Ultraviolet-catalyzed persulfate degradation of cellulosic ethanol wastewater

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ABSTRACT

To study environmental pollution problems, the effects of advanced treatment by an ultraviolet (UV) system, a persulfate (PS) system, and an ultraviolet/persulfate (UV/PS) system on cellulosic ethanol wastewater were compared. The results showed that the UV/PS system had the best removal efficiency. When the reaction temperature was 50°C, the initial pH was 6, the dosing of PS was 10 g/L, and the reaction time was 20 h. The maximum removal rate of chemical oxygen demand (COD) was 94.16%, and the effluent COD concentration was 39.6 mg/L. The removal capacity of the system was in accordance with the primary reaction’s kinetic equation. In addition, an optimization analysis of the composite system–degradation of cellulosic-ethanol-reduction in wastewater with alkali + UV-activated persulfate–was conducted. The results showed that the optimum reaction conditions were temperature of 50°C, NaOH dosage of 2 g/L, pH of 6, PS dosage of 6 g/L, and reaction time of 20 h. Under these conditions, the maximum COD removal rate was 97.59%, and the discharge standard of cellulosic ethanol wastewater was met. Therefore, this study can provide a reference for the treatment of cellulosic ethanol wastewater.

Keywords: UV; Persulfate; Cellulosic ethanol wastewater; Chemical oxygen demand; Dynamics; Advanced oxidation

1. Introduction

With the increasing severity of energy forms worldwide and the increasing maturity of cellulose-based substances for ethanol fuel production, the resulting wastewater problems are becoming increasingly serious [1–3]. Wastewater containing cellulosic ethanol is characterized by high salinity, strong acidity, strong discoloration, high turbidity, and pungent odor, which are typical for high concentrations, making it difficult to degrade industrial organic wastewater [4–6]. Therefore, the degradation of cellulose-based substances in wastewater became the key to treating wastewater containing cellulosic ethanol [7,8]. There is insufficient research on this type of wastewater treatment, both domestically and abroad, and the main treatment technology is still based on pretreatment and a biological method [9–13].

At present, the most cost-effective method is to use an appropriate pretreatment followed by an anaerobic–aerobic biological treatment; however, through this method, it is difficult to meet the discharge standard. In addition, after multi-stage biological treatment, the biochemical properties of wastewater were also significantly reduced, and the cost of subsequent deep treatment was high [14–18]. For example, Hu et al. [19] treated cellulosic ethanol wastewater with ozone oxidation and the final chemical oxygen demand (COD) degradation obtained was only 35%.

As advanced oxidation processes (AOPs) mature, they hold great potential for the decomposition and mineralization of organic pollutants [20]. AOPs use persulphate oxidants to generate sulfate radicals, which can mineralize refractory organic matter into CO₂ and H₂O, thereby increasing the removal rate of refractory organic matter from...
biochemical effluents. Currently, AOPs are mainly divided into hydroxyl radical-based (•OH) advanced oxidation processes (HR-AOPs) and sulfate radical-based (SO4•−) advanced oxidation processes (SR-AOPs). Compared to HR-AOPs, SR-AOPs have the advantages of a wide pH range, a wide range of degradable pollutants, and a low level of pollution to the environment [21–23]. In addition, the SO4•− radicals produced by SR-AOPs have a high redox potential ($E_0 = 2.5$–$3.1$ V) and are able to remove most organic pollutants from water at high rates. SR-AOPs also have higher selectivity and a longer half-life while allowing a longer contact time between SO4•− and pollutants, increasing the degree of pollutant degradation [24]. In SR-AOPs, persulfate (S2O82−) is a commonly used and efficient oxidant. One mol of persulfate can form 2 mol of SO4•− radicals under UV, thermal, alkali, and metal activation conditions. Qi et al. [25] used microwave radiation to activate peroxide monosulfate in order to degrade organic matter, and the results showed that sulfate had a positive effect on the degradation efficiency of BPA. In addition, the photogenerated electrons (e−) and photogenerated holes (h+) due to the excited photocatalyst decomposed persulfate into SO4•− radicals, enhancing the removal of organic pollutants from wastewater [26]. Ou et al. [27] used UV irradiation to degrade tris(2-chloroethyl) phosphate by decomposing persulfate into SO4•− radicals. The research found that UV/PS had a high conversion efficiency for the selective electron transfer reactions of the three main intermediates and was significant in the removal of tris(2-chloroethyl) phosphate from wastewater. The results showed that UV/PS had the advantages of low cost, stable performance, and free radical efficiency [28].

Therefore, this paper investigated the formulated cellulosic ethanol wastewater using UV/PS. The treatment characteristics of the UV-activated persulfate system were investigated, and a single-factor test was conducted for five reaction conditions: reaction system type, reaction temperature, initial pH, persulfate dosing amount, and reaction time. The optimal reaction conditions for the degradation of cellulosic ethanol wastewater by a UV/PS system were determined, and the experimental data were analyzed by the proposed first-order reaction kinetics [29]. An optimization analysis of the composite conditions was also conducted.

### 2. Experimental materials and methods

#### 2.1. Experimental water

Reduction wastewater was prepared according to the composition of main organic matter in cellulosic ethanol wastewater (Table 1).

#### 2.2. Experimental equipment

As shown in Fig. 1, the UV irradiation device was placed above the UV lamp in a box. During the experimental process, the working wavelength of UV light was 254 nm directly through a vertical light path to the surface of the water samples, which were placed directly below the light cylinder and stirred with a magnetic stirrer. During the experiment, the whole process was shaded to prevent the leakage of UV light.

#### 2.3. Experimental methods

COD was analyzed by rapid closed catalytic digestion method with a thermostatic digestion instrument. UV absorbance at 420 nm was measured by UV spectrophotometry with an ultraviolet visible spectrophotometer.

The analytical methods for COD was tested according to the Monitoring and Analysis Methods for Water and Wastewater [30].

#### 2.4. Optimization of treatment conditions for cellulosic ethanol wastewater

The effects of the reaction system type, reaction temperature, initial pH, persulfate dosing, and reaction time on the degradation of cellulosic ethanol-reduction wastewater were analyzed. Water was sampled at 4-h intervals over the 24-h reaction and was measured to determine the optimal reaction conditions.

#### 2.4.1. Optimization analysis

Reaction system: Three different systems were used: UV, persulfate, and UV/PS at a reaction temperature of 30°C and PS dosing of 10 g/L.

### Table 1

Main organic composition of cellulose ethanol wastewater

<table>
<thead>
<tr>
<th>Analyze the project</th>
<th>Molecular formula</th>
<th>Detection value (mass fraction)/%</th>
<th>Percentage of total COD/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td>/</td>
<td>0.156</td>
<td>2.43</td>
</tr>
<tr>
<td>Fibrous disaccharides</td>
<td>C12H18O11</td>
<td>0.111</td>
<td>1.70</td>
</tr>
<tr>
<td>Glucose</td>
<td>C6H12O6</td>
<td>0.0085</td>
<td>0.13</td>
</tr>
<tr>
<td>Xylose</td>
<td>C5H10O5</td>
<td>0.249</td>
<td>3.90</td>
</tr>
<tr>
<td>Formic acid</td>
<td>CH2O2</td>
<td>0.904</td>
<td>14.20</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>C2H4O2</td>
<td>1.104</td>
<td>17.40</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>C3H6O3</td>
<td>2.081</td>
<td>32.70</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>C3H6O2</td>
<td>0.013</td>
<td>0.20</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C2H5O2</td>
<td>0.261</td>
<td>4.10</td>
</tr>
<tr>
<td>Furfural</td>
<td>C5H4O2</td>
<td>0.009</td>
<td>0.14</td>
</tr>
<tr>
<td>5-Hydroxymethylfurfural</td>
<td>C6H10O3</td>
<td>0.007</td>
<td>0.11</td>
</tr>
</tbody>
</table>
Reaction temperature: Three different reaction temperatures were used: 30°C, 40°C and 50°C at the optimal reaction system and PS dosing of 10 g/L.

Initial pH: Five different initial pHs were used: 3, 4, 5, 6 and 7 at the optimal reaction system and reaction temperature. The dosing of PS was 10 g/L.

Persulfate dosage: Three different PS doses were taken: 5, 10, and 15 g/L at the optimal reaction system, reaction temperature, and optimal initial pH.

Reaction time: Water samples obtained every 4 h were measured under optimal reaction system, reaction temperature, initial pH, and PS dosing conditions.

2.4.2. Mathematical analysis

A reaction kinetic analysis of the treatment effect of cellulosic-ethanol-reduction in wastewater was carried out according to four influencing factors, namely, reaction systems, reaction temperatures, initial pH values, and persulfate dosage. The kinetic equation for the degradation of cellulosic-ethanol-reduction in wastewater through a persulfate-advanced oxidation system was established according to the kinetic equation, as shown in Eq. (1) [31].

\[
\ln \left( \frac{C}{C_0} \right) = a + bx
\]

where \( C \) – effluent COD concentration; \( C_0 \) – inlet water COD concentration; \( b \) – the kinetic constant of the proposed primary reaction.

2.4.3. Composite system optimization analysis

- Based on the optimal reaction system, temperature, initial pH, and persulfate dosing, three alkali activators (5 g/L of NaOH, CaCO3, and CaO) were added to determine the optimal alkali activator.
- Based on the optimal reaction system, temperature, initial pH, and persulfate dosage, the following concentrations of optimal alkali activator were added: 2, 5, 10, 15 and 20 g/L during the 24-h continuous experiments.

3. Results and discussion

3.1. Characterization of cellulose ethanol reduction wastewater treatment under UV/PS system

3.1.1. Effect of different systems on wastewater degradation

The effects of the UV system, the PS system, and the UV/PS system on the degradation of cellulosic-ethanol-reduction in wastewater were studied, and the results are shown in Fig. 2. All three systems had a good degradation effect on the reduced wastewater. The final COD degradation rates for the UV, PS, and UV/PS systems were 48.80% (UV/PS system), 42.51% (UV system), and 43.86% (PS system), respectively. The best degradation system was that with UV/PS, and the residual amount of peroxysulfate in the solution was 1.55 g/L after 24 h of reaction. The concentration of COD in the solution also decreased from the initial 702.54 to 359.68 mg/L because the wastewater contained organic acids that were easily degradable, in addition to lignin, cellobiose, and xylene, which were difficult to degrade. The degradation of large molecules into small molecules accelerated the degradation of cellulosic-ethanol-reduction in wastewater [32].

From an economic point of view, the cost of electricity consumed by UV and UV/PS fouling at different times was also evaluated. The electric energy (EE/O) value of each order is used as the index. EE/O was calculated using Eq. (2). The detailed steps of the calculation method are shown in the literature [33]. Finally, the EE/O values of UV and UV/PS were calculated (Table 2). As can be seen from the table, the energy consumption of COD degradation in the UV/PS system was lower than that in the UV system. Thus, the UV/PS system produces stronger, more diversified oxidants and consumes less electric energy [34].

\[
\frac{EE}{O} = \frac{P \times T \times 1,000}{V \times \log \left( \frac{C}{C_f} \right)}
\]
3.1.2. Effect of reaction temperature on wastewater degradation

Three temperatures variables were set at 30°C, 40°C and 50°C under the UV/PS system. The initial pH was not adjusted, and the persulfate dosing was 10 g/L for 24 h during the continuous experiment. The results are shown in Fig. 3. When the temperature was 30°C, the COD removal rate was 70.98%. When the temperature was increased to 40°C, the COD removal rate increased to 73.68%. When the temperature continued to increase to 50°C, the COD concentration was 67.65 mg/L, and the removal rate was 90.47%. The degradation rate of cellulosic ethanol wastewater increased with an increase in temperature. In addition, the higher the temperature, the lower is the residual amount of persulfate in the system and the better is the degradation of wastewater. Thermal activation occurs in the system when the temperature increases. The higher the reaction temperature, the greater the activation of persulfate and the more SO₄⁻• was generated, which could enhance the degradation of pollutants [35].

3.1.3. Effect of initial pH on wastewater degradation

In the UV/PS system, the reaction temperature was 50°C, and the amount of peroxynitrite was 10 g/L. Five groups of variables were set for 3, 4, 5, 6, 7, and 24-h continuous experiments. The results are shown in Fig. 4. With an increased initial pH, the utilization of persulfate and COD degradation rate under the UV/PS system showed a trend of increasing and then decreasing. The COD degradation rates were 61.65% (pH = 3), 67.36% (pH = 4), 77.16% (pH = 5), 100% (pH = 6) 82.05% (pH = 7), respectively. The UV/PS degradation of cellulosic-ethanol-reduction in wastewater was the best at an initial pH of 6. The solution COD concentration decreased from the initial 630.58 to 0 mg/L, and all the substances in the solution degraded. This is the same as the results of Hakim's experiments, where neutral conditions had a more favorable pH than acidic ones [36]. However, when the pH was decreased below 3, the degradation rate decreased instead, likely due to the conversion of persulfate to HS₂O₈⁻ in the system, which reduces the free radicals generated by activation. Further lowering the pH led to the reaction of PS with SO₄²⁻ and H⁺, which resulted in a lower SO₄²⁻ yield [37]. In addition, excess hydrogen ions can adversely affect AOPs by scavenging sulfate radicals [Eq. (3)]. Strong acid conditions can also inhibit the production of sulfate radicals via acid-catalyzed persulfate [Eqs. (4) and (5)]. This results in less effective degradation [38].

\[
\text{SO}_4^{2-} + \text{H}^+ + e^- \rightarrow \text{HSO}_4^- \quad (3)
\]

\[
\text{H}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow \text{HS}_2\text{O}_6^- \quad (4)
\]

\[
\text{HS}_2\text{O}_6^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{HSO}_4^- \quad (5)
\]

3.1.4. Effect of persulfate addition on wastewater degradation

In the UV/PS system, the reaction temperature was 50°C, the initial pH was 6, and the persulfate doses were set at 5, 10, and 15 g/L for 24 h (Fig. 5). The COD degradation rate increased significantly from 70.35% to 96.34% when the persulfate dosage was increased from 5 to 10 g/L. This may be because the 5 g/L dosage was not enough to...
Fig. 3. Effect of reaction temperature on wastewater degradation.

Fig. 4. Effect of initial pH on wastewater degradation.

Fig. 5. Effect of persulfate addition on wastewater degradation.
degrade the cellulosic-ethanol-reduction in wastewater. However, PS acts as the main donor for \( \text{SO}_4^{2-} \) generation, and the higher the PS concentration, the higher the \( \text{SO}_4^{2-} \) generation, the higher its steady-state concentration, and the higher the amount of \( \text{SO}_4^{2-} \) in contact with the reaction per unit volume, which is favorable for degradation [39]. The COD degradation rate decreased to 91.25% when continuing to increase the amount of persulfate dosing to 15 g/L. This could be due to the sharp increase in \( \text{SO}_4^{2-} \) production at a high PS concentration. Excess PS depleted the concentration, leading to a decrease in the concentration within the system, a weakening of the system’s oxidation capacity, and a decrease in the degradation rate [40].

3.1.5. Effect of reaction time on wastewater degradation

In the UV/PS system, the reaction temperature was 50°C, the initial pH was 6, the peroxysulfate dosage was 10 g/L, and it was a continuous reaction for 24 h (Fig. 6). The fastest reduction of persulfate content in the solution was observed from 16 to 20 h. At 20 h of reaction, the residual amount of persulfate in the solution was 0 g/L, indicating that at this time, all the persulfate in the solution had been utilized for conversion into sulfate radicals that participated in the treatment of cellulosic ethanol wastewater. The COD concentration in the solution was 39.6 mg/L, and the COD degradation rate was 94.16%. This is the same result as Bu’s study, where an increase in light duration stimulated the production of more reactive radicals, thus increasing the removal rate [41]. However, the degradation effect was slow because the UV lamp was mainly involved in wastewater degradation from 20 to 24 h.

In summary, the best reaction system for degrading cellulosic ethanol wastewater was the UV/PS system with an optimal reaction temperature of 50°C, an optimal initial pH of 6, an optimal persulfate dosage of 10 g/L, and an optimal reaction time of 20 h. The COD degradation rate was 94.16%. Under optimal conditions, the EE/O value of UV/PS decontamination was at a 162.12 kWh/m³·order. This indicates that the UV/PS process is cost effective in terms of EE/O.

3.2. Reaction kinetic analysis of UV/PS system

3.2.1. Kinetic analysis of the reaction under different systems

The fitted curves for the different reaction systems are shown in Fig. 7. The reaction rate constants for UV, PS, and UV/PS were 0.22607, 0.25606 and 0.27243 h⁻¹, respectively. All three systems contributed to the degradation of the organic matter in the treated cellulosic ethanol wastewater, but the UV/PS system had the largest effect.

3.2.2. Analysis of reaction kinetics at different temperatures

The fitted curves for the different reaction temperatures are shown in Fig. 8. The reaction rate constant at 30°C, 40°C and 50°C were 0.16395, 0.24437 and 0.07472 h⁻¹, respectively. The degradation of cellulosic ethanol wastewater using the UV/PS system gradually increased with an increase in reaction temperature, which was the same conclusion obtained by the COD degradation rate in solution. Thus, it
is clear that the degradation of organic matter in cellulosic ethanol-reduced wastewater was better promoted by the UV/PS system at 50°C.

### 3.2.3. Kinetic analysis of the reaction at different initial pH levels

The fitted curves for the different initial pH are shown in Fig. 9. As shown in Fig. 9, at a pH of 3, 4, 5, 6, and 7, the reaction rate constants were 0.18177, 0.3778, 0.28068, 0.20516, and 0.4227 h⁻¹, respectively. In addition, it was found that the degradation effect at different initial pH levels was in accordance with the kinetic equation of the proposed primary reaction, and the best degradation effect was found at an initial pH of 6.

### 3.2.4. Reaction kinetics analysis under different persulfate dosage

The fitted curves for the different persulfate doses are shown in Fig. 9. The reaction rate constants were 0.59461, 0.1903, and 0.27082 h⁻¹ when the amount of persulfate added was 5, 10, and 15 g/L, respectively. The best degradation effect was achieved when 10 g/L of persulfate was added.

### 3.3. Compound system optimization experiment

#### 3.3.1. Effect of alkali activator type on the treatment effect of the composite system

To investigate whether different alkali activators would have an effect on the degradation of cellulosic ethanol wastewater using the UV/PS system, the same concentration (5 g/L) of NaOH, CaCO₃, and CaO solids were added to the UV/PS system for the degradation of cellulosic ethanol wastewater under optimal reaction conditions after 24 h of reaction. The results are shown in Fig. 10. When the alkali activator was NaOH, the degradation rate of COD reached 60.48% and the COD concentration was 67.22 mg/L. When the alkali activator was Ca(OH)₂, the degradation rate of COD reached 52.43%. When the alkali activator was CaO, the degradation rate of COD reached 49.54%. This was the same as the results of Boczkaj and Fernandes [42], which favors the efficiency of the process when NaOH was the activator.

#### 3.3.2. Effect of alkali dosage on the treatment effect of the composite system

After obtaining the optimal alkali activator as NaOH, the effect of NaOH dosage on the degradation of cellulosic ethanol wastewater was investigated further by adding 2, 5, 10, 15, and 20 g/L of sodium hydroxide solids to the optimal system, and the results were obtained after 24 h of continuous reaction as shown in Fig. 11. When the NaOH dosage was 20 g/L, the COD degradation rate was 91.71%. When the NaOH dosage was 10 g/L, the COD degradation rate was 88.04%, and when the NaOH dosage was 2 g/L, the COD degradation rate was 87.31%. Although the degradation efficiency...
was not as high as that of 10 and 20 g/L, the amount of alkali activator and persulfate required was lower, and the treatment effect was similar. Therefore, the degradation of cellulose ethanol-reduced wastewater was better with 2 g/L. The experiments of Zhang et al. [43] also showed that the degradation rate of the wastewater was better at the alkali dosing level of 1.2 g/L. This indicates that these pollutants can be converted to less toxic substances under alkaline conditions.

Fig. 11. Effect of the type of alkali activator on the treatment effect of the composite system.

Fig. 12. Effect of alkali dosage on the treatment effect of the composite system.

Fig. 13. Effect of alkali activators at specific persulfate dosing levels.
As the peroxynitrite in the system had not completely reacted and nearly half the peroxynitrite dosage remained, the reaction time was prolonged by 4 h compared with that of the UV/PS system. The effect of NaOH dosage on the degradation of cellulose ethanol-reduced wastewater was investigated by the composite system when the peroxynitrite dosage = 6 g/L.

3.3.3. Effect of alkali activators at specific persulfate dosing levels

In the UV/PS system, the reaction temperature was 50°C, the initial pH was 6, the peroxynitrite dosing was 6 g/L, and the NaOH dosing was 2, 10, and 20 g/L. The results of the composite system optimization experiments are shown in Fig. 12. The ranking of the alkali dosage effect on the COD degradation rate of the lignin solution was: 2 > 10 > 20 g/L. When the dosage of the alkali activator was 2 g/L, the COD concentration of effluent decreased to 0 mg/L, and the COD degradation rate reached 100%. When the dosage of the alkali activator was 10 g/L, the COD degradation rate was 98.34%. When the alkali activator dosage was 20 g/L, the COD degradation rate was 97.59%.

In summary, in the alkali + UV-activated persulfate degradation of cellulose ethanol wastewater systems, the optimal reaction conditions were NaOH dosage of 2 g/L, a reaction temperature of 50°C, an initial pH of 6, a persulfate dosage of 6 g/L, and reaction time of 20 h. The COD degradation rate was 97.59%. By adding a small amount of alkali activator, the amount of persulfate used was reduced, and a very satisfactory degradation effect was also achieved.

4. Conclusion

The optimal reaction conditions of the UV/PS system were determined by experiments. The maximum degradation rate of COD was 94.16% at the optimum conditions of 50°C, initial pH of 6, peroxynitrite dosage of 10 g/L and reaction time of 20 h. The effects of temperature, pH and dosage on the reaction system were investigated, and it was confirmed that the COD removal capacity of the system was in accordance with the pseudo primary kinetic equation. And the compound conditions were optimized, and the best reaction conditions were obtained as follows: NaOH dosage = 2 g/L, reaction temperature = 50°C, initial pH = 6, peroxynitrite dosage = 6 g/L, and reaction time of 20 h. The final COD degradation rate was 97.59%. The effluent concentration was 12.84 mg/L, which could meet the discharge standard of cellulose ethanol wastewater. And it provided a more reasonable and effective solution for the treatment of cellulose ethanol wastewater.

Disclosures and declarations

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Author contributions

All authors contributed to the study conception and design. The formulation of the overall research goals and objectives was written by Likun Huang and Guangzhi Wang. Material preparation, data collection and analysis were performed by Jingfu Han, Zhe Li and Yuanyuan Xu. The first draft of the manuscript was written by Yue Hou and all authors commented on previous versions of the manuscript.

Availability of data and materials

Data and materials will be made available on reasonable request.

Authorship clarified

All authors have agreed to participate and all have explicitly agreed to submit.

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