Removal of citrate and hypophosphite binary components using Fenton, photo-Fenton and electro-Fenton processes

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Abstract
Both citrate and hypophosphite in aqueous solution were degraded by advanced oxidation processes (Fe2+/H2O2, UV/Fe2+/H2O2, and electrolysis/Fe2+/H2O2) in this study. Comparison of these techniques in oxidation efficiency was undertaken. It was found that Fenton process could not completely degrade citrate in the presence of hypophosphite since it caused a series inhibition. Therefore, UV light (photo-Fenton) or electron current (electro-Fenton) was applied to improve the degradation efficiency of the Fenton process. Results showed that both photo-Fenton and electro-Fenton processes could overcome the inhibition of hypophosphite, especially the electro-Fenton.

Key words: citrate; hypophosphite; wastewater; advanced oxidation processes; Fenton; photo-Fenton; electro-Fenton

Introduction
Electroless nickel (EN) plating technique provide wear and corrosion protection in various industrial applications (Chen et al., 2002). In contrast to traditional electroplating, it does not use external electric current to produce deposit. The conventional EN plating solutions contain nickel ions, reducing agents, complex agent, which prevent the precipitation of nickel hydroxide and other additives (to support the deposition) (Tarozaite et al., 2005; Cui et al., 2005). Hypophosphite (HP) has been mainly employed as a reducing agent in the EN plating industry (Li et al., 1999). Reducing ability of nickel electroplating solutions, however, decrease after repeated uses, and finally the electroplating solutions become unusable and need to be drained. Spent bath contains excess nickel ions, hypophosphite and ligands that would cause serious contamination if not removed before discharge. Because of metals are nondegradable that lead to residual solutions (Huynh and Tanaka, 2003; Njau et al., 2000). Heavy metals are extremely toxic and are bioaccumulate in the food chain. Ligands and nickel ions complex stably in EN plating bath. It is difficult to separate the metals from wastewater because of the complex form (Abd et al., 2005; Navarro and Tatsumi, 2002). Citrate is one of the most widely used ligand in EN plating solutions (Tarozaite et al., 2005). Therefore, the destruction of citrate is primary before processes of removing the nickel ion.

Fenton reaction has been widely used in the treatment of persistent organic pollutants in water owing to its “Green” chemical properties (De Laat and Gallard, 1999). Fenton is potentially useful for treating organic compounds in wastes because of the generated hydroxyl radical (·OH) is a powerful oxidant (2.8 V versus normal hydrogen electrode (NHE)). In the generally accepted mechanisms of Fenton reaction hydroxyl radicals are produced by interaction of H2O2 with ferrous salts (Walling, 1975):

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- 
\]

Fe3+ can react with H2O2 in the so-called Fenton-like reaction (Kim et al., 2006; Pekhonen et al., 1993; Zepp et al., 1992):

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{FeOOH}^{2+} + \text{H}^+ 
\]

\[
\text{FeOOH}^{2+} \rightarrow \text{HO}_2^- + \text{Fe}^{3+} 
\]

\[
\text{Fe}^{3+} + \text{HO}_2^- \rightarrow \text{Fe}^{3+} + \text{O}_2 + \text{H}^+ 
\]

Although Fe2+ is serving as a catalyst in Fenton process, it is well established that the reaction rate of Fe2+ ions regenerated from Fe3+ ions (Reaction (2), k is in the range of 0.01–0.001 L/(mol·s)) is very slow in comparing with the reaction rate in Reaction (1) (k = 76 L/(mol·s)). A larger concentration of Fe3+ ions can improve the decomposition rate of organic pollutants due to the greater amount of hydroxyl radicals produced by Reaction (1). However, the large amount of ferric hydroxide sludge was also produced in the same time which needed further handling and disposal. In recent years, there is a great interest which is by the use of electrochemistry (electro-Fenton) and photochemistry (photo-Fenton) to regenerate ferrous ions.

In photo-Fenton system, recent reports indicate that the illumination of the Fenton system (H2O2+Fe2+ + UV) can
significantly improve decomposition of many refractory organics (Kim et al., 2006). The improvement of organic decomposition is believed to be due to photolysis of aqueous complex \( \text{Fe(OH)}^{2+} \) to provide additional -OH by Reaction (5). \( \text{Fe(OH)}^{2+} \) is a major light absorber (absence of the other chelates) in the photo-Fenton process, has a relatively low quantum yield for the generation of \( \text{Fe}^{3+} \) (0.017 at 360 nm). Furthermore, \( \text{Fe}^{3+} \) complexes are known as playing an important role in producing \( \text{Fe}^{2+} \) because of its high molar absorptivity and quantum yield (Pekhonen et al., 1993; Zepp et al., 1992). The strong complexes (\( \text{Fe}^{3+} \)-citrate) can proceed rapid photochemical reactions in UV-Vis unit. Such photolysis of \( \text{Fe}^{3+} \)-citrate complexes can deduce \( \text{Fe}^{2+} \) formation and citrate decomposition (Reaction (6)), with a higher quantum yield of \( \text{Fe}^{2+} \) formation (0.21–0.28 at 436 nm) (Zepp et al., 1992).

\[
\text{Fe(OH)}^{2+} + \text{hv} \rightarrow \text{Fe}^{2+} + \bullet \text{OH} \quad (5)
\]

\[
2\text{Fe}^{3+} + 2\text{Cit}^{3-} + \text{hv} \rightarrow [\text{Fe(II) Cit}]^- + \text{Fe}^{2+} + 3\text{-oxoglutarate} + \text{H}^+ + \text{CO}_2 \quad (6)
\]

In electro-Fenton system, the degradation of different indirect electro-oxidation methods has been explored (Pignatello et al., 2006). Ferred-Fenton process is one of that \( \text{Fe}^{3+} \) are regenerated via Reaction (7) by contacting \( \text{Fe}^{3+} \) with the electrons which were supplied from the cathode (Hsiao and Nobe, 1993). We reported that this process was more efficient than the Fenton process in treating high concentration hexamine wastewater, because \( \text{Fe}^{3+} \) can be directly reduced to \( \text{Fe}^{2+} \) through electrolysis reduction. As a result, both the generation rate of hydroxyl radicals and the decomposition rate of organic are promoted (Chou et al., 1999; Huang et al., 1999).

\[
\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \quad (7)
\]

In our previous work we studied the treatment of chemical nickel plating wastewater on the application of electro-Fenton, containing a mixture of nickel ions, chelates and hypophosphite. A 93% removal efficiency of COD and a complete removal of nickel ions (> 99.9%) was obtained while using \( \text{IrO}_2/\text{RuO}_2 \) composite anode (Chang et al., 2004). The \( \text{O}_3 \) process, photo-degradation and different degradation sequences were proposed in treating citrate (Dodge and Francis, 2002). However, rarely studies have shown the application of \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) systems (Fenton, photo-Fenton, and electro-Fenton) and no comparison can be seen between the effectiveness of \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) systems when applied for the treatment of citrate and hypophosphite. This study examines the use of Fenton, photo-Fenton, and electro-Fenton methods in degrading the citrate in presence of hypophosphite. The oxidation of citrate in the presence and absence of hypophosphite was determined by COD measurement. The degradation efficiency of Fenton, photo-Fenton and electro-Fenton were also compared.

1 Experiment

1.1 Instruments

The Fenton reaction was carried out in a jar test reactor (1000 mL, Mei Cheng Acrylic Co., Ltd., Taiwan). The dosage of hydrogen peroxide was at beginning or using the continuous mode. All the reaction solutions were well mixed.

In photochemical processes, we immersed three UVA lamps (UVP BL-15 365 nm, Philips, the Netherlands) in reacting solution as an UV source of 365 nm (15 W × 3), the lamps were vertically located in the center of the reactor (2000 mL, Fig. 1a). Solution was well mixed in the reactor by a circulator pump.

In electrochemical processes, the reactions proceeded in a rectangular electrochemical reactor (3000 mL). Electrolytes were operated at constant current of 18 A using a DC power supply from Maxgood Industrial Company (Taiwan). The anode was composed by four cylindrical rods (150 cm², \( \text{Ti/RuO}_2/\text{IrO}_2 \)) and the cathode was composed by four cylindrical nets (460 cm², \( \text{Ti/RuO}_2/\text{IrO}_2 \), Fig. 1b). All the electrodes were dipped in the well mixed solution.

Fig. 1 Photo-Fenton reactor (a) and electro-Fenton reactor (b).
for experiments.

1.2 Reagents

Sodium phosphate monohydrate (82.0%–86.5%), trisodium citrate dihydrate (99%), sodium perchlorate monohydrate (98.5%) (Kanto Chemical Co., Inc., Japan), sodium hydroxide (50%, Mallinckrodt Baker, USA) and hydrochloric acid (37%, Scharlau Chemie, Spain) were used without further purification. FeCl₂ and H₂O₂ (purity, 50%) were obtained from Kanto Chemical Co., Inc., Taiwan and Chang Chun Petrochemical Co., Ltd., Taiwan, respectively. Aqueous solutions used for oxidation reactions were prepared with deionized water obtained from a Millipore Milli-Q system. Hypophosphite and citrate stock solutions (1 mol/L) were prepared and stored at 4°C for 1 week at most. FeCl₂ solution (1 mol/L) was prepared in 0.01 mol/L hydrochloric acid.

1.3 Experimental procedures

In each process, citrate and/or hypophosphite concentrated solutions were transferred to the electrochemical reactor. Amount of ferrous chloride was selected and dissolved in the solution. The initial pH value was adjusted to 3.0 by using concentrated hydrochloric acid. Hydrogen peroxide was applied initially or using continuous mode. Samples were taken into the tubes with sodium hydroxide to quench the reaction by increasing pH around 10.0. All trials were settled (30 min) and diluted for further measurements of COD and ionic concentration (IC).

1.4 Analysis

Before analysis, all trials were filtered with a 0.2-µm cellulose acetate from membrane filter (Advantec MFS Inc., Japan). COD was measured by the potassium dichromate method (NIEA W515.53A) (APHA, 1998). Hypophosphite, phosphite, phosphate and most of intermediates were separated and identified by ion chromatography using a 732 IC detector, and 4 mm × 250 mm (ID × L), and A SUPP 5-250 column (Metrohm Ltd., Switzerland).

To gain a better understanding on the oxidative ability of different processes, their removal efficiency for citrate and HP oxidation at a given sampling time t was determined as following Eqs. (8)–(12).

\[
R_{\text{total}} = \left(1 - \frac{\text{COD}_2}{\text{COD}_0}\right) \times 100\% \tag{8}
\]

\[
R_{\text{org}} = \left(1 - \frac{\text{COD}_{\text{org}}}{\text{COD}_{\text{org}_0}}\right) \times 100\% \tag{9}
\]

\[
R_{\text{HP}} = \left(1 - \frac{\text{COD}_{\text{HP}}}{\text{COD}_{\text{HP}_0}}\right) \times 100\% \tag{10}
\]

\[
R_{\text{PR}} = \left(1 - \frac{\text{COD}_{\text{PR}}}{\text{COD}_{\text{PR}_0}}\right) \times 100\% \tag{11}
\]

\[
\text{COD}_{\text{org}} = \text{COD}_T - \text{COD}_{\text{HP}} \tag{12}
\]

where, \(R_{\text{total}}\) is total COD removal efficiency; \(R_{\text{org}}\) is organic compound removal efficiency; \(R_{\text{HP}}\) is hypophosphite removal efficiency; \(R_{\text{PR}}\) is reduced phosphorus removal efficiency. COD_T, COD_organ, COD_HP, and COD_PR are the experimental measurement at time t and initial value for total COD, organic compound COD, HP COD, and reduced phosphorus COD, respectively. Reduced phosphorus COD was calculated assuming that one molecule of HP (COD = 32 (mgO₂·L)/mmol HP) and phosphite (COD = 16 (mgO₂·L)/mmol phosphite) requires 1 and 1/2 molecules oxygen to be completely oxidized to phosphate (COD = 0 (mgO₂·L)/mmol phosphate), respectively. Organic compound COD can be calculated according to Eq. (5).

2 Results and discussion

2.1 Fenton reaction

2.1.1 Influence of pH

pH is probably the most important parameter in Fenton process. High degradation efficiencies for various contaminants have been reported at acidic pH for Fenton reaction. For example, Gallard and De Laat (2000) have described the effects of iron speciation in Fenton reaction. They found that it is strongly dependent on pH. Thereby, the effect of pH on the efficiency of citrate degradation was examined. The experiment solution consisted of equal molar concentrations of citrate and HP (20 mmol/L). Ferrous ions (30 mmol/L) and H₂O₂ (260 mmol/L) were added initially. The final pH values of reaction solutions were ranged from 1.3 to 6.8. Figure 2 illustrates the total removal of COD in Fenton system as a function of pH. Obviously, the optimal solution pH was about 3.0. The results were similar to the previous publications (Kuo, 1992; Sevimli and Kinaci, 2002).

2.1.2 Influence of the \(C_{\text{Fe}^2+}^{0}/C_{\text{HP}}^{0}\) ratio

To elucidate the role of Fe²⁺ on removal of binary compounds, various experiments were performed at pH 3.0 by varying the \(C_{\text{Fe}^2+}^{0}/C_{\text{HP}}^{0}\) ratio from 0 to 5 at constant H₂O₂ concentration (260 mmol/L). The removal efficiency of total COD, organic compound, and hypophosphite with various \(C_{\text{Fe}^2+}^{0}/C_{\text{HP}}^{0}\) are illustrated in Fig. 3. It was found that the HP removal efficiency increased with increasing \(C_{\text{Fe}^2+}^{0}/C_{\text{HP}}^{0}\) ratio at lower \(C_{\text{Fe}^2+}^{0}/C_{\text{HP}}^{0}\) ratio (< 0.5) and HP
Reaction (1)). Therefore, keeping the phosphite can be removed completely by ferric ions (product in study, the phosphorus was removed by precipitation. If free ferrous ions to react with hydrogen peroxide. In this study, the removal efficiency increased progressively with increasing $C_{\text{Fe}^{2+}}/C_{\text{HP}}$ ratio. The total removal efficiency of COD can reach 59% when $C_{\text{Fe}^{2+}}/C_{\text{HP}}$ ratio is increased to 5. It was found that HP has a greater reactive constant with $\cdot$OH (Adams et al., 1965; Schaefer and Asmus, 1980). The reactions are as following (Reactions (13) to (16)).

$$\begin{align*}
\text{H}_2\text{PO}_3^- + \cdot\text{OH} & \rightarrow \text{HPO}_2^- + \text{H}_2\text{O} & \text{(13)} \\
\text{HPO}_2^- + \text{(further oxidation)} & \rightarrow \text{H}_2\text{PO}_4^- & \text{(14)} \\
\text{H}_2\text{PO}_4^- + \cdot\text{OH} & \rightarrow \text{H}_3\text{PO}_5^- + \text{H}_2\text{O} & \text{(15)} \\
\text{H}_2\text{PO}_5^- + \text{(further oxidation)} & \rightarrow \text{H}_2\text{PO}_4^- & \text{(16)}
\end{align*}$$

After oxidation by Fenton reaction, HP transformed into phosphate and phosphite which can be a complex with ferrous ions and ferric ions strongly, leading insufficient free ferrous ions to react with hydrogen peroxide. In this study, the phosphorus was removed by precipitation. If $C_{\text{Fe}^{2+}}/C_{\text{HP}}$ ratio is greater than 1.5 the phosphate and phosphite can be removed completely by ferric ions (product in Reaction (1)). Therefore, keeping the $C_{\text{Fe}^{2+}}/C_{\text{HP}}$ ratio at 1.5 to prevent waste of iron ions and increase the removal of phosphorus is our further work.

### 2.1.3 Influence of $\text{H}_2\text{O}_2$ concentration and dosage method

As Fig. 4 (curve a) shows, the rate of COD removal increases with the increase in initial concentration of hydrogen peroxide, where $\text{H}_2\text{O}_2$ dosage was altered from 0 to 20 mmol/L ($C_{\text{Fe}^{2+}} = 30$ mmol/L). When $C_{\text{H}_2\text{O}_2}$ in the range of 20–260 mmol/L, various amount of hydrogen peroxide has insignificant effects on the elimination rate of COD and the remaining COD was approximately 75%. The reason maybe due to that the solution pH (curve b) is much lower than optimum. A sharp drop in solution pH was observed when $\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2$ solutions were added into a binary solution of the citrate and hypophosphite. The drastic drop of pH (that is out of control) is due to a probable instantaneous formation of some acidic oxidation products. To control pH easily, experiments were carried out with a continuous $\text{H}_2\text{O}_2$ dosage at constant pH 3.0. Figure 4 (curve c) displays that when $C_{\text{Fe}^{2+}} = 30$ mmol/L and $C_{\text{H}_2\text{O}_2} = 260$ mmol/L (dosage continuously), the degradation efficiency increases with increasing $\text{H}_2\text{O}_2$ concentration because of more $\cdot$OH produced (Reaction (1)). Accordingly, we found that continuous dosage of $\text{H}_2\text{O}_2$ was better than one step dosage initially because of its well pH control.

### 2.1.4 Influence of single and binary systems

Figure 5 plots the removal efficiency against hydrogen peroxide concentration during the Fenton process in single (HP or citrate) and binary (HP and citrate) solutions. The optimum conditions of Fenton process were performed. In solution contained HP only, all HP and phosphorus are removed when dosage of hydrogen peroxide is larger than 40 mmol/L where HP can be oxidized by generated $\cdot$OH in Fenton reaction directly, and phosphorus can be removed by precipitation. When solution contained citrate only the $\cdot$OH can not mineralize the intermediates of citrate into $\text{H}_2\text{O}$ and $\text{CO}_2$, result to the removal efficiency remains about 70%. In binary system, the removal rates

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**Fig. 3** Removal efficiency for total COD, organic COD and hypophosphate for $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system as a function of $C_{\text{Fe}^{2+}}/C_{\text{HP}}$ ratio at pH 3.0. $C_{\text{citrate}}$: 20 mmol/L; $C_{\text{HP}}$: 20 mmol/L; $C_{\text{H}_2\text{O}_2}$: 260 mmol/L.

**Fig. 4** Total COD removal efficiency as a function of hydrogen peroxide concentration for different dosage method. $C_{\text{citrate}}$: 20 mmol/L; $C_{\text{HP}}$: 20 mmol/L; $C_{\text{Fe}^{2+}}$: 30 mmol/L.

**Fig. 5** COD and phosphorus removal efficiency as a function of hydrogen peroxide concentration for different solution systems. $C_{\text{citrate}}$: 20 mmol/L; $C_{\text{HP}}$: 20 mmol/L; $C_{\text{Fe}^{2+}}$: 30 mmol/L; pH: 3.0.
of COD increased significantly under the same condition. In comparison at the same H2O2 dosage (260 mmol/L), the removal efficiency (around 70%) of COD in citrate solution is much greater than it (around 42%) in binary solution, indicating that the present HP resist the mineralization of citrate.

2.2 Photo-Fenton process

In binary solution, different photochemical processes are shown in Fig. 6. As can be seen, the increase of H2O2 amount and the use of UV light can improve the reaction rate in presence of hypophosphite. It is clear that total COD removal can be reached around 90% within 420 min using the photo-Fenton process. In H2O2/UV system, total COD decreased with the irradiation time and a 66% of COD removal was achieved after 420 min reaction. However, comparing Fe3+/UV process (29%) and H2O2/UV process (66%), indicating that the presence of UV can significantly improve the oxidation of hypophosphite. Hence, in H2O2/UV process, a greater COD decrease was observed in binary solution. The presence of hypophosphite caused a great inhibition on citrate degradation in Fenton process. However, in the presence of UV, it is clear that COD would have been greatly degraded (binary solution) within 420 min by the photo-Fenton process. This shows that the COD decrease can largely be enhanced by the UV irradiation to binary solution.

2.3 Electro-Fenton process

The COD removals of different electrochemical processes of binary solutions are shown in Fig. 7. The electro-Fenton process shows a great COD removal over 90% even in the presence of hypophosphite, and the electron current can obviously improve the oxidation efficiency. Result shows that this electro-Fenton process can overcome the inhibition of hypophosphite on COD removal. Table 1 provides a comparison of the oxidation efficiency to remove COD of citrate or binary solutions by different oxidation processes (photochemical and electrochemical). As can be seen, H2O2/electro process is not a powerful method to production of hydroperoxyl radical by anode, the electro-Fenton is the most useful process in citrate degradation, especially in decomposition of binary solutions.

Table 1 Comparison of oxidation efficiency with different processes (reaction time: 420 min)

<table>
<thead>
<tr>
<th>Process</th>
<th>Oxidation efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenton</td>
<td>Photo-Fenton</td>
</tr>
<tr>
<td>Citrate solution</td>
<td>75.5</td>
</tr>
<tr>
<td>Binary solution</td>
<td>54.4</td>
</tr>
</tbody>
</table>

3 Conclusions

Different oxidation processes have been studied and compared for the oxidation of citrate and hypophosphite in aqueous solution. In Fenton process, the oxidation efficiency was influenced by many factors, such as the pH, the amount of hydrogen peroxide, and iron salt. The optimal pH obtained for the best degradation was about 3.0 for Fenton process. Fenton can not degrade citrate completely and even a series inhibition will be caused by HP. However, we found that the UV light and electron current (photo-Fenton and electro-Fenton) improved the degradation efficiency of the Fenton process. The application of UV light or electron current to Fenton process could overcome the inhibition of hypophosphite. Among all applied processes, electro-Fenton process was the most efficient, in which 95% of COD removal was obtained within 420 min. Photo-Fenton process was also effective in degradation of binary solution and around 90% of COD removal was achieved within the same time period. The decomposition of citrate in both single and binary solutions follows the sequence: electro-Fenton > photo-Fenton > Fenton.
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References


