Electro-photocatalytic degradation of amoxicillin using calcium titanate

Abstract: The electro-photocatalytic degradation of amoxicillin in aqueous solution was investigated using a single factor test by the potassium permanganate method for measuring the values of chemical oxygen demand (COD_{me}). Batch experiments were carried out successfully under different conditions, including initial amoxicillin concentration, calcium titanate dosage, pH, UV irradiation time, electrolyte and temperature. The experimental results show that there is a great difference between electro-photocatalytic and photocatalytic degradation. The maximum electro-photocatalytic degradation efficiency can increase to 79% under the experimental conditions of 200 mL amoxicillin solution (100 mg L^{-1}) with 0.5 g calcium titanate by pH=3 for 120 min irradiation and 0.058 g sodium chloride as electrolyte at 318.5 K. In addition, the reaction rate constant of 0.00848–0.01349 min^{-1}, activation energy of 9.8934 kJ mol^{-1} and the pre-exponential factor of 0.5728 were obtained based on kinetics studies, indicating that the electro-photocatalytic reaction approximately followed the first-order kinetics model.

Keywords: Electro-photocatalytic; Amoxicillin; Calcium titanate; Kinetics; Degradation.

1 Introduction

In recent years, more and more experts have called for the banning of the abuse of antibiotics due to seriously endangering the environment and endangering human health. Various antibiotics are detected in the medical wastewater, surface water, groundwater worldwide, and even in the drinking water [1–3]. Therefore, much attention has been focused on the research of antibiotic compounds in the environment, and methods for their treatment [4].

Amoxicillin is a commonly used β-lactam antibiotic, which is widely applied in medical, animal husbandry, aquaculture and other fields [5]. It is reported that amoxicillin has been analyzed in different water samples from different regions and countries [6]. Since the 1940s, many methods such as adsorption, precipitation, oxidation and microbial degradation were explored for antibiotic waste water treatment by researchers [7]. At present, light or electricity-assisted degradation methods are commonly used based on the advanced oxidation reaction. Rosenfeldt [8] proposed that providing ultraviolet light during antibiotics degradation using hydrogen peroxide can effectively increase the degradation ratio of antibiotics. Comparing with Fenton-like and Fenton methods on the removal of penicillin in dark and light conditions, advanced oxidation turned out to be an effective method for reducing the chemical oxygen demand in aqueous solution. When light is supplemented, extending processing time can continue to improve the degradation effect [9,10]. In 2016, a research was undertaken applying power with various current densities to the levofloxacin aqueous solution, and the content of levofloxacin effectively decreased by electro-Fenton method [11]. Light and electricity have played extremely important roles in the degradation of antibiotics, and have an extremely important role confirmed in lots of reports. Therefore, photocatalysis is an effective method used for degradation of antibiotics, until now, which
is primarily concerned with designing novel catalysts. The titanium dioxide (TiO₂), zinc oxide (ZnO), cadmium sulfide (CdS) and ferric oxide (Fe₂O₃) were commonly used as catalyst in amoxicillin photocatalytic degradation process [12]. Considering the limited performance for pure catalysts, researchers modified the photocatalyst by various ways, such as loading metal, inorganic salts and even organic matter [13-15]. In addition to modifying the developed catalysts, researchers have also explored other new catalysts, especially calcium titanate as a promising catalyst.

Calcium titanate with octahedral groups as basic structural unit is a typical perovskite type photocatalyst. The band gap of calcium titanate is 3.5eV higher than that of TiO₂ (3.2eV), showing the potential excellent catalytic performance in theory [16]. In recent years, a great number of researchers in various countries have begun to use pure or modified calcium titanate involving loaded metal and metal oxide for improving photodegradation of water, and several decent results are obtained [17-20]. However, how to realize the antibiotics degradation is still difficult by using calcium titanate, and the related reports are few. In this work, the amoxicillin degradation by calcium titanate in aqueous solution was studied by single factor experiment under UV irradiation with various current densities. Meanwhile, an extension study of application based on calcium titanate would be analyzed in this work, and more useful information could be provided for the kinetic study of amoxicillin degradation.

The 500 mL beaker with a magnetic stirring bar and under an illumination of 15 W UV lamp (Sitong, China) is taken as the photocatalytic reactor. In some cases, it is necessary to provide power supply to energize in aqueous solution. For each degradation experiment, various amounts of calcium titanate were added into 200 mL amoxicillin solution. PH was adjusted by H₂SO₄ and NaOH solutions and monitored by INESA PHS-3E pH meter (China). The suspension was agitated by magnetic stirring for 30min under dark conditions, and then irradiated by UV lamp. Amoxicillin concentrations, calcium titanate dosage, pH, UV irradiation time, electrolyte and temperature were optimized according to the values proposed in experimental design. After each experiment, the test solution was withdrawn and separated by a high speed centrifuge (Feige TGL-16GB, China) at 8000 r/min for 10 min.

In the course of experiment, the values of chemical oxygen demand (CODₜₐₙ) for various test solutions were measured according to potassium permanganate method [21]. The working curve of amoxicillin standard solutions is [CODₜₐₙ]=668.91c+5.1268, R²=0.9992, where [CODₜₐₙ] is the concentration of (mg L⁻¹) in test solution, and c (mg L⁻¹) is amoxicillin standard solution concentration from 0 mg L⁻¹ to 300mg L⁻¹.

The degradation efficiency of each test was calculated based on the following expression (Eq. (1)):

\[ \eta (%) = \frac{[\text{COD}_{\text{tini}}]_{\text{initial}} - [\text{COD}_{\text{tini}}]_{\text{final}}}{[\text{COD}_{\text{tini}}]_{\text{initial}}} \times 100 \]  

[CODₜₐₙ]_{initial} and [CODₜₐₙ]_{final} are the chemical oxygen demand values of the initial and final solutions respectively.

The degradation kinetics can usually be described by the zero-order, first-order and second-order kinetics models.

The reaction rate between amoxicillin concentration and time can be expressed by Eq. (2), Eq. (3) and Eq. (4), respectively.

\[ -r₀ = \frac{dc}{dt} = k₀ \]  

\[ -r₁ = \frac{dc}{dt} = k₁c \]  

\[ -r₂ = \frac{dc}{dt} = k₂c² \]  

Integrating between \( c = c₀ \) at \( t = 0 \) and \( c = c \) at \( t = t \), Eq. (2), (3) and (4) can be displayed as follows:

2 Experimental

Amoxicillin and calcium titanate (minimum 99.5%, 2μm) were purchased from Aladdin. And others were purchased from Chengdu Kelon Chemical Co., Ltd. Distilled water was used for the preparation of all test solutions.

An aqueous stock solution with 300 mg L⁻¹ amoxicillin was prepared. From this, calibration standards with concentrations of 1, 10, 20, 50, 100 and 200 mg L⁻¹ were prepared in distilled water before being filtered through 0.45mm nylon filter membranes from Jingteng (China). In order to eliminate the effect of calcium titanate self-adsorption, the adsorption experiment was carried out under dark conditions. In the adsorption process, the effect of initial amoxicillin concentrations of 100 and 300 mg L⁻¹ were investigated by batch experiments for a specific period of the contact time (0-300 min) at room temperature.
\[ c = c_0 - k_0 t \]  \hspace{1cm} (5)
\[ c = c_0 e^{k_1 t} \]  \hspace{1cm} (6)
\[ \frac{1}{c} = \frac{1}{c_0} + k_2 t \]  \hspace{1cm} (7)

\( c_0 \) and \( c \) are the concentrations of amoxicillin at initial and final testing, respectively (mg L\(^{-1}\)). \( k_0, k_1, k_2 \) are rate constants of the zero-order, first-order and second-order reaction respectively, \( t \) is irradiation time.

Assuming that the activation energy \( (E_a) \) of amoxicillin in the process of degradation is independent of temperature (\( T \)), the Arrhenius equation (Eq. (8) and (9)) can be used to calculate the activation energy \( (E_a) \) and the pre-exponential factor \( (A) \).

\[ k = A e^{\frac{-E_a}{RT}} \]  \hspace{1cm} (8)

or

\[ \ln k = \ln A - \frac{E_a}{R} \frac{1}{T} \]  \hspace{1cm} (9)

\( k \) is rate constants.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Adsorption of calcium titanate

Figure 1 shows the relationship of COD removal and adsorption time. It can be seen that at the first 30 min, the adsorption rate is very fast, and then changes slowly, ultimately to stabilize. And the COD removal is 1.3 and 1.9 mg L\(^{-1}\) with equilibrium time of 90 min for 200 mL amoxicillin in 100 mg L\(^{-1}\) and 300 mg L\(^{-1}\) concentration respectively. Moreover, at the beginning, the surface of calcium titanate with enough vacant sites effectively absorb amoxicillin molecules, and the adsorption rate is very fast, but the mutual repulsive forces of amoxicillin molecules made adsorption rate slow down obviously when adsorption capacity was close to maximum value. Adsorption experiments also show that the effect of adsorption on degradation experiment is little, so that it could be neglected in determination of degradation efficiency.

3.2 Effect of amoxicillin initial concentration

Clearly, as displayed in Figure 2, there is the similar degradation efficiency for 200 mL amoxicillin with initial concentration of 100 mg L\(^{-1}\) and 300 mg L\(^{-1}\). It can be found the degradation efficiency is not varied from a range of 25%~30%, because the intermediate products were hardly degraged by photocatalytic process. This result was different from reported conclusion that amoxicillin could be degraded completely under photocatalytic conditions in aqueous solution [22]. The reason is that the degradation efficiency reported is calculated based on the
3.3 Effect of pH

PH is considered as a significant factor to affect photocatalyst and the substrate of amoxicillin. Batch experiments were carried out as pH varied from 3 to 10. Figure 3 shows the effect of pH on degradation efficiency for 200 mL 100 mg L\(^{-1}\) amoxicillin solution with 0.5g calcium titanate at room temperature with various irradiation times. As shown in Figure 3, the degradation efficiency is 32%, 21% and 16% as pH is in 3, 7 and 10 after 150 min irradiation, respectively. and the optimum pH for amoxicillin degradation is pH=3, and the degradation efficiency increases with the pH decreasing. There are two reasons can explaining this. One is the oxidation potential of hydroxyl radicals (•OH) decreasing with the pH increasing, leading to the weak attack ability to organic [24-25]. The other is that amoxicillin may be relatively stable in high pH environment.

3.4 Effect of calcium titanate dosage

The dosage of calcium titanate varied from 0.1 g to 1.0 g and irradiation time from 10 min to 150 min and has a significant impact on degradation efficiency clearly seen in Figure 4. The degradation efficiency will reach the maximum value after 120 min irradiation for all samples, and there a similar changing tendency for degradation efficiency with calcium titanate dosage and irradiation time, showing that the low dosage of calcium titanate is not good enough for amoxicillin degradation. Additionally, it also can be found that the degradation efficiency increases with dosage of calcium titanate increasing from 0.1 g to 1.0 g, and which changes slightly as calcium titanate dosage is more than 0.5g. Therefore, the calcium titanate dosage of 0.5 g adding in 200 mL 100 mg L\(^{-1}\) amoxicillin solution was chosen for evaluating other factors effect on degradation efficiency in the experiment process.

3.5 Effect of electrolyte

It was discovered that the maximum value of degradation efficiency for 200 mL 100 mg L\(^{-1}\) amoxicillin solution with 0.5 g calcium titanate by pH=3 is about 36% (see in Figure 4) under the irradiation condition without current intensity for the reaction system, indicating that the degradation efficiency is unsatisfactory for amoxicillin solution without current intensity. sodium sulfate and sodium chloride were used as electrolyte for evaluation.
of amoxicillin degradation with various current densities. The Cu is used as electrode is, and the current density is 0.03mA/cm². Figure 5 shows the relationship between degradation efficiency degradation efficiency for 200 mL 100 mg L⁻¹ amoxicillin solution with 0.5 g calcium titanate by pH=3 and current intensities at room temperature. The irradiation time is 120 min. The degradation efficiency of sample with 0.142 g sodium sulfate is up to 73% better than that of samples with 0.058 g sodium chloride as electrolyte (ca. 37%), which is approximate compared with the blank samples. It can be found that with current intensity increasing the degradation efficiency changes lightly, which agrees with reports by Tang [26]. Thus the applying power with current density for amoxicillin solution contributes to improving the amoxicillin degradation, when a suitable electrolyte was selected.

### 3.6 Effect of temperature

The temperature of the reaction system was essential to a successful experiment. In this work, the batch experiments were carried out with the temperature range from 283.5 K to 318.5 K. as presented in Figure 6, the degradation efficiency increased with increasing temperature, indicating that the higher temperature is beneficial for amoxicillin degradation. The degradation efficiency will reach to 79% as temperature is controlled at 318.5 K at 120 min irradiation time with the current intensity in 0.03 mA cm². It is worth mentioning that the degradation efficiency has slightly decreased with irradiation time continuing to increasing more than 120 min, maybe this due to some intermediates generated in the system were difficult to degradation.

### 3.7 Effect of the other factors

In order to prove the electro-photocatalytic efficiency, electrolytic degradation and photocatalytic degradation experiments for 200mL 100 mg L⁻¹ amoxicillin solution with 0.5 g calcium titanate and 0.058 g sodium chloride by pH=3 in various irradiation time with current intensity in 0.03mA cm².

![Figure 5: The effect of electrolyte on degradation efficiency for 200 mL 100 mg L⁻¹ amoxicillin solution with 0.5 g calcium titanate by pH=3 with different current intensities at room temperature in 120 min irradiation time.](image)

![Figure 6: The effect of temperature on degradation efficiency for 200 mL 100 mg L⁻¹ amoxicillin solution with 0.5 g calcium titanate and 0.058 g sodium chloride by pH=3 in various irradiation time with current intensity in 0.03mA cm².](image)

**Table 1: Results of different degradation methods.**

<table>
<thead>
<tr>
<th>Method</th>
<th>Electrolysis Degradation</th>
<th>Photocatalytic Degradation</th>
<th>Electro-photocatalytic Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>57.3%</td>
<td>35.8%</td>
<td>79.1%</td>
</tr>
<tr>
<td>2</td>
<td>56.9%</td>
<td>36.3%</td>
<td>78.5%</td>
</tr>
<tr>
<td>3</td>
<td>57.7%</td>
<td>36.2%</td>
<td>78.7%</td>
</tr>
<tr>
<td>Average Value</td>
<td>57.3%</td>
<td>36.1%</td>
<td>78.8%</td>
</tr>
<tr>
<td>R</td>
<td>0.56%</td>
<td>0.39%</td>
<td>0.24%</td>
</tr>
</tbody>
</table>
Table 2: Kinetic parameters and modeling of amoxicillin electro-photocatalytic degradation at various temperatures.

<table>
<thead>
<tr>
<th>T/K</th>
<th>Zero-order kinetics</th>
<th>First-order kinetics</th>
<th>Second-order kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k_f (mg L⁻¹ min⁻¹)</td>
<td>R²</td>
<td>k (min⁻¹)</td>
</tr>
<tr>
<td>283.5</td>
<td>5.235×10⁻⁸</td>
<td>0.9687</td>
<td>0.00848</td>
</tr>
<tr>
<td>297.5</td>
<td>5.868×10⁻⁸</td>
<td>0.9529</td>
<td>0.01077</td>
</tr>
<tr>
<td>308.5</td>
<td>6.167×10⁻⁷</td>
<td>0.9454</td>
<td>0.01212</td>
</tr>
<tr>
<td>318.5</td>
<td>6.241×10⁻⁷</td>
<td>0.9045</td>
<td>0.01349</td>
</tr>
</tbody>
</table>

3.8 Kinetics of electro-photocatalytic degradation

To study the kinetics of electro-photocatalytic (0.03 mA cm⁻²) degradation of amoxicillin, experiments were conducted under optimum operating conditions that 0.5 g calcium titanate and 0.058 g sodium chloride were added into 200 mL 100 mg L⁻¹ amoxicillin solution by pH=3 for 120 min irradiation. The temperature controlled in the range of from 283.5K to 318.5K. The reaction rate constant (k) and correlation coefficient (R²) of zero-order of first-order and second-order reaction were calculated by equation (5), (6) and (7), respectively under different temperatures shown in Table 2. The results suggest that the electro-photocatalytic reaction approximately followed the first-order kinetics, the reaction rate constant is 0.00848–0.01349 min⁻¹, which are similar with the results reported in references [27] and [28]. Meanwhile, the linearity of the plots demonstrated in Figure 7 suggests that the fitting equation is y=−1899.97×0.5573, R²=0.9864. The activation energy 9.8934 kJ mol⁻¹ and the pre-exponential factor 0.5728 were calculated from equation (9).

4 Conclusion

In this work, the electro-photocatalytic degradation of amoxicillin in aqueous solution was demonstrated by using potassium permanganate method and analyzing values of chemical oxygen demand (COD_Mn). Firstly, the effect factors involving initial amoxicillin concentration, calcium titanate dosage, pH, UV irradiation time, electrolyte and temperature were studied to obtain the optimum operational conditions for amoxicillin degradation. The results show that the optimized degradation efficiency is about 36% with only irradiation, and up to 79% at 318.5K, when sodium chloride was added for amoxicillin electro-photocatalytic degradation. In addition, the kinetics of electro-photocatalytic amoxicillin degradation was studied at different temperature and irradiation time. The results display that the electro-photocatalytic reaction approximately follow the first-order kinetics. The reaction rate constant, activation energy and pre-exponential factor were 0.00848–0.01349 min⁻¹, 9.8934 kJ mol⁻¹ and 0.5728, respectively.

Acknowledgment: Financial support of the work by the Opening Project of Key Laboratory of Green Catalysis of Sichuan Institutes of Higher Education (Nos. LYJ1605, LZJ1803), the program projects funded of Sichuan University of Arts and Science (No. 2018SCL001Y), the opening project of Key Laboratories of Fine Chemicals and Surfactants in Sichuan Provincial Universities (Nos. 2018JXZ01, 2016JXZ03) and the Opening Project of Material Corrosion and Protection Key Laboratory of Sichuan Province (No. 2017CL02) were gratefully acknowledged.

Conflict of interest: Authors declare no conflict of interest.
References


