



Article

Study of the Degradation of Trimethoprim Using Photo-Fenton Oxidation Technology

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Abstract: Trimethoprim is one of the representative drugs within the pharmaceutical and personal care products (PPCPs) group. The photo-Fenton oxidation technology was used to degrade trimethoprim in wastewater and the extent of degradation was analyzed by using high-performance liquid chromatography, then experimentally obtained the optimal conditions. Analysis of the experimental data showed that, under the single-factor experimental conditions, the optimal conditions for degradation were a pH of 4, an H₂O₂ concentration of 3.0 mmol/L, an FeSO₄ concentration of 0.06 mmol/L, an initial trimethoprim concentration of 0.0689 mmol/L, and an ultraviolet (UV) intensity (UVA) of 12 mW/cm². The interaction of pH and the concentration of H₂O₂ and Fe²⁺ have been further explored, it was obtained the following response surface results through the central composite design experiment: pH = 4.56, H₂O₂ concentration = 0.09 mmol/L, and Fe²⁺ concentration = 0.09 mmol/L. Under these conditions, it can be obtained a degradation rate of 99.95% after 6 min. There were similar results for three sets of parallel experiments, indicating that these simulation conditions were feasible.

Keywords: photo-Fenton oxidation; trimethoprim; pharmaceutical and personal care products (PPCPs); advanced oxidation processes (AOPs)

1. Introduction

With the rapid development of the economy, the problem of environmental pollution became a major research focus. Pharmaceutical and personal care products (PPCPs) represent a type of environmental pollutant that has “subtle, potential, and cumulative impact” [1]. The content of PPCPs is very low in the natural environment as a whole, but it can be detected in water, soil, and the atmospheric environment [2]. PPCPs include a range of chemical substances; for example, there are currently about 4500 different types of medicines that are widely used in the prevention and treatment of various diseases. The main sources of PPCPs in the environment include the mass use of chemicals, human and animal excreta, and the residual material in PPCP production processes [3]. Although the concentration of PPCPs in the environment is very low in most cases, with the accumulation of organisms, the concentration of PPCPs will become increasingly larger over time, and ultimately will have a profound impact and irreversible effect on ecosystems [4]. PPCPs continuously flow into

the natural environment, leading to an upward trend in their residual environmental concentrations. Studies indicated that PPCPs have a certain potential physiological hazard to animals, plants, and microorganisms [5,6].

Advanced oxidation processes (AOPs) are a commonly used method for the treatment of PPCPs in water. The final product of the AOPs reaction is water, carbon dioxide, and inorganic ions, and there is no residual concentration of matter [7]. Fenton oxidation and photocatalytic oxidation were successfully applied for the removal of pharmaceutical compounds [8]. Various photocatalytic models were also applied to treat multifarious effluents which are commonly from various industries, including forest industry, agriculture, and municipal wastewater, such as the photocatalytic reactor with ultraviolet (UV) lamp module [9]. The photo-Fenton oxidation process, which combines ultraviolet radiation with a Fenton reagent, is widely used because of its excellent oxidation performance. The synergistic effect of UV on the Fenton system increases the rate of the whole reaction, reduces the dosage of the Fenton reagent, shortens the reaction time, and reduces the amount of sludge produced, which allows the organic matter to be better degraded and mineralized [10]. The main disadvantage of photo-Fenton technology is the need for removing the dissolved iron from the treated sewage. At present, after oxidation treatment, the wastewater is treated by alkalization to form insoluble $\text{Fe}(\text{OH})_3$, which is precipitated in the form of iron sludge [11,12].

Trimethoprim is a representative antibiotic within the PPCP group and one of the main pollutants in pharmaceutical wastewater, mainly used in synergistic antibacterial activities [13,14]. It is used individually in the treatment of respiratory tract infections, urinary tract infections, intestinal infections, and other diseases. The presence of trimethoprim in the environment, especially in water bodies, caused the emergence of bacteria that are resistant to antibiotics as a result of developing a resistance gene [15]. As a large amount of pharmaceutical wastewater containing trimethoprim is discharged into the aquatic environment, pollution with this chemical is becoming more and more serious. Trimethoprim was found in municipal wastewater treatment plants at concentrations of 2 mg/L and in surface waters at concentrations up to 0.48 mg/L [16,17]. The concentration is higher in pharmaceutical wastewater. Trimethoprim is one of the fourteen pharmaceuticals which were classified as “high risk” with hazard quotient (HQ) >10 in hospital wastewater; thus, it is necessary to remove trimethoprim from water bodies [18].

Trimethoprim is detected with high frequency in wastewater, indicating that conventional wastewater treatment processes do not effectively remove trimethoprim [19]. The photo-Fenton oxidation method was considered as a treatment with high efficiency [10]. According to References [20,21], during degradation, noxious nitrogen oxide (NO_x) species are released during the AOP treatment of trimethoprim with several N heteroatoms in its structure. However, it is lower than the concentration of nitrogen in the pollutant, and cannot be considered hazardous. Several oxidation by-products during the photo-Fenton treatment of trimethoprim are in low concentration, and cannot be considered hazardous either [15]. Furthermore, up to now, there is no reported study on the use of response surface methodology (RSM) to optimize the optimal conditions of photo-Fenton oxidation degradation of trimethoprim. In this paper, the design of experiments and RSM were used to study and optimize the conditions of the photo-Fenton oxidation degradation of trimethoprim (including pH; the concentration of Fe^{2+} , H_2O_2 , and trimethoprim; and UV intensity). Then, the degradation rate of trimethoprim using the photo-Fenton oxidation technology and the optimal conditions were also acquired.

2. Materials and Methods

2.1. Experimental Drugs

Trimethoprim is an antibacterial agent, with the typical form of a white or white crystalline powder, which is odorless, with a bitter taste. The molecular formula of trimethoprim is $\text{C}_{14}\text{H}_{18}\text{N}_4\text{O}_3$; it has a molecular weight of 290.32, and its chemical structure is shown in Figure 1.

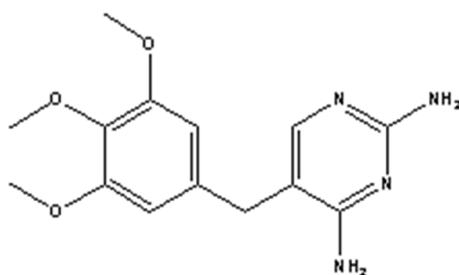


Figure 1. Trimethoprim chemical structure.

2.2. Reagents and Instruments

The main reagents of the experiment are listed below. Trimethoprim (JS14829) was purchased from Shanghai Jinsui Biotechnology Co., Ltd. (Shanghai, China). HPLC-grade CH₃OH was purchased from Tianjin Siyou Fine Chemicals Co., Ltd. (Tianjin, China). H₂O₂ was obtained from Jiangsu Tong Sheng Chemical Regent Co., Ltd. (Yixing, China). FeSO₄·7H₂O was purchased from Shantou Xilong chemical Co., Ltd. (Shantou, China). H₂SO₄ was obtained from Quzhou Juhua Reagent Co., Ltd. (Quzhou, China). HCOOH was purchased from Shanghai Chemical Regent General Co., Ltd. (Shanghai, China). H₂O₂, FeSO₄·7H₂O, H₂SO₄, and HCOOH used in the experiment were analytical pure grade.

All the glassware was rinsed and dried in a constant-temperature oven (DGG-9420, Ningbo's Science and Technology Co., Ltd., Ningbo, China). During the process of the experiment, Barnstead purification (MILLIQ, Millipore Company, Molsheim, France) was necessary. An electronic balance (AL-204, Shanghai Mettler-Toledo Instruments Co., Ltd., Shanghai, China), ultraviolet analyzer (ST510, Taiwan Xianchi Company, Taiwan, China), and ultraviolet lamp (Philips TL 8 W-08 FAM, Philips Corporation, Amsterdam, Holland) were also used throughout the process, as well as a pH Meter (MODEL6250C, Shanghai Ren's Electronics Co., Ltd., Shanghai, China), magnetic agitator (ET606, Lovibond Company, Düsseldorf, Germany), and high-performance liquid chromatograph (Type 2695 pump, PDA2996 type, Waters Corporation, Milford, MA, USA).

2.3. Experimental Method

2.3.1. Solution Preparation

To prepare the trimethoprim stock solution, 200 mg of trimethoprim powder was dissolved in ultrapure water. The medicine completely dissolved with the help of an ultrasonic cleaning machine. Then, the ultrapure water was used to maintain a constant volume in a 1-L volumetric flask. Then, 200 mg of solid FeSO₄·7H₂O was dissolved in the ultrapure water to prepare the FeSO₄ intermediate fluid. The ultrapure water was used to maintain a constant volume in a 1-L volumetric flask under acidic conditions. Next, 1 mL of 30% H₂O₂ was dissolved in a 100-mL volumetric flask to obtain the H₂O₂ intermediate fluid, and the resultant concentration of H₂O₂ was 0.1 mol/L. Finally, 0.5 mL of HCOOH was dissolved in a 100-mL volumetric flask to generate the HCOOH solution.

2.3.2. Experimental Apparatus

The 100-mL reaction solution was placed on a magnetic mixer. The magnetic mixer was helpful for mixing the reaction solution. The UV lamp with an iron bench was conveniently mobile, and emitted UVA light in the wavelength region 320–400 nm with $\lambda_{\max} = 360$ nm. The experimental device was arranged in a darkroom and outside interference was avoided to protect the subjects from UV irradiation experiments. Because different beaker positions may affect the degradation of trimethoprim, all degradation experiments were fixed in a position to prevent effects caused by the different location of the degradation.

2.3.3. Analytical Test Methods

In this experiment, the concentration after degradation was determined with the W2695 high-performance liquid chromatograph (Waters Corporation, Milford, MA, USA), with a photodiode array detector (PDA2996, Waters Corporation, Milford, MA, USA) and pillars (C18, Waters Corporation, Milford, MA, USA) [22]. Scanning the full wave band of 210–450nm, the mobile phase was 1% HCOOH:CH₃OH = 7:3. The flow rate was 1.0 mL/min, and the quantity of sampling was 10 µL. The Empower software was used to integrate the peak area, and the peak area ratio was used to calculate out the removal rate. The three-dimensional (3D) scan of trimethoprim showed that chromatography was a suitable method for trimethoprim purification and separation. According to the result, the maximum absorption wavelength of trimethoprim was 270.2 nm, which was used as the characteristic absorption peak of trimethoprim in this study. The trimethoprim retention time was 4.60 min.

The removal percentage of each sampling point could be calculated according to the following calculation formula:

$$\text{Removal percentage } \eta = 1 - C_i/C_0, \quad (1)$$

where C_i is the concentration of trimethoprim at different time points (mmol/L), and C_0 is the concentration of trimethoprim at time zero (mmol/L).

Then, the removal percentage was compared over the same period of time to reflect the quality and degradation effect of trimethoprim. In this case, a higher removal rate resulted in a better degradation effect.

2.4. Experimental Program

2.4.1. Photo-Fenton Blank Experiment

As this study was aimed at high-concentration pharmaceutical wastewater, a higher concentration of trimethoprim was used in the experiment. The reaction solution was 100 mL, the trimethoprim concentration was 0.0689 mmol/L, and photo-H₂O₂, photo-Fe²⁺, photo-Fenton, Fenton, and UV were used in the reaction. The type of UV used in the experiment was UVA, because UVA can remove more waste than UVC under the same conditions [23]. The degradation times were 0, 2, 4, 6, 10, 20, and 30 min, and the degradation percentage was measured in each case.

2.4.2. Photo-Fenton Single-Factor Optimization Experiment

For this experiment, the trimethoprim concentration was initially 0.0689 mmol/L, while the concentration of H₂O₂ was 2.0 mmol/L, and the concentration of Fe²⁺ was 0.04 mmol/L; the pH was adjusted to 2.5, 3.0, 3.5, 4.0, and 4.5. Then, the degradation experiments were carried out under the UV lamp. When the degradation times were 0, 2, 4, 6, 10, 20, and 30 min, 1-mL samples were taken into the sample bottle, which contained 100 µL of methanol for quenching [24]. Then, the degradation percentage of trimethoprim was determined with HPLC. Then, under the previous optimized conditions, we sequentially changed one of the conditions in turn, and kept the other conditions the same. The specific experimental conditions were as follows: the concentrations of H₂O₂ were 0, 0.5, 2.0, 3.0, and 5.0 mmol/L; the concentrations of Fe²⁺ were 0, 0.02, 0.04, 0.06, and 0.08 mmol/L; the concentrations of trimethoprim were 0.0344, 0.0517, 0.0689, 0.0861, and 0.1033 mmol/L; and the irradiation distance of the UV lamp was also adjusted to change the UV intensity to carry out the degradation experiment.

2.4.3. Central Composite Experimental Design

To take into account the interaction of pH and the concentrations of H₂O₂ and Fe²⁺, a central composite experimental design approach was used to explore the optimal degradation conditions. In this study, the optimal conditions in different pH, H₂O₂ concentrations, and Fe²⁺ concentrations

were analyzed with response surface methodology (RSM). The central composite experimental design parameters were determined according to the single-factor optimization experiment results.

3. Results and Discussion

3.1. Photo-Fenton Blank Experiment

The experiments were conducted in the presence of UV, Fenton, photo-H₂O₂, photo-Fe²⁺ and photo-Fenton (Figure 2). The experimental results indicate that, when using photo-Fe²⁺ or UV alone, the reaction was barely carried out. When using Fenton, the degradation effect was improved, but it was not completely degraded. When using photo-H₂O₂, it was completely degraded in 30 min. In comparison, the trimethoprim was degraded substantially using photo-Fenton, and it was completely degraded in 10 min, indicating that the degradation effect was considerable. This result shows that the addition of UV irradiation has a synergistic effect on the Fenton system. During the Fenton reaction, Fe²⁺ ions are converted to Fe³⁺ ions; however, when UV was added to the reaction system, Fe²⁺ was regenerated via the photo-reduction of Fe³⁺ [25]. The newly generated ferrous ions reacted with H₂O₂ in the next cycle.

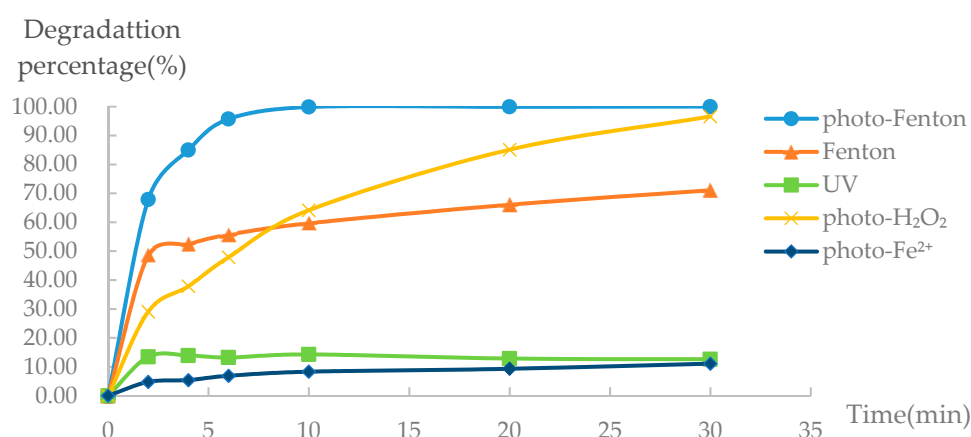


Figure 2. The degradation of trimethoprim under different conditions.

Under the conditions of the photo-Fenton system, UV radiation can directly decompose H₂O₂ into hydroxyl radicals as follows:



Fe²⁺ can be partially converted to Fe³⁺; the transformation of Fe³⁺ in acidic medium can be hydrolyzed to produce hydroxyl Fe(OH)²⁺. Moreover, the high concentration of Fe³⁺ also contributes to consuming a higher amount of H₂O₂, which releases the weaker oxidant HO₂· [26]. Under UV light (<300 nm), Fe(OH)²⁺ can be converted to Fe²⁺, and produce ·OH at the same time.



The above formula indicates that the decomposition rate of H₂O₂ is much greater than a simple addition of the decomposition rates due to Fe²⁺ or UV. Because of the above factors, the treatment efficiency of the photo-Fenton system is affected by much more than Fenton alone.

3.2. Photo-Fenton Single-Factor Optimization Experiment

3.2.1. The Influence of pH on Removal Efficiency

The Fenton reagent method needs to be carried out under acidic conditions, largely because the acidic environment is favorable for the existence of Fe²⁺. The precipitation of iron catalysts as iron hydroxide stops the extent of the Fenton reaction when it is carried out under alkaline conditions.

Most of the literature shows that the Fenton reaction is optimal when the pH is about 3; at this pH, the solution can produce a large number of $\text{Fe}(\text{OH})^+$ ions, which has an activity higher than Fe^{2+} [27]. Therefore, the pH range examined in this paper was from 2.5 to 4.5.

The experimental results (Figure 3) under different pH conditions show that the best degradation of the trimethoprim occurred at pH values from 3.0 to 4.0. When $\text{pH} > 4.0$, the removal was limited by the lower catalyst activity, resulting from the presence of relatively inactive iron oxohydroxides and the formation of ferric hydroxide precipitate [28]. The Fe^{2+} rapidly forms ferric hydroxide precipitation or other forms of iron that cause Fe^{2+} decline, and the reaction between Fe^{2+} and hydrogen peroxide forms hydroxyl radicals that slow down and otherwise influence the Fenton reaction [29]. However, with the pH as low as 2.5, the degradation effect decreased. This is because a low pH reduces the stability of H_2O_2 and may release a proton to form hydronium (H_3O^+), enhancing its stability; however, this can reduce the reactive activity of Fe^{2+} when it participates in the degradation process [30]. Finally, in order to reduce the cost of acid, a pH of 4.0 was chosen as the best condition.

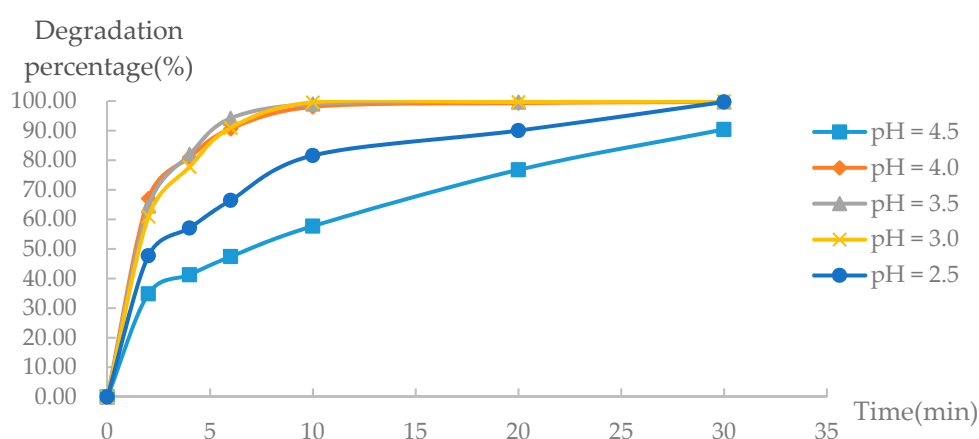


Figure 3. The influence of pH (2.5–4.5) on the degradation of trimethoprim.

3.2.2. The Influence of H_2O_2 Dosage on Removal Rate

The hydroxyl radical produced by the reaction of hydrogen peroxide in the Fenton reaction is one of the important factors that influence the reaction. The key principle of the Fenton reagent method is that the hydroxyl radical oxidizes organic compounds to readily biodegradable intermediate products. Therefore, the concentration of hydroxide free radicals directly affects the whole reaction system. In this study, concentrations of H_2O_2 ranging from 0 to 5 mmol/L were examined for the removal rate of trimethoprim (Figure 4).

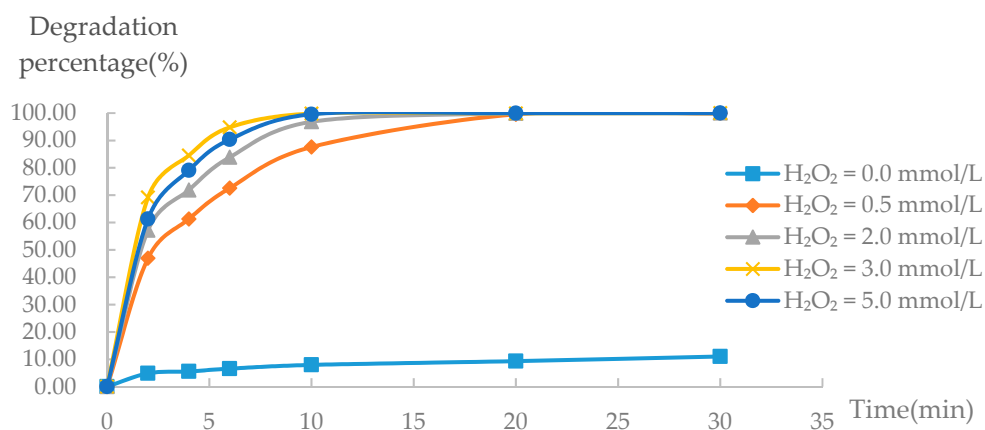


Figure 4. The influence of H_2O_2 concentration (0–5 mmol/L) on trimethoprim degradation.

The experimental results show that, with the increase of the dosage of H_2O_2 , the degradation effect gradually improved. When the concentration of H_2O_2 was 3 mmol/L, trimethoprim was completely removed within 10 min. However, the treatment effect did not increase with the increase of H_2O_2 ; it shows that when the H_2O_2 concentration was 5 mmol/L, the degradation rate began to decline slightly. This may be because an excess of H_2O_2 and $\cdot\text{OH}$ will react to generate $\text{H}_2\text{O}\cdot$, and $\text{H}_2\text{O}\cdot$ is easy to produce with the $\text{HO}\cdot$ reaction, which not only consumes the $\text{HO}\cdot$, but also prevents H_2O_2 decomposition. Finally, the optimal concentration of H_2O_2 was chosen as 3 mmol/L.

3.2.3. The Influence of FeSO_4 Dosage on Removal Rate

Ferrous iron ions are generally believed to play a catalytic role in the Fenton reaction because they can cause H_2O_2 to generate hydroxyl radicals. The concentration of Fe^{2+} was varied between 0 and 0.08 mmol/L.

The results (Figure 5) show that, with the increase of the dosage of Fe^{2+} , the degradation effect of trimethoprim improved. This trend is mainly associated with the scavenging effect of Fe^{2+} at higher $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ ratios [31]. When the Fe^{2+} concentration was 0 mmol/L, the degradation process did occur, but its rate was much slower than the reaction with added Fe^{2+} . When the concentration of Fe^{2+} was 0.06 mmol/L, the trimethoprim was almost completely degraded within 10 min and the degradation rate reached 98.01%. Because too much Fe^{2+} discharged into the water body will cause water pollution and increase the burden on the environment and the cost of degradation, the optimal Fe^{2+} concentration was chosen as 0.06 mmol/L.

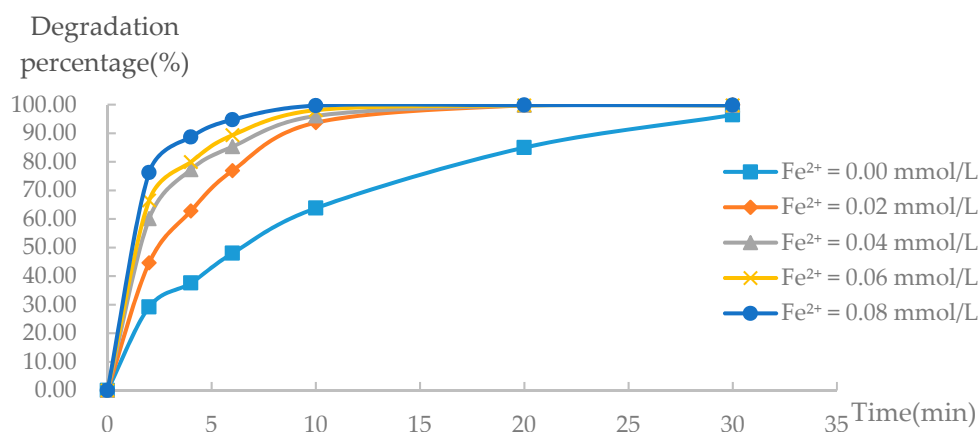


Figure 5. The influence of Fe^{2+} concentration (0–0.08 mmol/L) on trimethoprim degradation.

3.2.4. The Influence of the Initial Concentration of Trimethoprim on the Removal Rate

The concentration of trimethoprim in water is not fixed in practice nor is it fixed under field conditions, and different initial concentrations will also affect the degradation. Therefore, it is of practical importance to study the optimal initial concentration of trimethoprim. In this experiment, the concentration of the trimethoprim was varied between 0.0344 mmol/L and 0.1033 mmol/L, before being degraded under the optimized photo-Fenton conditions.

The experimental results (Figure 6) show that, with the increase of the dosage of trimethoprim, the degradation of trimethoprim decreased. On the one hand, under the optimal conditions in terms of the amount of catalyst, too much trimethoprim consumed a large amount of hydroxyl radicals in the initial reaction, thus reducing the catalytic effect. On the other hand, an increased initial trimethoprim concentration reduced the intensity of the irradiation on the surface of the catalyst, and caused a reduction of the photocatalytic effect. However, this effect should be very small due to the fast kinetics. When the concentration of trimethoprim was 0.0689 mmol/L, the trimethoprim was almost completely degraded within 10 min, and the degradation rate reached 98.08%. Thus, 0.0689 mmol/L was selected as the optimal initial trimethoprim concentration for degradation.

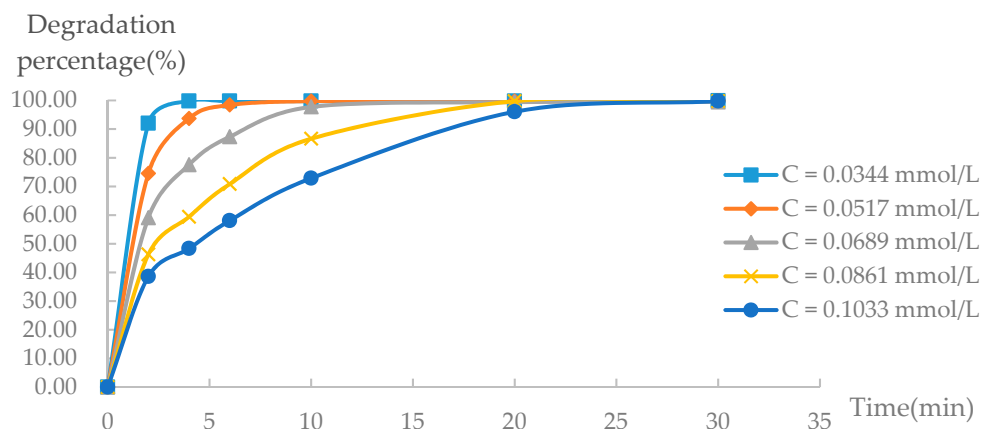


Figure 6. The influence of different initial trimethoprim concentrations (0.0344–0.1033 mmol/L) on trimethoprim degradation.

3.2.5. The Influence of Different UV Light Intensities on Trimethoprim Degradation

It is clear from the blank experiment that UV irradiation had a synergistic effect on the Fenton system alone. Different UV light intensities have an effect on the promotion of the degradation experiment. Therefore, we needed to determine the optimal intensity of UV light degradation of trimethoprim. To achieve this, the UV intensity was changed by altering the distance between the iron stand and the sample, before measuring the light intensity at different locations. The experimental results (Figure 7) show that, with the increase of UV intensity, the degradation effect of trimethoprim was greater because UV promoted trimethoprim decomposition. The stronger the light intensity was, the greater the promotion effect became. The optimal condition of light intensity was UVA = 12 mW/cm².

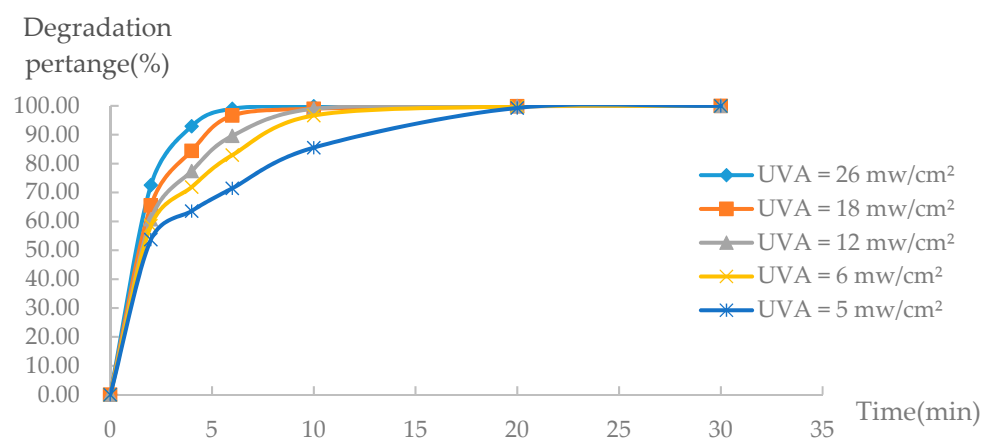


Figure 7. The influence of different ultraviolet (UV) light intensities (5–26 mW/cm²) on trimethoprim degradation.

3.3. Central Composite Experimental Design Optimization

Taking into account the interaction of pH and the H₂O₂ and Fe²⁺ concentrations, the central composite experimental design approach was used to explore the optimal degradation conditions. Response surface analysis can greatly improve the test efficiency and obtain the expected results. According to the single-factor optimization experiment, the optimal conditions were as follows: pH = 4; H₂O₂ concentration = 3 mmol/L; Fe²⁺ concentration = 0.06 mmol/L; and UVA = 12 mW/cm². Through a preliminary experiment, the three factors and five levels of central composite design were used to optimize the possible existence of the optimal degradation conditions. This design is shown in Table 1.

Table 1. Details of the central composite design optimization by Design Expert 8.0.5b software.

Factor	Unit	−1 ¹	0	1	Alpha (−)	Alpha (+)
pH		2.5	4	5.5	1.47731	6.52269
H ₂ O ₂ concentration	mmol/L	1.5	3	4.5	0.477311	5.52269
Fe ²⁺ concentration	mmol/L	0.03	0.06	0.09	0.009542	0.110454

Notes: ¹ −1, 0, 1, Alpha (−), and Alpha (+) are the levels of the factor.

Design Expert 8.0.5b software (Stat-Ease, Inc., Minneapolis, MN, USA) was used to design the experimental sequence and produce the 20 groups of complete factors of the experiment. Then, the experiment was carried out according to the order of the experimental design group (Table 2), and the degradation rate after 6 min was determined. The test results of each group are shown in Table 2. The highest degradation rate was 97.62% when the experimental conditions were pH = 4.00, H₂O₂ concentration = 5.5 mmol/L, and Fe²⁺ concentration = 0.06 mmol/L. Under these conditions, the consumption of H₂O₂ and Fe was too large, resulting in high cost; thus, it was necessary to optimize the condition.

Table 2. Central composite design experimental groups.

Design Sequence	Operation Sequence	pH	H ₂ O ₂ Concentration (mmol/L)	Fe ²⁺ Concentration (mmol/L)	Degradation Rate (%)
18	1	4.00	3.0	0.06	87.98
17	2	4.00	3.0	0.06	89.97
10	3	6.52	3.0	0.06	75.23
14	4	4.00	3.0	0.11	92.96
12	5	4.00	5.5	0.06	97.62
16	6	4.00	3.0	0.06	89.21
19	7	4.00	3.0	0.06	88.75
6	8	5.50	1.5	0.09	92.03
3	9	2.50	4.5	0.03	70.74
11	10	4.00	0.5	0.06	84.27
2	11	5.50	1.5	0.03	37.21
5	12	2.50	1.5	0.09	83.37
7	13	2.50	4.5	0.09	89.79
13	14	4.00	3.0	0.01	65.81
8	15	5.50	4.5	0.09	95.98
20	16	4.00	3.0	0.06	87.38
9	17	1.48	3.0	0.06	71.40
4	18	5.50	4.5	0.03	54.74
1	19	2.50	1.5	0.03	57.06
15	20	4.00	3.0	0.06	91.33

The ANOVA results of the trimethoprim degradation model are shown in Table 3.

Table 3. ANOVA results for the trimethoprim degradation model; df—degrees of freedom.

Source	Sum of Squares	df	Mean Square	F-Value	p-Value Prob > F
Model	4306.57	9	478.51	8.20	0.0014 significant
Residual	583.46	1	58.35		
Pure Error	10.06	5	2.01		
Corrected Total	4890.04	19			
Standard Deviation	7.64		R ²	0.8807	
Mean	80.14		Adjusted R ²	0.7733	
Adequate Precision	9.358				

Through ANOVA, the model F-value of 8.20 implies that the model was significant, and the coefficient of variation ($R^2 = 0.88$) indicates a comparatively high correlation between the observed

and predicted values. Adequate precision compares the range of the predicted values at the design points to the average prediction error. Ratios >4 indicate adequate model discrimination [32]. It was found that $p = 0.0014$, suggested the experimental model was statistically significant at the 0.05 level. The regression equation of the predicted trimethoprim degradation percentage is shown below.

$$\text{Degradation percentage} = 89.37 - 1.07A + 13.70C + 6.34AC - 7.30A^2 - 5.15C^2. \quad (4)$$

The levels of A, B, and C were computed with the following equations: $a = (A - 4) / 1.5$; $b = (B - 3) / 1.5$; $c = (C - 0.06) / 0.03$, a, b, c represent the actual independent variable. Then, the equation was transformed to the actual values.

$$\text{Degradation percentage} = 3.00155 + 16.54958 \times \text{pH} + 753.69973 \times \text{Fe} + 140.81851 \times \text{pH} \times \text{Fe} - 3.24243 \times \text{pH}^2 - 5722.90348 \times \text{Fe}^2. \quad (5)$$

The analytical results of the interaction between pH, H_2O_2 concentration, and Fe^{2+} concentration are shown in Figures 8–10.

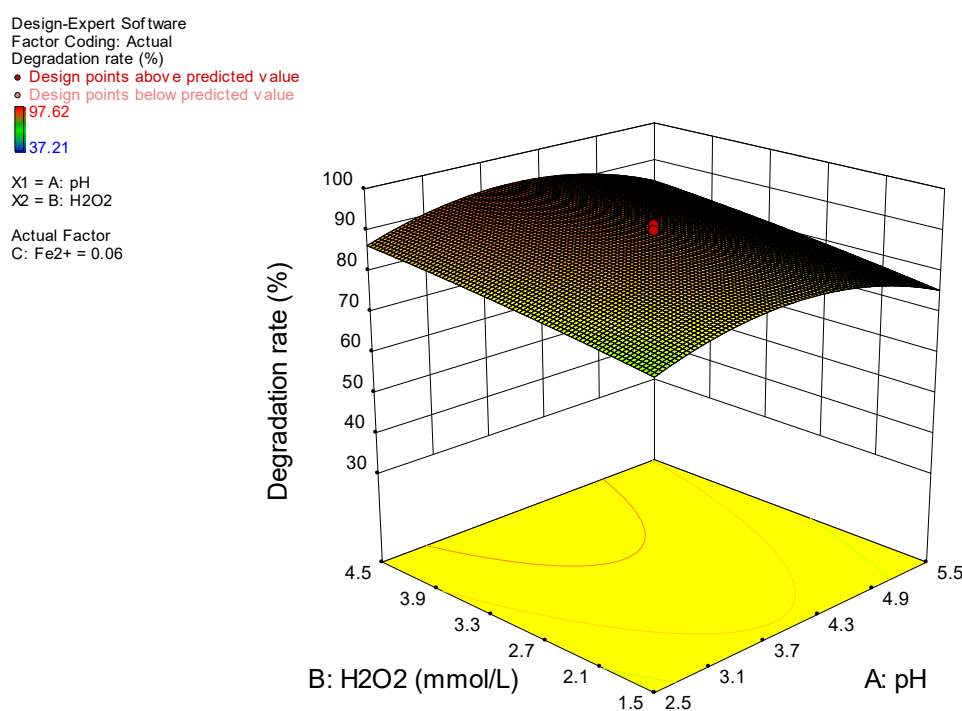


Figure 8. The influence of pH and H_2O_2 concentration on trimethoprim degradation.

Figure 8 shows that, under the same H_2O_2 concentrations, the degradation rate increased with the increase in pH and then decreased. At the same value of pH, the degradation rate of trimethoprim increased with the increase in H_2O_2 concentration. This shows that the degradation under the Fenton reaction requires a suitably acidic pH. If the pH is too high, the oxidation potential of hydroxyl radicals will decrease with the increase of pH, whereas, if the pH is too low, the stability of H_2O_2 will decrease and this could release a proton and form a stable hydrated proton, which is not conducive to the reaction.

Figure 9 shows that, at the same pH, the degradation rate increased with the increase in Fe^{2+} concentration, while, under the same Fe^{2+} concentration, the degradation rate increased with the increase in pH and then decreased. Fe^{2+} plays the role of catalyst in the Fenton reaction; the greater the concentration of Fe^{2+} is, the more hydroxyl radicals can be generated, which improves the degradation efficiency. When the pH increases, Fe^{2+} will form ferric hydroxide precipitation quickly, which leads

to a decrease in Fe^{2+} concentration. The reaction of Fe^{2+} and hydrogen peroxide to form hydroxyl radicals will slow down and influence the Fenton reaction.

Design-Expert Software
 Factor Coding: Actual
 Degradation rate (%)
 • Design points above predicted value
 • Design points below predicted value
 97.62
 37.21
 X1 = A: pH
 X2 = C: Fe^{2+}
 Actual Factor
 B: $\text{H}_2\text{O}_2 = 3$

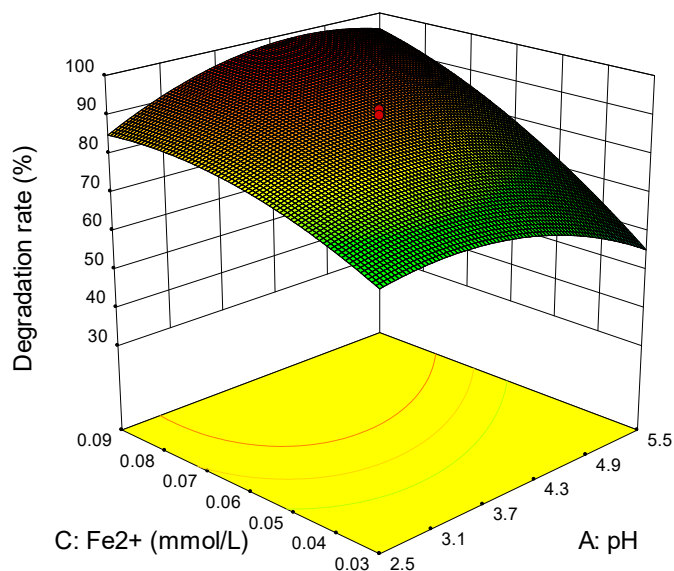


Figure 9. The influence of pH and Fe^{2+} concentration on trimethoprim degradation.

Design-Expert Software
 Factor Coding: Actual
 Degradation rate (%)
 • Design points above predicted value
 • Design points below predicted value
 97.62
 37.21
 X1 = B: H_2O_2
 X2 = C: Fe^{2+}
 Actual Factor
 A: pH = 4

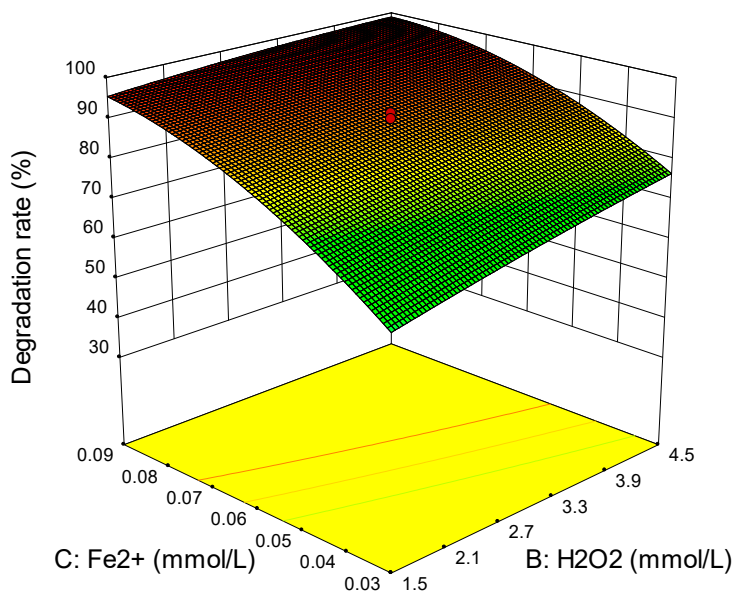


Figure 10. The influence of Fe^{2+} and H_2O_2 concentration on trimethoprim degradation.

It is clear from Figure 10 that, under the same Fe^{2+} concentration, the degradation rate increased with the increase in H_2O_2 concentration, while, under the same H_2O_2 concentration, the degradation rate increased with the increase in Fe^{2+} concentration. Hydrogen peroxide produces hydroxyl radicals in the Fenton reaction and participates in the degradation reaction; thus, the more hydroxyl free radicals there are, the quicker the reaction will be.

The optimal degradation conditions optimized by Design Expert 8.0.5b were as follows: pH = 4.56, H₂O₂ concentration = 0.09 mmol/L, and Fe²⁺ concentration = 0.09 mmol/L. Under these conditions, the optimal degradation rate was 99.95%. Three sets of tests were carried out under the optimal degradation conditions after determining the optimal degradation conditions of the software. The results were close to the design value, which shows that the optimal conditions can be realized.

4. Conclusions

The experimental analysis showed that the photo-Fenton reagent can effectively degrade trimethoprim in wastewater. The blank experiment proved that the addition of UV irradiation has a synergistic effect on the Fenton system. This study shows that response surface methodology is a factual and error-free approach for the optimization of media composition to obtain the best performance for the degradation of trimethoprim. Taking into account the possible interactions of pH, Fe²⁺ concentration, and H₂O₂ concentration, Design Expert 8.0.5b was used to optimize the optimal degradation conditions as follows: pH = 4.56, H₂O₂ concentration = 0.09 mmol/L, and Fe²⁺ concentration = 0.09 mmol/L. Under these conditions, the optimal degradation rate was 99.95%. Then, three sets of tests were carried out under the optimal degradation conditions. The results were close to the design value, which indicates that the optimal conditions can be realized.

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