Advanced treatment of effluents from an industrial park wastewater treatment plant by ferrous ion activated persulfate oxidation process
Songmei Zhu, Zhen Zhou, Haitao Jiang, Jianfeng Ye, Jiamin Ren, Lingyun Gu and Luochun Wang

ABSTRACT
The advanced oxidation technology, ferrous ion (Fe(II)) activated persulfate (PS) producing sulfate radicals, was used for the advanced treatment of effluent from an integrated wastewater treatment plant in a papermaking industrial park. Separate and interactive effects of PS dosage, Fe(II)/PS ratio and initial pH on chemical oxygen demand (COD) removal were analyzed by the response surface methodology (RSM). The results showed that Fe(II)-PS system was effective in COD removal from the secondary effluent. PS dosage was the most dominant factor with positive influence on COD removal, followed by initial pH value. The optimum conditions with COD removal of 54.4% were obtained at PS/COD of 2.2, initial pH of 6.47 and Fe(II)/PS of 1.89. UV-visible spectrum analysis showed that after RSM optimization, Fe(II)-PS system effectively degraded large organic molecules into small ones, and decreased humification degree of the effluent. Three-dimensional fluorescence analysis demonstrated that aromatic protein and fulvic substances were fully decomposed by the Fe(II)-PS treatment.

INTRODUCTION
The zoned developmental pattern of modern industries has resulted in large resource consumption, especially of freshwater, and pollutant emissions, particularly from wastewater discharge, in a small area (Tong et al. 2013). Wastewater treated through the integrated wastewater treatment plants (WWTPs) was more cost-effective than individual ones and has been adopted by most industrial parks (Yuan et al. 2010). The combined influent in the industrial park WWTP features a large flow, complex composition and non-degradable characteristics (Zhu et al. 2015). Traditional physical, chemical and biological technologies can efficiently degrade most pollutants, but there are still considerable amounts of residual pollutants in the effluent from industrial park WWTP (Bagal & Gogate 2014). Therefore, it is necessary to carry out advanced treatment to ensure compliance discharge and even water reuse.

Advanced oxidation processes (AOPs) that generate highly activated radicals, such as hydroxyl radicals (·OH), hydroperoxyls (·O₂) and sulfate radicals (SO₄²⁻), have been applied successfully for the removal or degradation of non-degradable substances (Shi et al. 2012; Schulze-Hennings & Pinnekamp 2013; Bagal & Gogate 2014). AOP technologies based on the generation of SO₄²⁻ have emerged over the past years as a promising technique to degrade organic pollutants owing to their advantages of high oxidation potential (2.5–3.1 eV), safety and wide pH adaption (Anipsitakis & Dionsisou 2003; Shi et al. 2012; Zhou et al. 2013). Ferrous iron (Fe(II)) activated persulfate (PS) (Fe(II)-PS, Equation (1)) is a cheap and non-toxic AOP system (Long et al. 2014), and has the potential to be employed in full-scale WWTPs for advanced treatment of effluent. Many intensive efforts were conducted to investigate the effects of Fe(II)-PS system on organic pollutant removal, but most of the previous studies were tested with synthetic wastewater (Criquet et al. 2010; Marchesi et al. 2012; Jiang et al. 2013; Long et al. 2014). More detailed research is needed for real wastewater.
to investigate the feasibility of Fe(II)-PS system for advanced treatment of effluent from a full-scale WWTP.

\[
S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+} + SO_4^{2-}
\]  

(1)

In this study, Fe(II)-PS system was employed for advanced treatment of effluent from a centralized WWTP in a papermaking industrial park to reduce chemical oxygen demand (COD) to below 80 mg/L according to the discharge standard of pollutants for urban wastewater treatment plant of China (GB 18918-2002). Separate and interactive effects of PS dosage, Fe(II)/PS ratio and pH on the removal of COD were evaluated with real effluent by response surface methodology (RSM). Detailed characterization of dissolved organic matter (DOM) after Fe(II)-PS treatment was carried out by UV-visible (UV-vis) spectrum analysis and three-dimensional excitation-emission matrix (EEM) fluorescence spectroscopy. The results obtained in this study are expected to provide an advanced treatment technology and elucidate the DOM degradation mechanism for real effluent.

**METHODS**

**Wastewater sample**

The wastewater sample used for the experiment was taken from effluent of a papermaking industrial park WWTP in Liuyang, China. The WWTP was designed with treatment capacity of 20,000 m³/d fed by 85% wastewater from recycled paper mills and 15% domestic wastewater. In the WWTP, the treatment processes comprised an equalization tank, hydrolytic acidification tank, anoxic tank, aerobic tank and secondary settler. The 24-h composite sample was collected from the effluent, transferred to the laboratory within 90 min after sampling, and then stored at 4 °C. All the experiments were conducted using the same sample. The main characteristics of effluent sample used in the experiment were as follows: pH of 7.90 ± 0.20, COD of 100.0 ± 5.0 mg/L, ammonia nitrogen (NH₄-N) of 1.55 mg/L and total phosphorus (TP) of 0.02 mg/L.

**Batch experimental procedure**

Batch experiments were performed with a sample volume of 200 mL in an air bath thermostats oscillator (TS-200B, Tiancheng, China) at 20 °C to determine effects of PS/COD, Fe(II)/PS and initial pH on COD removal of the effluent. In each test, the effluent sample was firstly preheated to 20 °C, and then an appropriate amount of PS and Fe(II) (Na₂S₂O₈ > 98.0%, FeSO₄·7H₂O > 99.0%, Sinopharm Chemical Reagents Co., China) was added. Seven PS/COD ratios (1.0, 1.5, 2.0, 2.5, 3.0, 4.0 and 5.0) were used to study the effect of PS dosage on COD removal. The dosage of Fe(II) and initial pH were maintained at 88.7 mg/L and 7.90, respectively. Six Fe(II)/PS ratios (0.4, 0.8, 1.2, 1.6, 2.0 and 3.0) were chosen to evaluate the effect of Fe(II)/PS ratio on COD removal under PS dosage of 209 mg/L and initial pH of 7.90. Seven initial pH values (6.0, 6.5, 7.0, 7.5, 8.0, 8.5 and 9.0) were used to evaluate the effect of pH on oxidation performance of SO₄²⁻ with dosage of PS and Fe(II) of 209 and 88.7 mg/L, respectively. All the experiments were carried out for 2 h at mixing speed of 180 rpm.

**Experimental design**

On the basis of the range with significant change determined by single-factor tests, the three-factor three-level Box-Behnken design (BBD) was used as experimental design for the RSM to find out the optimal level of the factors. The three factors selected in the experiment were PS/COD (A: 0.5–2.5), Fe(II)/PS (B: 0.5–2) and pH (C: 6–10), and the response variable was COD removal (Y). The experimental levels of each variable were lower limit, median and upper limit of the selected range. In total, 17 runs were conducted for the experimental design and are shown in Table 1. The obtained data were analyzed by Design Expert® software version 8.0.6.1 for regression analysis and model development.

**Analytical methods**

Concentrations of COD, NH₄-N and TP were analyzed according to standard methods (Chinese NEPA 2012). The pH was monitored using a portable meter (HQd30, Hach, USA). The three-dimensional EEM fluorescence spectra were measured using a fluorospectrophotometer (RF-5301pc, Shimadzu, Japan). UV-vis spectra were analyzed by a spectrophotometer (UV-2600, Shimadzu, Japan).

**RESULTS AND DISCUSSION**

**Single-factor experiments**

Some single-factor runs were performed to achieve optimal levels of a single factor (SFopt). Figure 1 shows effects of PS
dosage, Fe(II)/PS ratio and pH value on COD removal of the effluent by Fe(II)-PS treatment. As shown in Figure 1(a), COD decreased firstly and then rose again with increasing PS/COD ratio, and remained constant after PS/COD > 3.0. The maximum COD removal of 30.9% was achieved at PS/COD = 1.5. As a source of SO4^2-/COD, PS generates more reactive radicals at higher dosage, and enhances COD removal. If excessive PS dosage is added, the generated SO4^2- will collide with each other and be annihilated (Equation (2)) (Yang et al. 2010), or react with PS and be consumed (Equation (3)) (Liang & Su 2013; Long et al. 2014).

\[
\text{SO}_4^{2-} + \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} \tag{2}
\]

\[
\text{SO}_4^{2-} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{2-} + \text{S}_2\text{O}_8^{2-} \tag{3}
\]

As shown in Figure 1(b), COD decreased from 73.5 to 67.1 mg/L with Fe(II)/PS ratio increasing from 0.4 to 1.2, but then increased to 79.5 mg/L at Fe(II)/PS = 3.0. A slight increase of COD was observed at Fe(II)/PS = 4.0. The COD removal reached its maximum of 37.5% at Fe(II)/PS = 1.2. At a given PS dosage, increasing Fe(II) corresponds to a higher production of SO4^2-; however, COD removal decreased when Fe(II)/PS ratio exceeded 1.2. This was because destruction and/or consumption of SO4^2- by excessive Fe(II) via Equation (4) limited its ultimate oxidation capacity (Vicente et al. 2011; Long et al. 2014).

\[
\text{SO}_4^{2-} + \text{Fe}^{2+} \rightarrow \text{SO}_4^{2-} + \text{Fe}^{3+} \tag{4}
\]

when pH was below 8, COD removal fluctuated in a narrow range of 43.9%–52.1%, indicating that Fe(II)-PS oxidation could be conducted for the effluent without pH regulation. As shown in Figure 1(c), the COD removal decreased greatly at pH > 8.0, and dropped to 14.0% at pH = 9.0. In the Fe(II)-PS system, variations of pH resulted in the conversion of SO4^2- to -OH, and influenced the oxidation activity of the system.

Table 1 | The design matrix based on coded and real variables for experimental factors and response

<table>
<thead>
<tr>
<th>Test no.</th>
<th>PS/COD</th>
<th>Fe(II)/PS</th>
<th>pH</th>
<th>Removal of COD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>1.25</td>
<td>8.0</td>
<td>40.00</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>1.25</td>
<td>8.0</td>
<td>41.54</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>1.25</td>
<td>8.0</td>
<td>46.67</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>1.25</td>
<td>8.0</td>
<td>45.13</td>
</tr>
<tr>
<td>5</td>
<td>2.5</td>
<td>1.25</td>
<td>10.0</td>
<td>37.44</td>
</tr>
<tr>
<td>6</td>
<td>2.5</td>
<td>0.50</td>
<td>8.0</td>
<td>37.44</td>
</tr>
<tr>
<td>7</td>
<td>2.5</td>
<td>2.00</td>
<td>8.0</td>
<td>43.59</td>
</tr>
<tr>
<td>8</td>
<td>0.5</td>
<td>0.50</td>
<td>8.0</td>
<td>28.41</td>
</tr>
<tr>
<td>9</td>
<td>1.5</td>
<td>1.25</td>
<td>8.0</td>
<td>39.99</td>
</tr>
<tr>
<td>10</td>
<td>1.5</td>
<td>0.50</td>
<td>6.0</td>
<td>38.00</td>
</tr>
<tr>
<td>11</td>
<td>1.5</td>
<td>2.00</td>
<td>6.0</td>
<td>54.36</td>
</tr>
<tr>
<td>12</td>
<td>0.5</td>
<td>1.25</td>
<td>6.0</td>
<td>16.92</td>
</tr>
<tr>
<td>13</td>
<td>1.5</td>
<td>0.50</td>
<td>10.0</td>
<td>31.79</td>
</tr>
<tr>
<td>14</td>
<td>2.5</td>
<td>1.25</td>
<td>6.0</td>
<td>48.72</td>
</tr>
<tr>
<td>15</td>
<td>0.5</td>
<td>1.25</td>
<td>10.0</td>
<td>11.79</td>
</tr>
<tr>
<td>16</td>
<td>1.5</td>
<td>2.00</td>
<td>10.0</td>
<td>37.44</td>
</tr>
<tr>
<td>17</td>
<td>0.5</td>
<td>2.00</td>
<td>8.0</td>
<td>19.99</td>
</tr>
</tbody>
</table>

As shown in Figure 1, COD concentration decreased at pH between 7.0 and 8.0, and increased at pH > 8.0. When the pH value increased from 7.0 to 8.0, COD concentration decreased from 85.0 to 70.0 mg/L, and increased from 70.0 to 85.0 mg/L when pH > 8.0. The COD concentration fluctuated in a narrow range of 70.0–85.0 mg/L when pH was below 7.0.
Zhao et al. (2015) also observed that the degradation efficiency of p-nitroaniline by SO$_4^{2-}$ was high under acid and neutral conditions, but decreased greatly under alkaline conditions. A reason for this phenomenon was that SO$_4^{2-}$ predominating under acidic and neutral conditions react with OH$^-$ to form -OH under alkaline conditions via Equations (5) and (6) (Lee et al. 2012), but -OH has a very poor reactivity to degrade organic substances under alkaline conditions (Zhao et al. 2015). Another reason was that alkali converts Fe(II) to precipitates or complexes without catalytic ability (Anipsitakis & Dionysiou 2003), and decreases the production of SO$_4^{2-}$.

$$\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \cdot\text{OH}$$  \hspace{1cm} (5)  

$$\text{SO}_4^{2-} + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \cdot\text{OH}$$  \hspace{1cm} (6)  

**Response surface analysis**

The relationship between COD removal efficiencies obtained from BBD experiments (Table 1) and input parameters was fitted by a full second-order polynomial model given below:

$$Y = 42.67 + 11.26A + 2.47B - 4.94C + 5.64AB + 1.54AC - 2.68BC - 10.99A^2 + 0.69B^2 - 2.96C^2$$  \hspace{1cm} (7)  

The coefficient of determination ($R^2$) of Equation (7) was 0.91, which implied a high correlation between experimental and predicted data. An analysis of variance (ANOVA) was further applied to evaluate the significance and adequacy of the model, with statistical results summarized in Table 2. The model $F$-value of 7.7 with a low associated $p$-value of 0.0068 implied that the model terms were significant. Simultaneously, the ‘lack of fit’ $F$-value of 5.55 ($p$-value = 0.066) suggested that the lack of fit was insignificant, which also showed the model adequately described the experimental data (Zhou et al. 2014).

The contour plots shown in Figure 2 were used to investigate the optimal level and interactive effects of variables on $Y$. The U-shape plots in Figure 2(a) and 2(b) suggested that an optimal PS/COD (2.2 at Fe(II)/PS of 2.0) could benefit $Y$, which was consistent with the results of single-factor analysis. Figure 2(c) shows that $Y$ was enhanced with the decreasing pH and increasing Fe(II)/PS, and the maximum was achieved at pH of 6.0 and Fe(II)/PS of 2.0. Figure 2 and ANOVA analysis in Table 2 also showed that PS/COD was the most dominant process parameter with positive influence on $Y$ ($p < 0.01$). The effect of pH on $Y$ was also significant at $p < 0.05$ level.

The predicted optimal results for $Y$ by RSM ($\text{RSM}_\text{opt}$) were obtained using PS/COD of 2.2, Fe(II)/PS of 1.89 and initial pH of 6.47, resulting in maximum $Y$ of 54.4% and COD in the effluent of 43.1 mg/L. The costs of sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8 > 99.0\%$) and ferrous sulfate ($\text{FeSO}_4\cdot\text{H}_2\text{O} > 93.0\%$) were estimated at $\$865$/ton and $\$45$/ton, respectively. Therefore, the operating costs for effluent were $\$0.21$/ton and $\$3.68$/kg COD. Zhu et al. (2015) proposed a novel electro-oxidation reactor for industrial park effluent treatment with COD decreasing from 154.7 to 58.8 mg/L, and the operating costs were $\$0.57$/ton and $\$5.94$/kg COD. The cost of Fe(II)-PS system in this study is slightly lower than the reported electro-oxidation method.

The single-factor experiment also yielded $S\text{F}_\text{opt}$ at PS/COD of 1.5, Fe(II)/PS of 1.2 and initial pH of 8.0, but the predicted $Y$ was only 11.8%. COD removal efficiencies under $\text{RSM}_\text{opt}$ and $S\text{F}_\text{opt}$ were checked experimentally and resulted in 55.0% and 12.1% $Y$. The low relative deviation (2.5% and 1.1%) between the predicted and experimental results verified the validity of the response model and the existence of an optimal point.

**Spectrum analysis for the optimized Fe(II)-PS system**

**UV-vis spectrum analysis**

The change in UV-vis spectrum of the effluent samples after Fe(II)-PS treatment is shown in Figure 3. The remaining

<table>
<thead>
<tr>
<th>Item</th>
<th>Mean square</th>
<th>$F$-value</th>
<th>$p$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>212.3</td>
<td>7.7</td>
<td>0.0068</td>
</tr>
<tr>
<td>A: PS/COD</td>
<td>1,013.7</td>
<td>36.6</td>
<td>0.0005</td>
</tr>
<tr>
<td>B: Fe(II)/PS</td>
<td>48.7</td>
<td>1.8</td>
<td>0.2262</td>
</tr>
<tr>
<td>C: pH</td>
<td>195.4</td>
<td>7.1</td>
<td>0.0326</td>
</tr>
<tr>
<td>AB</td>
<td>53</td>
<td>1.9</td>
<td>0.2088</td>
</tr>
<tr>
<td>AC</td>
<td>9.5</td>
<td>0.3</td>
<td>0.577</td>
</tr>
<tr>
<td>BC</td>
<td>28.7</td>
<td>1</td>
<td>0.3423</td>
</tr>
<tr>
<td>A$^2$</td>
<td>508.9</td>
<td>18.4</td>
<td>0.0036</td>
</tr>
<tr>
<td>B$^2$</td>
<td>2</td>
<td>0.1</td>
<td>0.7968</td>
</tr>
<tr>
<td>C$^2$</td>
<td>36.8</td>
<td>1.3</td>
<td>0.2869</td>
</tr>
<tr>
<td>Residual</td>
<td>27.7</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pure error</td>
<td>9.4</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>52.06</td>
<td>5.55</td>
<td>0.066</td>
</tr>
</tbody>
</table>
peaks at the UV-region after Fe(II)-PS treatment have shifted to lower wavelength, confirming the formation of more polar and less aromatic compounds (Azizi et al. 2015). The absorbance ratio $A_{254}/A_{365}$ reflects molecular weight distributions of DOM, with higher ratio indicating smaller molecules in DOM (Peuravuori & Pihlaja 1991). The $A_{254}/A_{365}$ ratios of raw effluent, SF$_{opt}$ and RSM$_{opt}$ were 2.86, 3.70 and 6.91, respectively. The greatly higher $A_{254}/A_{365}$ in RSM$_{opt}$ indicated that Fe(II)-PS treatment effectively degraded macromolecules into small ones after RSM optimization. UV absorbance at 254 nm (UV$_{254}$) represents an index of humic content in DOM, while $A_{300}/A_{400}$ reflects humification degree of DOM, with higher ratio indicating lower humification (Li et al. 2014). The RSM$_{opt}$ obtained greatly higher UV$_{254}$ removal (71.2%) than did SF$_{opt}$ (23.1%), while $A_{300}/A_{400}$ ratios of raw effluent, SF$_{opt}$ and RSM$_{opt}$ were 2.28, 3.90 and 7.65, respectively. These results indicated that SO$_4^{\cdot}$ generated by PS could decrease humification degree of DOM in the effluent from the industrial park WWTP. The results also showed that RSM optimization greatly improved the oxidation ability of the Fe(II)-PS system.

**Three-dimensional fluorescence analysis**

Typical EEM fluorescence spectra and their corresponding fractions extracted from the raw effluent and effluent treated with Fe(II)-PS are shown in Figure 4. The raw and treated effluents under SF$_{opt}$ were both diluted five times for EEM analysis. As shown in Figure 4(a) and 4(b), four fluorescent peaks identified from fluorescence spectra of DOM were located at Ex/Em of 245/(360–365), 285/(350–355), (280–285)/425 and (320–325)/(415–425) nm, which were related to aromatic protein (Peak A), tryptophan protein (Peak B), fulvic (Peak C), and humic (Peak D) substances (Chen et al. 2005; Ren et al. 2015; Zhou et al. 2015). Compared to raw effluent, fluorescence intensities (FI) of Peak B, C and D decreased by 43.4%, 34.2% and 33.6% in DOM from samples of SF$_{opt}$, while FI of Peak A was almost unchanged. In the undiluted sample of RSM$_{opt}$ (Figure 4(c)), only two fluorescent peaks were identified.
and located at Ex/Em of 280/380 and 355/435 nm, which were related to tryptophan protein (Peak E) and humic (Peak F) substances. The results suggested that aromatic protein and fulvic substances were fully decomposed by the Fe(II)-PS treatment. Peak E was red-shifted in emission wavelength in comparison to Peak B. Compared to Peak D in raw effluent, the peak F in RSMopt was red-shifted in both excitation and emission wavelengths. The results suggested that, although some complicated aromatics could not be decomposed by Fe(II)-PS treatment, they were oxidized by the SO₄²⁻ with the carbonyl and carboxyl groups bound on the aromatic structure (Wei et al. 2015).

**CONCLUSION**

This study showed that Fe(II)-PS system is effective (COD reduced to <80 mg/L) in COD removal from effluent of an industrial park WWTP. Applying RSM to investigate the Fe(II)-PS AOP revealed that PS/COD was the most dominant factor with positive influence on COD removal, followed by initial pH value. The optimum conditions with COD removal of 54.4% were obtained at PS/COD of 2.2, initial pH of 6.47 and Fe(II)/PS of 1.89. Fe(II)-PS process effectively degraded macromolecules in DOM into small ones after RSM optimization, and decreased humification degree of the effluent. Three-dimensional fluorescence analysis showed that aromatic protein and fulvic substances were fully decomposed by the Fe(II)-PS treatment.

**REFERENCES**


![Figure 4](https://iwaponline.com/wst/article-pdf/74/2/535/461098/wst074020535.pdf)


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