Treatment of real wastewater using semi batch (Photo)-Electro-Fenton method

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ABSTRACT

INTRODUCTION

A large portion of wastewater generated by many university laboratories has many kinds of high concentration complex organic constituents, but the conventional method such as coagulation is not useful for removal of total organic carbon (TOC) and chemical oxygen demand (COD) [1]. Alternative technology has been developed to help solving the problem. Advanced oxidation processes (AOPs) are frequently used to oxidize complex organic constituents found in wastewaters which are difficult to be degraded biologically into simpler end products [2]. Fenton oxidation is particularly attractive because of its simplicity without requirement for special equipment and high efficiency in organic pollutant removal [3]. In Fenton reaction, highly reactive hydroxyl radicals (-OH) are generated (Eq. 1).

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

(1)

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

(2)

To avoid the disadvantages of traditional Fenton oxidation such as potential risk in transportation of \( \text{H}_2\text{O}_2 \), a loss of reactive activity and sludge production, a modified process called Electro-Fenton method (EF) has been developed. The EF method has the advantage of allowing a better control of hydroxyl radical production; in the EF method, soluble \( \text{Fe}^{2+} \) can be cathodically reduced to \( \text{Fe}^{3+} \) which is known as electrochemical catalysis with \( E^{\circ} = 0.77 \text{ V/SHE} \) [4]. Thus, the fast generation of \( \text{Fe}^{3+} \) accelerates the production of \( \cdot \text{OH} \) according to Eq. 3.

\[ \text{Fe}^{3+} + e^{-} \rightarrow \text{Fe}^{2+} \]  

(3)

Recently there are several applications of EF process. These can be generally divided into four categories of Fenton reagents externally added to electrochemical reactor [5]. In the first category, ferrous ion is externally applied, hydrogen peroxide and ferrous ion are concurrently generated at cathode [6-11]. In the second category, hydrogen peroxide is externally applied while a sacrificial iron anode is used as ferrous ion source [12]. In the third category, hydrogen peroxide is externally applied and ferrous ion was electro
generated via the reduction of ferric ion or ferric hydroxide sludge [13]. In the fourth category, both ferrous ion and hydrogen peroxide are electro-generated at sacrificial anode and cathode.

In this study, the solution in the Photo-Electro Fenton method (PEF) is treated under EF conditions and simultaneously irradiated with UVA light to accelerate the mineralization rate of organics via photo-Fenton process. UVA light can induce the photo degradation of some oxidation by-products or their complexes [4]. PEF process can be used to attain high removal TOC and COD with low amount of sludge production [14]. The reaction of PEF is shown as Eq. 4, higher production rate of OH resulting from the greater photon intensity supplied to the system can enhance the ability of oxidation in highly contaminated wastewater.

\[
\text{Fe(OH)}^{2+} + hv \rightarrow \text{Fe}^{3+} + \cdot\text{OH} \quad (4)
\]

The aim of this work was to treat real wastewater from Sustainable Environment Research Center (SERC) which is responsible for the treatment of laboratory waste liquid collected from universities in Taiwan. To fulfill the effluent standards of industrial wastewater specified by Taiwan government, where the COD is less than 200 mg L\(^{-1}\), the EF and PEF methods through a newly designed reactor were used to investigate the ability to treat SERC wastewater as compared with the traditional coagulation process. Through this study, the technologies in complex wastewater treatment could be established, and the cost will be evaluated and provided as well.

**MATERIALS AND METHODS**

1. Wastewater Solutions

In this work, wastewater was from SERC in Taiwan. The center is responsible for the treatment of laboratory hazardous waste liquid collected from universities in Taiwan. The quality of wastewater is shown in Table 1 with Fig. 1 showing the ion chromatography diagram of the wastewater. The TOC and COD values of this wastewater were high as 16500 and 24000 mg L\(^{-1}\), respectively.

2. Experimental Procedure and Apparatus

Figure 2 shows the schematic diagram of the experimental reactor. The reactor was designed with the dimensions of 14 x 14 x 41 cm (L x W x H). The reaction solutions were mixed by a circulation pump with 2000 mg L\(^{-1}\) ferric sulfate (FeSO\(_4\)-7H\(_2\)O, Merck), and the continuous H\(_2\)O\(_2\) (50 wt%, Union Chemical Works) dosage was supplied to the system at room temperature. The anode (Φ = 0.625 cm) was titanium rod coated with IrO\(_2/\)RuO\(_2\) (DSA) and the cathode (Φ = 5 cm) was a cylindrical Ti-DSA grid. The UV light (λ = 365 nm) was fixed inside a cylindrical Pyrex tube. All the experimental used the same reactor and the volume of solution was about 4 L for each trial. After all the chemicals were well mixed and the pH of solution were adjusted (pH = 2 avoiding Fe(OH)\(_3\) generation), the power supply and UV light were turned on to initiate the reaction. Simultaneously hydrogen peroxide was continuously supplied into the system.

**Fig. 1.** Ion Chromatography of wastewater diluted 1000 times (4 = Cl\(^-\); 6 = NO\(_3\); 9 = SO\(_4\)).

**Fig. 2.** Schematic diagram of experimental set up.
3. Analytical Methods

TOC was determined by using a TOC analyzer (Ge Sievers Innovox). Calibration of the analyzer was achieved with potassium hydrogen phthalate solution. COD was determined by colorimetric, dichromate oxidation using UV-Vis-spectrophotometers according to the standard methods [15].

RESULTS AND DISCUSSION

1. Coagulation Process

Treatment of wastewater by coagulation is a well-established technology which is suitable for wastewater that contains large amount of colloids and suspended matters. Ferric salts have been found to be economically preferable in wastewater treatment [16]. The results presented in Fig. 3 show the relation between various concentrations of ferric and ferrous salt and the TOC removal. It was found that the FeSO₄·7H₂O is slightly better for TOC removal than Fe₂(SO₄)₃·5H₂O where the TOC removal was about 18% for FeSO₄·7H₂O and 10% for Fe₂(SO₄)₃·5H₂O. In general case, the coagulation method is not so effective to remove high organic solution. Moreover, the huge amount of ferric and ferrous salt used in coagulation method will be totally against the purpose of sludge decrement and removal of organic compound [1]. The results proved the fact illustrated above and indicated that conventional process like coagulation cannot be used to treat this high concentration organic wastewater.

Fig. 3. Coagulation (pHe = 8.5; time = 10 min; 100 rpm).

2. Treatment Efficiency of Fenton Methods

Fenton method is the traditional AOPs. The highly reactive OH in Fenton reaction generation generated (Eq. 1) will oxidize the organic compounds into CO₂, H₂O and inorganic ions. Figure 4 data show the changes of TOC and COD on semi batch Fenton systems. The initial pH was set at 2 for avoiding Fe(OH)₃ generation and achieving the best current efficiency as indicated in the previous study [1]. In the Fenton systems, the TOC and COD removal efficiencies were 96 and 95%, respectively at 2520 min. In this experiment we could not use higher H₂O₂ dosing rate because the solution would overflow due to the violent oxidation. The amount of H₂O₂ used in this experiment was the same.

Fig. 4. Change of organic matter with time for Fenton system, ([Fe²⁺] = 2000 mg L⁻¹; H₂O₂ dosing rate = 0.15 mL min⁻¹; pH = 2; I = 20 A). (a) TOC, (b) COD.

3. Treatment Efficiency of Photo Fenton (PF) Methods

In this study, the UV lights (λ = 365 nm) is used to accelerate the mineralization process. The UVA irradiation destroyed organic products more rapidly. Meanwhile, the derived ferrous complex can be regenerated into ferrous and hydroxyl radicals via Eq. 4. Figure 5 data show the changes of TOC and COD on semi batch PF systems. The initial pH was set at 2. The results show that in the PF system at 1620 min, the TOC and COD removal efficiencies were 97 and 95%, respectively. Also, the H₂O₂ dosing rate was properly conditioned to prevent the solution from overflow due to the violent oxidation.

4. Treatment Efficiency of EF and PEF Methods

With applied electricity in the system, ferrous ions are generated more via Eq. 3 in the solution, and therefore the hydroxyl radical is consumable efficiently. Figure 6 data show the changes of TOC and COD on
5. Cost Estimation

The equation applied to calculate the energy cost of electricity is as follows:

\[
\text{Energy cost (kWh)} = (V \cdot I \cdot t_e) + (V \cdot I \cdot t_{AV}) + (V \cdot I \cdot t_r)
\]  

\[
\text{Cost} = \text{energy cost} \times \text{price}
\]

Where $V$ is the voltage applied until time $t$ (V), $I$ is the electric current (A) used in this study, $t$ is the reaction time (h), $E$ is the electrical power used, $UVA$ is the light power used in this experiment, and $P$ is the pump used in this experiment.

Table 2 shows the cost of electricity of different types of Fenton processes. All treatments were using the same amounts of ferrous salt and hydrogen peroxide. From the table, PF method has the highest cost because it needs longer time to archive high TOC removal and prevent the overflow due to the violent oxidation. Fenton process is the cheaper one to treat wastewater but needs long time to obtain high TOC removal. With the use of semi batch EF method about 98% TOC was removed in 7 h, while 99% TOC was archived using semi batch PFE method. The cost of EF and PEF is higher than Fenton and PF methods, but EF can effectively reduce the reaction time. Moreover, the treated wastewater with PEF can meet the effluent standard of TOC in Taiwan (150 ppm). Therefore, although the cost of PEF is cheaper than PF method, PEF still has the competitiveness.

Table 2. Cost of electricity in many types of Fenton process

<table>
<thead>
<tr>
<th>Method</th>
<th>Time (h)</th>
<th>TOC (%)</th>
<th>Cost (NT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenton</td>
<td>42</td>
<td>96</td>
<td>2.1</td>
</tr>
<tr>
<td>Photo Fenton (PF)</td>
<td>27</td>
<td>97</td>
<td>4.9</td>
</tr>
<tr>
<td>Semi Batch Electro Fenton (EF)</td>
<td>7</td>
<td>98</td>
<td>2.5</td>
</tr>
<tr>
<td>Semi Batch Photo-Electro Fenton (PEF)</td>
<td>7</td>
<td>99</td>
<td>3.2</td>
</tr>
</tbody>
</table>

1 USD = 30 NT

CONCLUSIONS

Coagulation was undoubtedly ineffective in the removal of this type of highly polluted wastewater. With the treatment of PEF, the COD of treated wastewater can meet the effluent standard in Taiwan (200 mg L\(^{-1}\)). In the Fenton systems at 2520 min, the TOC and COD removal efficiencies were 96 and 95%, respectively. In the PF systems at 1620 min, the TOC and COD removal efficiencies were 97 and 95%, respectively. However, the TOC and COD removal efficiencies were 98 and 97% by EF, while 99% of TOC and 99% COD can be further removed by PEF. The optimum conditions were \([\text{Fe}^{2+}] = 2000 \text{ mg L}^{-1}, \text{H}_2\text{O}_2\) dosing rate = 6 mL min\(^{-1}\); pH = 2; $I = 20 \text{ A}$ and $t = 420 \text{ min}$. The cyclically electro-generated Fe\(^{2+}\) efficiently produced the hydroxyl radicals and could prevent $\text{H}_2\text{O}_2$ from overflow. Although the cost is higher than tradi-
tional Fenton method, EF and PEF have the advantages of short reaction time and highest efficiency which can fulfill the effluent standard of COD.

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REFERENCES


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