OA. At pH 6.0, EDTA completely inhibited the Fenton-type reaction (IR = 99%). The inhibition effect decreased with a decline in pH. The IR at acidic condition was 70% at pH 2.5 and 17% at pH 2.0. Thus, EDTA strongly inhibited the Fenton-type reaction at pH 2.5 or higher.

The profile of HEDP was quite different from those of OA and EDTA. The R_{dx} at pH 6.0 was almost equal to the control, but the R_{dx} at pH 2.5 was 2.2 times higher. Thus, HEDP enhanced the Fenton-type reaction at acidic pH.

Table 1 summarizes the stability constants of iron complexes. The stability constants of iron-EDTA complexes and iron-HEDP complexes at [ML]/[M][L] system, in which M and L mean a metallic ion and a ligand, respectively, are much higher than those of iron-OA complexes. This is because the stability of a metal-ligand complex generally strengthens with an increase in the dentate number of ligand, which is known as chelate effect (Basolo and Johnson, 1986). Table 1 shows that the stability constant of Fe^{2+}-protonated EDTA complex ($10^{6.82}$ M^{-1}) is lower than that of Fe^{2+}-EDTA complex

Table 1 - Stability constants of iron complexes.

Metal-ligand	System	Stability constant (log K)
Fe^{2+}-OA	[ML]/[M][L]	3.05*
	$[ML_2]/[M][L]^2$	5.08*
Fe^{3+}-OA	[ML]/[M][L]	7.53 - 7.74*
	$[ML_2]/[M][L]^2$	13.81*
	$[ML_3]/[M][L]^3$	18.6*
Fe^{2+}-EDTA	[ML]/[M][L]	14.30*
	[MHL]/[M][HL]	6.82*
Fe^{3+}-EDTA	[ML]/[M][L]	23.8 - 25.1*
	$[MHL]/[ML][H^+]$	1.3*
	$[ML]/[M(OH)L][H^+]$	7.39 - 7.53*
	$[M_2(OH)_2L_2]/[M(OH)L]^2$	2.8*
Fe^{2+}-HEDP	[ML]/[M][L]	12.9**
	$[MHL]/[ML][H^+]$	4.87**
	$[MH_2L]/[MHL][H^+]$	3.3**
Fe^{3+}-HEDP	[ML]/[M][L]	14.1*
	$[MHL]/[ML][H^+]$	3.2***
	$[M(OH)L]/[ML][OH^-]$	8*
	$[M(OH)_2L]/[M(OH)L][OH^-]$	3*

* National Institute of Standards and Technology (2004). ** Deluchat *et al*. (1997), *** Lacour *et al*. (1998)

($10^{14.30}$ M^{-1}), because the protonated EDTA acts as a quinquedentate ligand, whereas non-protonated EDTA is sexidentate. As the protonation is promoted by a decline in pH, it was inferred that the acidification lowered the stability of Fe^{2+}-EDTA complexes and enhanced the Fenton-type reaction.

Cornell and Schindler (1987) reported the speciation of iron-OA complexes in bulk solution in goethite-OA system under acidic condition. At pH 2, half of iron was free Fe^{2+}, and the rest was $[Fe(C_2O_4)]$, but at pH 2.5 free Fe^{2+}, $[Fe(C_2O_4)]$, and $[Fe(C_2O_4)_2]^{2-}$ occupied about 20, 60, and 20% of total iron, respectively. Main iron species was $[Fe(C_2O_4)_2]^{2-}$ at pH over 4. Considering our experimental results in Fig. 3, $[Fe(C_2O_4)]$ was inferred to be more reactive with HOCl than $[Fe(C_2O_4)_2]^{2-}$.

Figure 4 shows the pH-dependent speciation of Fe^{2+}-HEDP and Fe^{3+}-HEDP complexes based on the stability constants in Table 1. Figure 4 illustrates that the predominant species of Fe^{2+}-HEDP complex at pH 2.5 is $[Fe(H_2\text{-HEDP})]$, which differs from the predominant species of the complex, $[Fe(HEDP)]^{2-}$, at pH 6.0. In this study the speciation might differ from Fig. 4, because an abundance of HEDP was expected to increase the number of HEDP coordinated with Fe^{2+}. However, the protonation to the Fe^{2+}-HEDP complex in this study was also expected with a decline in pH in a similar manner to Fig. 4. The protonation to the Fe^{2+}-HEDP complex may increase its reactivity with HOCl. However, the reactivity change alone cannot explain the enhancement effect of HEDP on 1,4-dioxane degradation at pH 2.5, because it does not bring the generation of ·OH more than the initial amount of Fe^{2+}.

Enhancement Effect of HEDP on the Fenton-type Reaction

There are two assumptions to explain the enhancement effect of HEDP on 1,4-dioxane degradation. The one is that HEDP reacts with HOCl and produces an oxidant that degrades 1,4-dioxane. The other is that HEDP regenerates Fe^{2+} from Fe^{3+}. Accordingly, a series of experiments was performed to elucidate the influence of HEDP on the 1,4-dioxane degradation. Figure 5 shows the R_{dx} at various HEDP doses (D_{HEDP}) and $D_{Fe(II)}$. When Fe^{2+} was not added, 1,4-dioxane degradation was not observed.

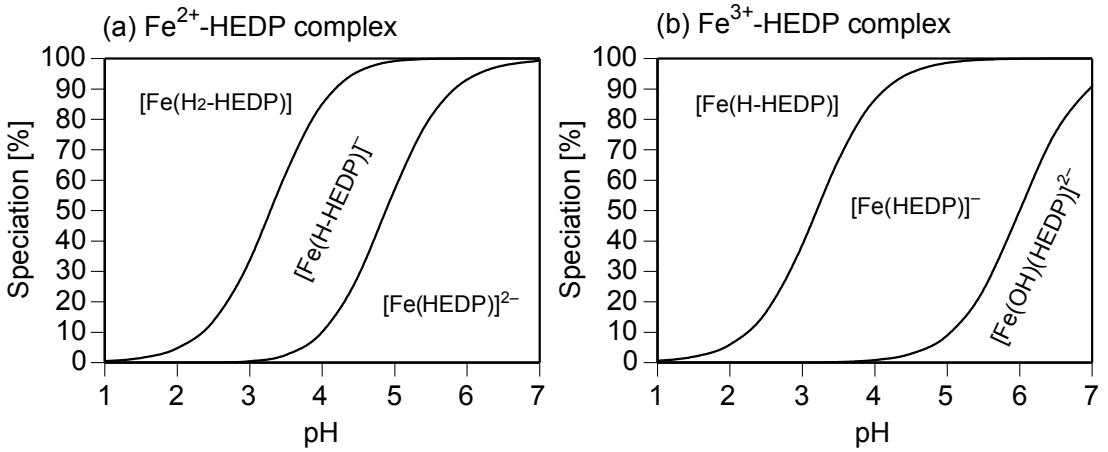

Fig. 4 - Speciation of HEDP-coordinated iron complexes based on stability constants in Table 1. Total HEDP concentration is the same as total iron concentration.

Consequently, the assumption of 1,4-dioxane degradation by a reaction of HEDP and HOCl was rejected.

The experiments with the addition of Fe^{2+} revealed that the R_{dx} increased with an increase in D_{HEDP} at pH 2.5. Figure 6 is a photograph of samples, whose HOCl and iron ions were quenched by the addition of sodium sulfite and sodium hydroxide after 0 – 10 minutes of treatment. It should be noted that the color of the sample was not changed by the addition of sodium sulfite and sodium hydroxide, although the color tone deepened. Moreover, no precipitation was observed by the addition of sodium hydroxide. Accordingly, all iron ions formed stable chelate compounds with HEDP before and after the addition of sodium sulfite and sodium hydroxide. Figure 6 demonstrates that Fe^{2+}-HEDP complex was rapidly transformed into Fe^{3+}-HEDP complex at pH 2.5 within 5 minutes. Thus, the Fe^{2+}-HEDP complex was inferred to react with HOCl rapidly at pH 2.5, which generated ·OH and Fe^{3+}-HEDP complex. At D_{HEDP} of 1 mM, HEDP acts as a bidentate ligand at pH 2.5 and quadridentate ligand at pH 6.0, and HEDP forms a complex of [Fe(H_2-HEDP)] at pH 2.5 and $[Fe(HEDP)]^{2-}$ at pH 6.0 (Fig. 4). As the chelate effect usually strengthens with an increase in the dentate number,

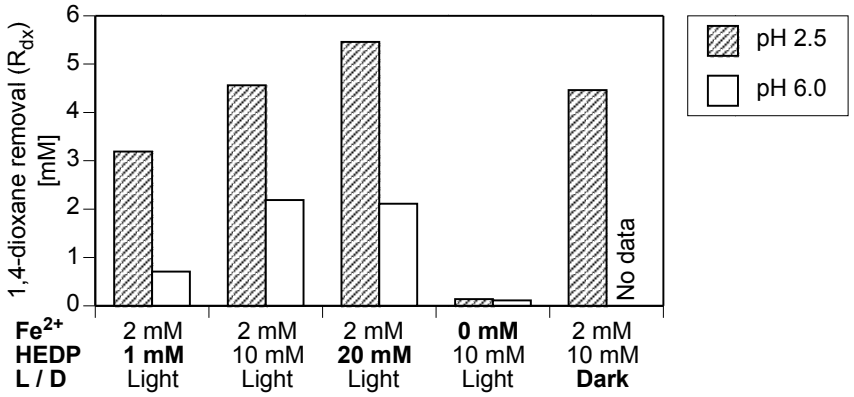

Fig. 5 - Removal of 1,4-dioxane by the Fenton-type reaction with the addition of HEDP. The D_{HOCl} was set at 10 mM.

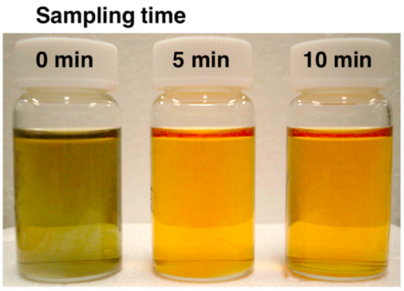

Fig. 6 - Photograph of samples. Excess HOCl and iron ions were quenched by the addition of sodium sulfite and sodium hydroxide. ($D_{Fe(II)}$: 2.0 mM, D_{HEDP}: 10 mM, D_{HOCl}: 10 mM, initial pH 2.5).

[Fe(H_2-HEDP)] at pH 2.5 is inferred to be more reactive with HOCl than $[Fe(HEDP)]^{2-}$. Thus, the reactivity change at different pH was thought to be responsible for the pH-dependent R_{dx} at D_{HEDP} of 1 mM.

At pH 2.5 and D_{HEDP} of 10 – 20 mM, the R_{dx} was larger than $D_{Fe(II)}$ of 2 mM. Accordingly, it was inferred that Fe^{2+} regenerated from the Fe^{3+}-HEDP complex and further degradation of 1,4-dioxane occurred. Zee *et al*. (1993) reported that Fe^{3+} combined with chelators was reduced to Fe^{2+} by ligand-to-metal charge transfer processes excited by light exposure. Fischer (1993) also observed the photodegradation of Fe^{3+}-HEDP complex in acidic solution. As the experiments in this study were performed under fluorescent light, the photodegradation of Fe^{3+}-HEDP complex by the fluorescent light might be expected. However, it was rejected, since the R_{dx} in the dark did not differ from the R_{dx} under the fluorescent light (Fig. 5). Thus, the mechanism of Fe^{2+}-regeneration is not clear at present. Perhaps the regeneration of Fe^{2+} might be caused by a chemically excited degradation of the Fe^{3+}-HEDP complex by HOCl.

Contrary to the experiments at pH 2.5, R_{dx} at pH 6.0 reached a plateau around 2 mM that was equal to $D_{Fe(II)}$, even if D_{HEDP} increased to 20 mM. This indicates that the Fe^{2+}-HEDP complex formed under the HEDP-rich condition at pH 6.0 reacted with HOCl and changed into the Fe^{3+}-HEDP complex. Then, the Fe^{3+}-HEDP complex remained in the solution without any further reaction with HOCl. Contrary to the HEDP-rich condition, the Fe^{2+}-HEDP complex of $[Fe(HEDP)]^{2-}$ at D_{HEDP} of 1 mM was unreactive with HOCl, because R_{dx} at pH 6.0 and D_{HEDP} of 1 mM was around 1 mM, which was equal to free Fe^{2+} concentration. Figure 7 shows the absorption spectra of the mixtures of Fe^{2+} and HEDP without HOCl. The spectrum of the mixture of Fe^{2+} and HEDP at D_{HEDP} of 10 mM under pH 6.0 had a shoulder around 440 nm, which disappeared at D_{HEDP} of 1 mM. Thus, the structure of Fe^{2+}-HEDP complex changed with the HEDP/Fe^{2+} molar ratio. Probably, a kind of bridging complex was formed under the high HEDP/Fe^{2+} molar ratio. As a result of the structure change, the reactivity of the Fe^{2+}-HEDP complex with HOCl changed at different D_{HEDP} under pH 6.0. The reaction of the Fe^{2+}-HEDP complex with HOCl generates the Fe^{3+}-HEDP complex. Considering that the photodegradation of Fe^{3+}-HEDP complex is caused under acidic condition (Fischer *et al*., 1993), the Fe^{3+}-HEDP complex may be more stable at pH 6.0 than at acidic condition. From Fig. 4 the main species of the Fe^{3+}-HEDP complex at pH 6.0 are $[Fe(OH)(HEDP)]^{2-}$ and $[Fe(HEDP)]^{-}$, although formation of some bridging complexes is also expected at D_{HEDP} of 10 – 20 mM. In aqueous solutions, the most common complexes are octahedral, namely the coordination number of six (Paoletti, 1984). The remaining coordination sites are occupied by water molecules. Since the number of water molecules which coordinated with Fe^{3+} at pH 6.0 is smaller than that at pH 2.5 due to the hydroxylation at pH 6.0 and protonation at pH 2.5, the small number of water molecules which coordinated with Fe^{3+} at pH 6.0 was inferred to result in less reactivity with HOCl.

Thus, the effect of HEDP on the Fenton-type reaction depended on pH and D_{HEDP}. Acid and D_{HEDP} promoted the Fenton-type reaction, probably resulting from the Fe^{2+} regeneration via the degradation of Fe^{3+}-HEDP complex. However, the Fenton-type reaction was inhibited when the HEDP/Fe^{2+} molar ratio was less than one at around neutral pH.

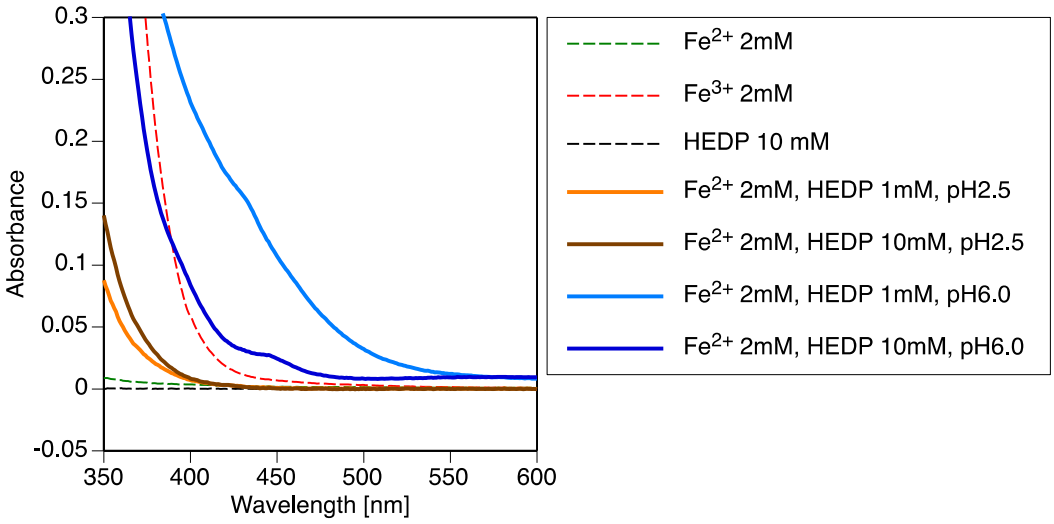

Fig. 7 - Absorption spectrum of each solution without HOCl.

CONCLUSIONS

The influence of three chelating agents on 1,4-dioxane degradation by the Fenton-type reaction using Fe^{2+} and HOCl was investigated in this research. The obtained results are summarized as follows:

(1) The R_{dx} of the Fenton-type reaction with no chelating agent was equal to the initial dose of limiting reactant, Fe^{2+} or HOCl, since HOCl could not regenerate Fe^{2+} from Fe^{3+}.

(2) The Fenton-type reaction was strongly inhibited by OA and EDTA at pH 6.0. However, the inhibition effect was deteriorated at acidic pH. Changes in chelating ability by protonation of carboxyl groups of the chelating agents accounted for the decrease in the inhibition effect at acidic pH.

(3) Acid and D_{HEDP} promoted the Fenton-type reaction, probably resulting from the Fe^{2+}-regeneration via the degradation of Fe^{3+}-HEDP complex. However, the Fenton-type reaction was inhibited at the HEDP/Fe^{2+} molar ratio less than one at pH 6.0.

Consequently, the iron-chelating agents affect the Fenton-type reaction by chelation. However, a decrease in the operational pH is useful to avoid the inhibition by the chelating agents.

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