The Effect of UV Degradation of Ketoprofen and Its Influencing Factors

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Abstract. This paper mainly studies the removal effect of ketoprofen in UV-degraded water and explores the influence of light turbidity, light intensity and other factors on the degradation efficiency of ketoprofen. The results show that deep ultraviolet treatment has a good degradation effect on ketoprofen, which accords with the pseudo-first-order kinetic equations. After irradiation with 1700 μw/cm² UV lamps for 40 minutes, the maximum removal rate can reach 99.59%. Besides, UV lamps with different irradiation strengths (1300μw/cm²/1700μw/cm²) have similar treatment effects on ketoprofen. Low turbidity (1-5NTU) solutions will reduce the degradation rate of ketoprofen, while high turbidity (5-9NTU) solutions will enhance the degradation rate of ketoprofen. Solution turbidity is increased after UV degradation of ketoprofen.

1. Introduction
Non-steroidal anti-inflammatory drugs (NSAIDs) have been widely used in medicine because of their good analgesic effects and small side effects, while some unabsorbed drugs enter the natural environment with human excretion. The existence of non-steroidal anti-inflammatory drugs in the natural environment is recognized as a thorny problem. At a small amount of concentration, it can also have harmful effects on public health and environment; but the biochemical treatment process of traditional sewage treatment plants has no obvious effect on such substances [1]. There will even be a “negative removal” phenomenon due to the accumulation and release of sludge [2]. Ketoprofen (KET), as a typical NSAIDs, is currently widely used in rheumatism and rheumatoid arthritis, ankylosing spondylitis, rheumatism, dysmenorrhea, etc. It is also effective for trauma and post-surgery pain and its annual dosage is up to 92t [3]. Owing to its wide application of ketoprofen, it is often detected in sewage [4].

The literature points out that KET is difficult to be biodegraded or mineralized and requires advanced treatment to remove KET from sewage. [5]. Compared with other sewage depth treatment methods, ultraviolet depth treatment has the characteristics of small land area, mild reaction conditions, energy saving, simple equipment, convenient maintenance and small secondary pollution, which is suitable for application in rural micro-sewage treatment stations.

This study is based on the deep treatment of ultraviolet light to investigate the effects of ultraviolet light intensity, light time, water turbidity, and hydroxyl radical trapping agent p-hydroxybenzoic acid (HBA) on the removal rate of ketoprofen. In addition, the kinetic analysis of the ketoprofen degradation process is carried out [6].
2. Materials and methods

2.1. Instruments and reagents
Main instruments: U3000 high performance liquid chromatograph, 10W 254nm ultraviolet lamp, 24W 254nm ultraviolet lamp, UV-C single-channel ultraviolet irradiation, turbidity meter.
Main medicines: Ketoprofen, HBA, Formazin turbidity standard solution, preparation water is ultrapure water.

2.2. Analysis and monitoring methods
Ketoprofen, HBA concentration: high performance liquid chromatography; solution turbidity: turbidity meter; ultraviolet intensity: ultraviolet irradiator.

2.3. Drawing the standard curve
Precisely configure ketoprofen solutions with concentrations of 2mg/L, 4mg/L, 8mg/L, and 16mg/L, use high performance liquid chromatography to detect and read the peak area. The ketoprofen standard curve is drawn to use peak area concentration and ordinate, with the curve equation \( y = 1.21157x - 1.35474 \) and \( R^2 = 0.9997 \).

2.4. Experimental setup
The experimental device is divided into two parts: (1) The reactor part. It is composed of a three-mouth glass reaction vessel (diameter 6 cm, length 25 cm), quartz glass sleeve (diameter 3 cm, length 30 cm), and ultraviolet lamp; (2) Stirring device composed of PTFE magnetic rotor and magnetic stirrer.
When studying the effect of UV intensity on the reaction, different lamp adjustments are replaced. With 24W ultraviolet lamp, the average ultraviolet intensity in the device is 1700μw/cm²; with 10W ultraviolet lamp, the average intensity is 1300μw/cm². The ultraviolet lamp is energized for half an hour in advance before reaction and the experiment is performed after the light stabilizes. When studying the effect of turbidity on the reaction, formadrazid turbidity standard fluid is used to adjust solution turbidity. Samples are sampled according to time and a 22μm filter membrane. All samples are repeated three times and take the average for graphing.

3. Results and discussion

3.1. The influence of the initial concentration of ketoprofen
Experiment was performed using 24W UV lamps with an average UV intensity of 1700w / cm². The initial concentration of ketoprofen was set to five concentration gradients of 16mg/L, 8mg/L, 4mg/L, 2mg/L, and 1mg/L for the experiment. The results of experiment are shown in Figure 1 and Table 1.
Ultraviolet rays have a good degradation effect on ketoprofen. Ultraviolet rays can degrade ketoprofen at concentrations of 16mg/L, 8mg/L, 4mg/L, 2mg/L, and 1mg/L to 0.91%, 2.98%, 1.75%, 2.18% and 3.55% within 3 minutes. They degraded to 0.46%, 1.25%, 1.17%, 1.33%, 3.30% after 20 minutes and no longer decreased. The final degradation rate of ketoprofen decreases with the increasing ketoprofen concentration. Kinetic analysis shows that UV degradation of ketoprofen complies with the pseudo-primary reaction kinetics and that the ketoprofen degradation rate (Kobs) promotes with increasing concentration. Therefore, the degradation of ketoprofen by ultraviolet rays is a direct photolysis and the degradation rate varies greatly between each concentration. It shows that under the condition of 24W UV lamp irradiation, it is the concentration of ketoprofen that limits the degradation rate. The degradation rate of high-concentration ketoprofen solution is higher than that of low-concentration solution, which indicates that after increasing the concentration, the absorption effect of ketoprofen on UV light is enhanced and then increases the reaction rate.
3.2. The influence of UV light intensity on the removal rate of ketoprofen

24W and 10W UV lamps were used to irradiate 16mg/L, 8mg/L and 4mg/L ketoprofen solutions respectively to compare the degradation effects of the two light intensities. The results are shown in Figure 2 and Table 2.

![Figure 2. Degradation effect of different power UV lamps](image)

### Table 2. The kinetics of degradation of different concentrations of ketoprofen by 10W UV

| Mass concentration | Quasi-first-order kinetic equation | R2   |
|--------------------|-----------------------------------|------|
| 16mg/L             | \( \ln \left( \frac{c}{c_0} \right) = 1.6203t + 0.00124 \) | 0.99761 |
| 8mg/L              | \( \ln \left( \frac{c}{c_0} \right) = 1.68064t \) | 0.9989 |
| 4mg/L              | \( \ln \left( \frac{c}{c_0} \right) = 0.85458t \) | 0.99943 |

The use of 10W ultraviolet lamp still has a good treatment effect on ketoprofen, which can respectively degrade ketoprofen of 16mg/L, 8mg/L and 4mg/L to 1.97%, 0.96%, 0.92% in 3min and it is finally degraded to 0.93%, 0.73% and 0.65% after 20min. Then it does not decrease any more. Kinetic analysis shows that the rate of ketoprofen degradation still complies with pseudo-first-order kinetic equation when irradiated with a 10W ultraviolet lamp. However, Kobs changes little at 16mg/L and 8mg/L, which indicates that at these two concentrations below, 10W ultraviolet lamp cannot have an effect on all the ketoprofen in the solution. At this time, the factor that affects the degradation rate is radiation intensity. Comparing the fitted kinetic equations in Figure 2 and Table 2, it is found that 4mg/L ketoprofen solution has the same Kobs under two different lighting conditions, which indicates that this degradation rate is the maximum degradation rate under the current conditions.
3.3. The effect of solution turbidity on the degradation rate of ketoprofen

Use 24W UV lamp to degrade 16mg/L ketoprofen solution, adjust the turbidity of the solution with formazin turbidity standard solution. The turbidity is adjusted to 1NTU, 3 NTU, 5 NTU, 7 NTU, and 9 NTU respectively. The results are shown in Table 3.

Table 3. 24W UV degradation of 16mg/L ketoprofen with different turbidity effects and turbidity changes (Note: "-" means not detected or exceeded the detection limit.)

| Turbidity | Time | Ultra-pure water (0.14NTU) | 1NTU | 3 NTU | 5 NTU | 7 NTU | 9 NTU |
|-----------|------|-----------------------------|------|-------|-------|-------|-------|
| 1         | 1    | 4.82%                       | 1.24%| 7.18% | 6.78% | 2.06% | 4.75% |
|           | 2    | 1.27%                       | 0.21%| 1.73% | 0.62% | 0.18% | 0.22% |
|           | 3    | 0.91%                       | 0.04%| 0.08% | 0.03% | -     | -     |
|           | 5    | 0.84%                       | 0.08%| 0.02% | -     | -     | -     |
|           | 7    | 0.75%                       | 0.05%| 0.03% | -     | -     | -     |
|           | 10   | 0.63%                       | 0.19%| 0.01% | -     | -     | -     |
|           | 15   | 0.50%                       | 0.08%| -     | -     | -     | -     |
|           | 20   | 0.46%                       | 0.10%| -     | -     | -     | -     |
|           | 30   | 0.41%                       | 0.01%| -     | -     | -     | -     |
|           | 40   | -                           | 0.01%| -     | -     | -     | -     |
| Turbidity after 40 min | 3.08NTU | 6.56 | 10.61 | 13.76 | 17.86 | 19.74 |

After 15 minutes of irradiation for 3NTU solution, ketoprofen exceeded the detection limit and could not be detected; 5NTU solution could not be detected after 5 minutes of irradiation; 7NTU and 9NTU solutions could not be detected after 3 minutes of irradiation ketoprofen. Compared with degradation effect in aqueous solution and 1NTU solution, 1NTU solution was higher than in aqueous solution. After 40 minutes, 1NTU solution was degraded to 0.01%. It is better than 0.41% at the same time in aqueous solution. In 1-5NTU solution, ketoprofen degradation effect of phenanthrene decreases with the increase of turbidity. Under 5-9NTU, degradation effect increases with the increase of turbidity. The above experiment shows that higher turbidity can increase the utilization of ketoprofen to ultraviolet light. 1NTU ketoprofen solution still conforms to the pseudo first-order kinetic equation, the equation is \( \ln \frac{c}{c_0} = 1.76768t+0.24412 \) (R2=0.95198). However, Kobs decreases from 3.01009 to 1.76768, which indicates that the turbidity of solution increases and the UV degradation of ketoprofen have a negative impact.

3.4. The effect of free radical scavengers on the degradation rate of ketoprofen

20ml 1000 mg/L HBA was added to 16mg/L ketoprofen solution and with a fixed capacity to 1000ml. A 24W UV lamp was used for 24W UV degradation and loss of the hydroxytrap in the presence of hydroxytrap in solution. The results are shown in Figure 3 and Table 4.
The degradation effect of ketoprofen changed greatly after adding HBA. Compared with no HBA solution, after adding HBA ketoprofen solution for 1 min, 3 min, and 20 min, ketoprofen surplus rate rose from 4.82% to 25.58%, from 0.91% to 6.74% and then from 0.42% to 0.76%. The remaining rate of HBA was 79.72%, 57.27%, and 21.17%. The Kobs of ketoprofen decreased from 3.01009 to 1.2587. The degradation of HBA also conformed to pseudo first-order kinetics and Kobs was 0.09074. The above results indicate that in addition to the direct photolysis of ultraviolet radiation, •OH produced by the degradation of ketoprofen will promote its own degradation during the degradation process of ultraviolet radiation. After adding HBA, •OH will preferentially combine with HBA to react. Advanced oxidation process that occurs under the action of ultraviolet is inhibited, so the degradation rate of ketoprofen is affected.

### 3.5. The effect of UV degradation of ketoprofen on water

Formal fluid turbidity solution was added to the configured 16mg/L ketoprofen solution. Solution turbidity was adjusted to 1NTU, 3NTU, 5NTU, 7NTU and 9NTU respectively. Changes in turbidity were measured and recorded after 40 min of irradiation with a UV lamp at 24W. The results are shown in Table 4: the turbidity of 16mg/L, 8mg/L, 4mg/L, 2mg/L and 1mg/L ketoprofen solution during the degradation process was measured. Moreover, the changes were recorded. The results are shown in Figure 4.
Above results show that the turbidity of ketoprofen at different concentrations changes after UV degradation. It can be seen from Table 3 that after 40 minutes of reaction, the turbidity of high-concentration solution changed greatly. The turbidity of 16mg/L and 8mg/L solutions increased from 0.41, 0.15 to 3.08, 1.41. The turbidity of low-concentration ketoprofen solution changed little. The turbidity of 4mg/L, 2mg/L, and 1mg/L solutions increased from 0.29, 0.33, 0.29 to 0.73, 0.59, 0.57. Besides, the color of solution in the reactor gradually changed from colorless and transparent to brown and yellow within 0-15 minutes. The magnitude of high concentration ketoprofen change was significantly greater than that of low concentration ketoprofen solution, consistent with turbidometer measurements. In other ketoprofen solutions with adjusted turbidity, the greater the turbidity of solution before the reaction, the greater the range of change in the turbidity of solution.

3.6. Analysis of the mechanism of UV degradation of ketoprofen

Ketoprofen, as a multifunctional compound containing a benzene ring, its ultraviolet degradation process is mainly composed of two parts: direct photolysis and hydroxyl radical oxidation [7]. Among them, direct photolysis is that it is exposed to ultraviolet light after ketoprofen, hydroxyl group connected to the carbonyl group in the structure is prone to breakage after absorbing UV to form •OH and •OH will further promote its own advanced oxidation reaction [8]. Therefore, a higher concentration of ketoprofen will produce more •OH, so after 20 minutes of UV irradiation, the final removal rate of ketoprofen solution with a high initial concentration is also higher.

The carbonyl group used to connect benzene ring will form a conjugated double bond with carbon-carbon double bond on the benzene ring and deepen the chromaticity of water. The hydroxyl group as an auxochrome group will further increase the turbidity of aqueous solution, so after the ketoprofen solution is irradiated with ultraviolet light, the color and turbidity will change greatly [9]. In addition, under the action of stirring, H2O2 will diffuse to water layer far away from the lamp tube, which results in advanced oxidation of UV/H2O2. Finally ketoprofen in the region of lower UV intensity will produce advanced oxidation. The degradation rate of ketoprofen becomes lower after adding hydroxyl trapping agent HBA because hydroxyl radicals generated by the photolysis of ketoprofen are preferentially combined with HBA during the reaction. HBA is consumed and UV/H2O2 advanced oxidation reaction is also inhibited. Therefore, when HBA is still present in large quantities, the degradation rate of ketoprofen is greatly reduced. As HBA content decreases, UV/H2O2 advanced oxidation process begins to gradually recover, so the degradation rate begins to increase. However, because most of the
ketoprofen has been photodegraded at this time, •OH has been consumed in large quantities and UV/H2O2 advanced oxidation occurs. The reaction is still small. At the same time, unreacted HBA has the effect of robbing •OH. Therefore, under the same conditions, the final degradation effect of the ketoprofen solution with HBA added is less than the final degradation effect of the ketoprofen solution without addition.

4. Conclusions and recommendations
1) UV light degradation rate of ketoprofen was over 96%, and each concentration of ketoprofen met the quasi-primary kinetic equation (R2> 0.9), and when the ketoprofen concentration increased from 1 to 16 mg/L, Kobs rose from 0.61886 to 3.01009. Univariate experiments showed that the maximum rate of 4 mg/L ketoprofen for UV degradation by UV254 was Kobs=0.85458.

2) When the ketoprofen concentration is gradually increased from 1 to 16 mg/L, the solution turbidity increases from 0.29 to 0.08 after 30 i n m of the reaction. Therefore, in addition to conventional indicators, close attention should be paid to the color, turbidity and other factors that affect the look and feel of effluent from the advanced treatment in practical applications.

3) The high-efficiency degradation of ketoprofen by advanced ultraviolet treatment is due to the structure of ketoprofen. The same process cannot achieve similar effects when processing other drugs. Therefore, more research is needed when performing advanced ultraviolet treatment to degrade other substances.

4) Different deep processing methods handle the same NSAIDs, but they have different effects and products. In future research, the decomposition process and products of specific drugs should be studied in depth.

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