

# Efficiency and mechanism of UV / CH<sub>3</sub>COOOH for advanced treatment of wastewater in Waterworks

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**Abstract.** In this paper, advanced oxidation technology based on radical catalysis was used to study the efficiency and mechanism of advanced treatment of refractory pollutants in the wastewater of waterworks by coupling the ultraviolet chemical reaction system with peroxyacetic acid. In this paper, the first-order photodegradation kinetics of UV / PAA system was revealed; The efficiency characteristics of UV / PAA system were analyzed with high quantum yield and excellent degradation rate constant; From the point of view of PAA activating free radicals, the contribution of pollutants degradation was quantitatively analyzed, and the reaction mechanism of UV / PAA system was given. This paper proves the feasibility and superiority of UV / PAA advanced treatment of wastewater in waterworks, and provides an important theoretical basis for practical process design.

**Keywords:** peracetic acid, ultraviolet rays, radical, wastewater, degradation of pollutants.

## 1. Introduction

With the full development of the 14th five-year plan, the battle of pollution prevention and control has entered a profound historical critical period. With the introduction of the new environmental protection law, people pay more and more attention to the impact of sewage discharge on the ecological environment. The sewage purification technology is constantly mature, the sewage treatment system is constantly improved, and the industrial, agricultural and domestic wastewater has been effectively collected and purified on the technical level.

However, with the diversification of social life, the sources of wastewater are becoming more and more diverse, the composition of sewage is becoming more and more complex, and the harmful chemical substances in sewage are more and more difficult to degrade. From the source, the traditional wastewater treatment methods (physical adsorption, chemical precipitation, biodegradation, etc.) are made, it is easy to produce a large number of secondary sewages which is not completely degraded and forms wastewater of water plant with low concentration of pollutants but great environmental harm. On the one hand, if the wastewater of the waterworks cannot be effectively purified, it cannot be recycled with higher water quality requirements, which means the waste of economic resources; On the other hand, a large amount of wastewater is discharged into the natural water environment, which will cause serious secondary pollution and cause irreversible harm to the ecological environment and human activities.

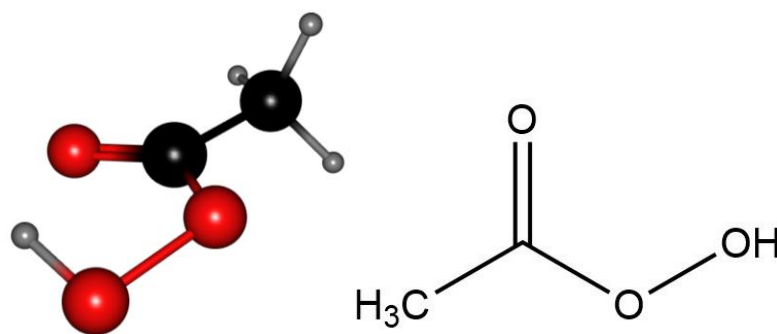
Advanced oxidation process (AOPs) based on free radical catalysis is a kind of environment-friendly water treatment technology. It has strong degradation effect on organic pollutants [1]. Hydroxyl radical (HO·), superoxide radical ( $\cdot\text{O}_2^-$ ), peroxide hydroxyl radical (HO<sub>2</sub>·) and alkyl radical (RO·) can mineralize many organic pollutants with high reaction rate, At the same time, the minimum secondary pollution [2] is produced.

Among them, the reaction conditions of advanced photochemical oxidation process are mild. The free radicals generated by photocatalysis can degrade pollutants by using water vapor and oxygen in the air at room temperature. Organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), chlorophenols (CPS) and alkylphenols (APS) can be effectively degraded [2]. Among them, ultraviolet (UV) as a means of activating free radicals, which belongs to the type of relatively energy-saving and low-cost, and the degradation efficiency is relatively high. In addition, there is no input of harmful chemicals in the reaction system of UV oxidation technology, and the free radical participating in the reaction has a very short life, which can minimize the formation

of harmful by-products, thus making it more environmentally friendly and has certain ecological benefits.

As a new oxidant and disinfectant, peracetic acid (PAA) owns high oxidation capacity and antibacterial activity [3], which has been widely used in many fields such as wastewater treatment in food processing, medical, chemical, textile and papermaking industries. Kim J[4] reviewed the rate constants of PAA oxidation of organic compounds, whose reactivity to 123 kinds of organic compounds was evaluated. It was proved that PAA could activate a large number of effective free radicals under suitable reaction conditions, thus completing the degradation of organic pollutants. The results showed that the redox potential of PAA and hydrogen peroxide were 1.96 eV and 1.78 eV respectively, indicating that the oxidation capacity of PAA was higher than that of H<sub>2</sub>O<sub>2</sub>, and the antibacterial activity of PAA was much greater than that of H<sub>2</sub>O<sub>2</sub>[5].

As an oxidant of UV photooxidation, peracetic acid has an asymmetric structure containing O-O bond, which is similar to PMS in structure. Compared with traditional oxidants H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, Fenton reagent and PMS, PAA has a higher efficiency of free radical generation[6], and can produce active factors better in the oxidation reaction, which can be optimized in both consumption and cost; On the other hand, as a broad-spectrum fungicide, peracetic acid is an excellent substitute for chlorine based oxidants due to its limited formation of harmful disinfection byproducts[7], negligible mutagenicity or genotoxicity to aquatic organisms, and no persistent residues in the environment.



**Figure 1.** Structural formula of peracetic acid

Therefore, this project plans to use PAA as a new oxidant of UV photooxidation reaction system, coupled with AOPs technology, to construct ultraviolet / peracetic acid system (UV / PAA system), and carry out research on advanced treatment of water plant wastewater. Taking the photochemical degradation process of typical pollutants as the research object, the efficiency and mechanism of UV / PAA system in treating water plant wastewater are summarized.

## 2. Research preparation

### 2.1. Chemical properties of peracetic acid

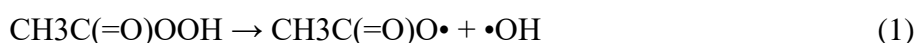
#### 2.1.1. free radical reaction theory of peracetic acid

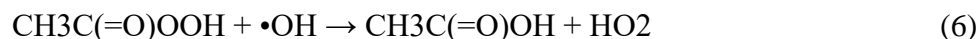
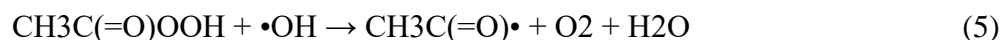
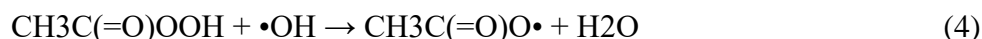
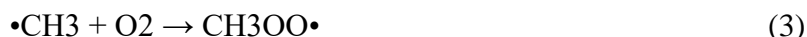
The free radical reaction of peracetic acid can be inferred theoretically [9] [10].

In the case of only considering direct decomposition, the initial reaction of the radical chain reaction of peracetic acid is the homogeneous cleavage of O-O bond, resulting in CH<sub>3</sub>C(=O)O•(formula (1)); Subsequently, CH<sub>3</sub>C(=O)O• was rapidly dissociated to methyl radicals(•CH<sub>3</sub>)and CO<sub>2</sub>(formula (2));•CH<sub>3</sub> combines with oxygen to produce a weak peroxy radical CH<sub>3</sub>OO•(formula (3)).

At the same time, •OH may attack PAA molecule (formula (4-6)) to produce various alkyl radicals.

CH<sub>3</sub>C(=O)O• may also react with PAA to produce acetyl peroxide radical CH<sub>3</sub>C(=O)OO•(formula (7)).





Of course, in the UV / PAA system, the free radical reaction of peracetic acid will be more complex. We can take the theoretical free radical reaction as a reference to investigate the actual free radical reaction of UV / PAA system.

### 2.1.2. Chemical state of peracetic acid

There are two forms of PAA in solution [8]: PAA0, which is not dissociated from PAA. When pH is less than 3.17, PAA0 can account for more than 99% of the total PAA in solution; PAA<sup>-</sup> is a quasi-dissociated species of PAA, also known as the biocide form of PAA. When pH > 8.2, PAA<sup>-</sup> can be considered as the main form of PAA. When pH value reaches 9.93, PAA<sup>-</sup> accounts for more than 98% of the total PAA.

### 2.1.3. Properties of peracetic acid solution

PAA is unstable, especially at low concentrations. In general, solutions containing 40% PAA lose about 1-2% of the active ingredient [11] per month.

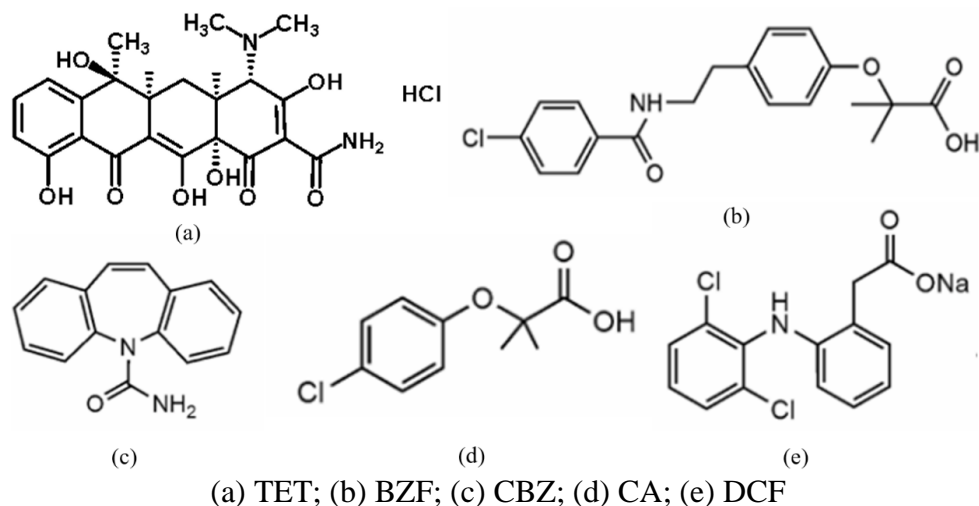
Commercial PAA disinfectants are generally a mixture of PAA, H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>COOH. Similarly, acetic acid and hydrogen peroxide coexist in the higher purity peracetic acid stock solution. Therefore, the reaction kinetics and mechanism of UV / PAA process involve a higher degree of complexity.

The peroxyacetic acid stock solution used in this paper was purchased from Tianjin Zhongsheng challenge Biotechnology Co., Ltd. It contains about 39% acetic acid, the content of H<sub>2</sub>O<sub>2</sub> is less than 6%, and stored at 5°C.

## 2.2. Selection of research objects

This paper intends to use UV / PAA system to treat the wastewater of water plant, and complete the research on efficiency and mechanism. Firstly, we measured the photodegradation of PAA under UV irradiation from the UV / PAA system itself, constructed the photodegradation kinetic model of PAA, and determined the mechanism of UV activation of PAA; Secondly, we selected typical refractory pollutants in common domestic sewage and medical wastewater. These pollutants are very easy to appear in the wastewater of waterworks whose wastewater treatment capacity is not up to standard. The degradation effect of pollutants by UV / PAA system was studied by combining experiment and kinetic simulation. The reactive species responsible for pollutant degradation under UV / PAA system were systematically evaluated. The reaction mechanism was elucidated and the action path of free radical species in the UV / PAA system was evaluated.

In this paper, tetracycline hydrochloride (TET), bezafibrate (BZF), carbamazepine (CBZ), chlorofibre acid (CA), diclofenac (DCF) was selected as the pollutants in the wastewater of typical waterworks.



**Figure 2.** structure of pollutants in wastewater of typical waterworks

## 2.3. research methods

### 2.3.1. calibration method of PAA solution concentration

PAA stock solution (39% PAA and 6% H<sub>2</sub>O<sub>2</sub>, stored at 5°C) was calibrated for PAA concentration [12] using a combination of iodometric titration and acid potassium permanganate titration. Firstly, the concentration sums of PAA and H<sub>2</sub>O<sub>2</sub> was measured by iodometric titration. Free iodine was produced by adding potassium iodide (with ammonium molybdate as catalyst), and then iodine was titrated with sodium thiosulfate; Then, under acidic conditions, H<sub>2</sub>O<sub>2</sub> in PAA stock solution was titrated with potassium permanganate. The actual concentration of PAA in PAA stock solution can be obtained by subtracting the results of two titrations.

10 g / L PAA working solution was prepared by diluting the standardized PAA stock solution, which was stored at 5°C and used in the experiment.

The concentration of PAA stock solution should be calibrated regularly, and the working solution should also be calibrated.

### 2.3.2. quantitative method of residual PAA in the experiment

The residual PAA was quantified by N, N'-diethyl-p-phenylenediamine (DPD) Colorimetry [13]. After being treated with iodine, the concentration of potassium iodide can be measured in proportion to the absorbance of potassium iodide.

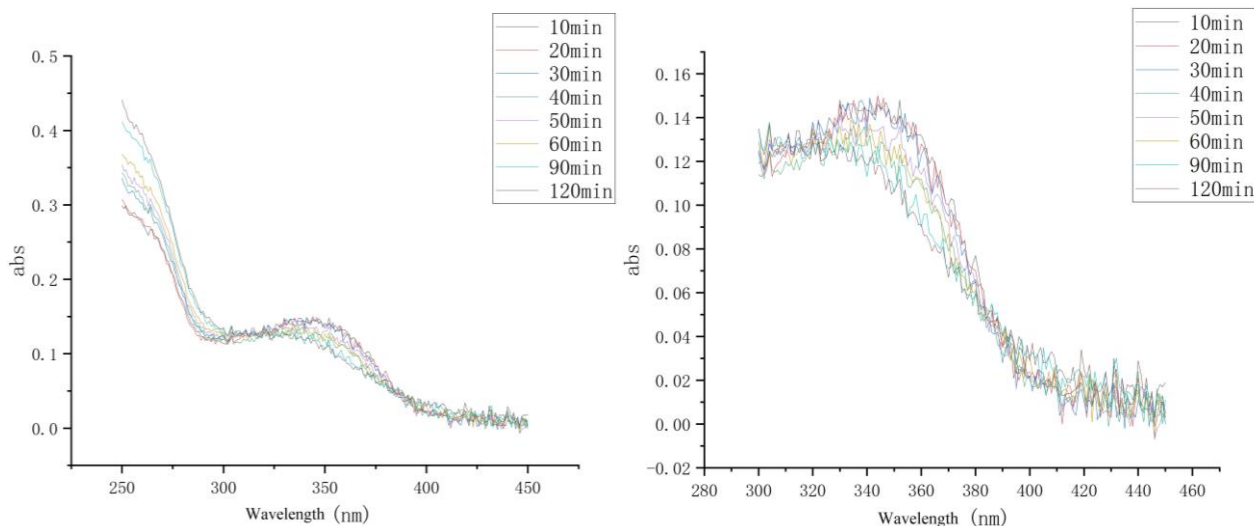
Take 8 50ml colorimetric tubes, add about 40ml pure water, then add 0ml, 0.10ml, 0.20ml, 0.30ml, 0.40ml, 0.60ml, 0.80ml, 1.00mL peracetic acid working solution (10.00mg / ml), add pure water to the scale, and mix well. When using, mix ferric chloride solution and N, n-diethyl-p-phenylenediamine solution according to (1 + 20) as the color developing solution. Add 1.0 ml color developing solution to water sample tube and standard tube respectively, shake up immediately, and place for 20min. Under the circumstance of the wavelength of 665 nm and a 3 cm cuvette used with pure water as reference, the absorbance of standard series solution was measured and the calibration curve was drawn.

Take 50ml uniform water sample, or take appropriate amount of water sample and dilute it to 50ml with pure water. According to the sample configuration steps of standard curve, determine the absorbance, and find out the residual PAA content in the sample from the calibration curve.

### 2.3.3. determination method of pollutant concentration in the experiment

The concentration of each pollutant was determined by UV spectrophotometry.

According to Lambert Beer law, the absorbance of a substance at a specific wavelength is directly proportional to its concentration. In the experiment, we first completed the characteristic absorption peak scanning spectrum of each pollutant, and confirmed it with the characteristic peak wavelength in the literature. The characteristic absorption peak wavelengths of Tet, BZF, CBZ, Ca and DCF were 350, 235, 285, 227 and 219 nm, respectively, which is consistent with the literature.



**Figure 3.** scanning spectrum of characteristic absorption peak of TET

### 2.3.4. determination methods of H<sub>2</sub>O<sub>2</sub>, PAA<sup>0</sup>, PAA<sup>-</sup> in the experiment of photolysis determination of PAA

The molar absorption coefficient [14] was calculated.

Molar absorptivity ( $\epsilon$ ) is a measure of the absorption capacity of a substance to light at a certain wavelength. The molar absorption coefficient is numerically equal to the product of the absorption coefficient ( $a$ ) and the molecular weight ( $m$ ) of the substance

In the experiment, the characteristic absorption peaks of PAA<sup>0</sup> and PAA<sup>-</sup> are unknown, which need to be determined by scanning spectrum. Therefore, it is necessary to adjust the pH value of PAA solution to 3.17 and 9.93 respectively, and calculate the molar absorptivity of PAA<sup>0</sup> and PAA<sup>-</sup> according to the known concentration of PAA working solution calibration. On this basis, in the experiment of photodegradation of PAA, the kinds of substances were determined according to different absorption peak wavelengths, and the concentration of each substance was determined according to the absorbance and the molar absorption coefficient, so as to calculate the quantum yield of each substance, and evaluate the efficiency of UV / PAA system from the perspective of photolysis of oxidant.

### 2.3.5. determination method of free radical contribution in UV / PAA system

The contribution of free radical [15] in the reaction process was determined by adding free radical quenching agent.

In the experiment, in order to determine the influence of various free radicals on the reaction process, we can set up two reaction systems, one of which is added with the corresponding free radical quenching agent to react rapidly with the free radicals generated in the system, so that it does not participate in the degradation of pollutants, compared with the system without the addition of free radical quenching agent.

The free radical quenching agents used in the experiment are: tert butyl alcohol (TBA)  $\cdot\cdot\cdot$ OH quenching agent.

### 2.3.6. preparation method of UV / PAA system solution

A phosphate buffer solution (10mM) is used to prepare the drug. The reactor is then placed in a light chamber with an operating magnetic stirrer. A certain amount of PAA solution was added to the reactor immediately to start the reaction.

### 2.3.7. sample post-treatment methods for UV / PAA system

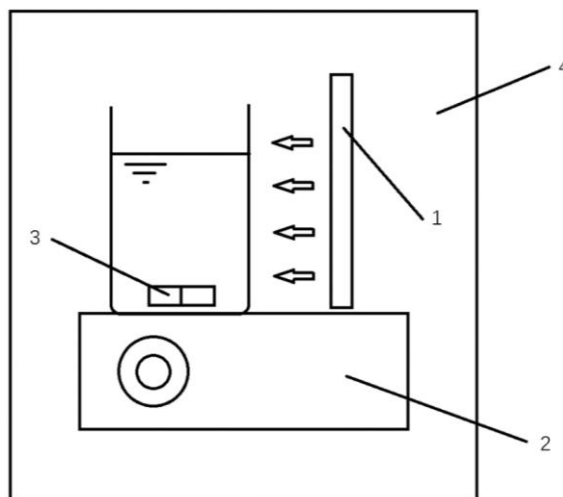
Because of the strong reactive free radicals in the system, if the reaction is not stopped immediately, the reaction will continue, resulting in inaccurate measurement of pollutant concentration and wrong reaction kinetics equation. Therefore, it is necessary to quickly put the sample into an amber glass vial

containing excessive sodium thiosulfate ( $[Na_2S_2O_3] / [PAA^0] > 5$ ), All the oxidants and free radicals in the system were removed.

### 2.4. Experimental device

Philips 8W ultraviolet lamp (according to the ultraviolet germicidal lamp gb19258, when the electric power in the input lamp is 100 watts, the ultraviolet radiation efficiency is 60%), and the ultraviolet lamp is 254nm band.

During the experiment, we built a 100 ml cylindrical quartz reactor with magnetic stirring and rotating light coating



1-UV lamp; 2-rotating chassis; 3-magnetic stirrer; 4-airtight light room

**Figure 4.** Schematic diagram of UV photooxidation reactor

In photochemical reaction, we need to pay attention to the effective optical path length and incident light intensity of the reaction device, so as to calculate the quantum yield of photolysis materials, and then evaluate the treatment efficiency of UV / PAA system according to the comparison of quantum yields.

The effective light intensity is calculated as follows [16]

$$I_{\lambda} = \frac{I_{\lambda}' \cdot D \cdot H}{V} \cdot \frac{1}{N_A \cdot \frac{h \cdot c}{\lambda}}$$

$I_{\lambda}$  -Effective light intensity, Einstein·L-1· s-1

$I_{\lambda}'$  -Average light intensity of area measurement,  $I_{\lambda}' = \frac{\frac{1}{4}\pi D^2}{D} = 0.25\pi D$ , W·cm-2;

D – reactor diameter, cm;

H – solution height, cm;

V – volume of reaction solution, cm<sup>3</sup>;

$N_A$  - Avogadro constant, 6.022×10<sup>23</sup>;

h – Planck constant, 6.626×10<sup>-34</sup>m<sup>2</sup>·kg·s-1;

c – speed of light, 3×10<sup>8</sup>m·s-1;

$\lambda$  - characteristic absorption peak wavelength of corresponding substance, m;

According to the measured parameters of the experimental device, the effective light intensity of the system is 2.12×10<sup>-6</sup>Einstein·L-1·s-1.

The calculation formula of quantum yield is as follows [17]

$$\Phi_{\lambda} = \frac{k_d \cdot A}{(I_{\lambda} \cdot (1 - 10^{-A \cdot L}) \cdot \epsilon_{\lambda}}$$

Among them:

$$A = \epsilon_{PAA^0}[PAA^0] + \epsilon_{PAA^-}[PAA^-] + \epsilon_{H_2O_2}[H_2O_2]$$

$\Phi_\lambda$  - quantum yield, mol·Einstein<sup>-1</sup>;

$k_d$  - the direct photolysis rate of corresponding substance, s<sup>-1</sup>;

$\epsilon_\lambda$  - molar absorptivity at the characteristic absorption peak, M<sup>-1</sup>·cm<sup>-1</sup>;

According to the above formula, only the molar absorptivity of PAA<sup>0</sup> and PAA<sup>-</sup> corresponding to the absorption peak wavelength and the degradation rate under UV irradiation can be calculated.

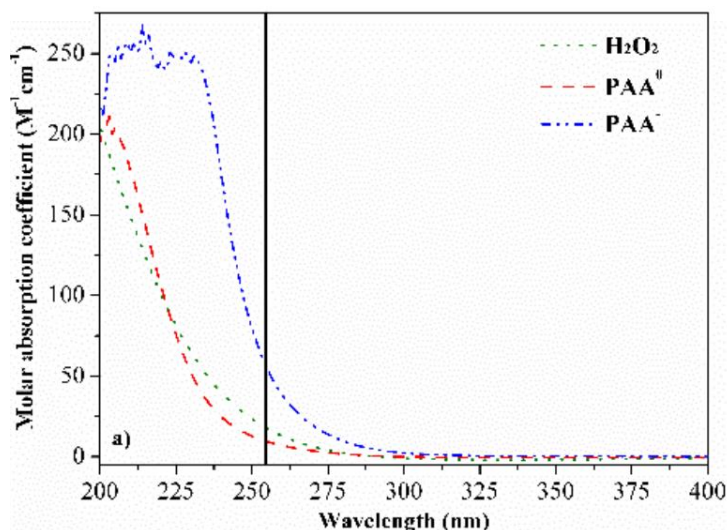
### 3. Research results and discussion

#### 3.1. photolysis of PAA under UV irradiation

In order to fully understand the degradation mechanism of UV / PAA, it is necessary to understand the photolysis of PAA under UV irradiation.

##### 3.1.1. Determination of molar absorptivity of PAA<sup>0</sup> and PAA<sup>-</sup>

It can be seen from the literature investigation [18] that the spectrum of PAA solution system can be directly scanned by spectrophotometer, and the 254 nm of ultraviolet lamp in the experimental device is taken as the characteristic absorption peak wavelength. According to the concentration of PAA in the working solution of known concentration, the molar absorptivity of PAA<sup>0</sup> and PAA<sup>-</sup> in the system can be determined.



**Figure 5.** the molar absorption coefficients of PAA<sup>0</sup> and PAA<sup>-</sup> at 200-400nm

Therefore, we directly measured the absorbance of PAA working solution at 254nm at pH = 3.17 (all PAA<sup>0</sup>) and pH = 9.93 (all PAA<sup>-</sup>) in the solution. According to the PAA concentration (10mg / ml), the molar absorptivity of PAA<sup>0</sup> and PAA<sup>-</sup> were calculated. The calculation results are as follows:

**Table 1.** Molar absorptivity of PAA<sup>0</sup> and PAA<sup>-</sup>

	PAA <sup>0</sup> (pH = 3.17)	PAA <sup>-</sup> (pH = 9.93)
Absorbance (abs)	0.113	0.592
molar absorptivity(M <sup>-1</sup> ·cm <sup>-1</sup> )	9.65	58.37

It can be found that PAA<sup>-</sup> has a higher molar absorptivity, indicating a higher UV absorption capacity.

##### 3.1.2. Photodegradation kinetics of PAA<sup>0</sup> and PAA<sup>-</sup>

In order to study the photolysis of PAA<sup>0</sup> and PAA<sup>-</sup> under UV irradiation, the photolysis processes of PAA<sup>0</sup> and PAA<sup>-</sup> were studied.

Solutions with pH = 3.17 and pH = 9.93 were placed in the device for ultraviolet irradiation. Samples were taken every 20 minutes. The absorbance of PAA<sup>0</sup> and PAA<sup>-</sup> were measured at the

wavelength of 254 nm, and their concentrations were calculated. The kinetic curve of photolysis reaction was drawn as follows:

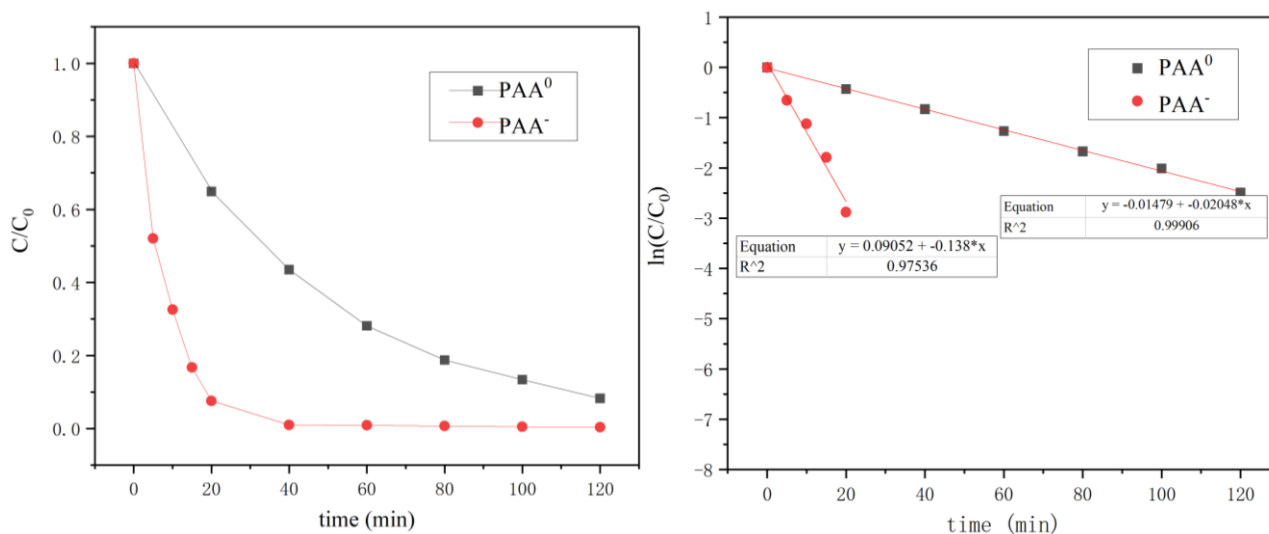


Figure 6. photodegradation kinetic curves of PAA<sup>0</sup> and PAA<sup>-</sup>

From the logarithmic fitting curve in Fig. 5, it can be concluded that the photolysis of PAA<sup>0</sup> and PAA<sup>-</sup> follows the first-order reaction kinetics (first-order kinetic reaction), and the first-order dissociation constants of PAA<sup>0</sup> and PAA<sup>-</sup> can be obtained:

$$k_{PAA^0} = 0.02048 \text{ min}^{-1}$$

$$k_{PAA^-} = 0.138 \text{ min}^{-1}$$

First-order dissociation rate of PAA<sup>-</sup> is higher than that of PAA<sup>0</sup>.

### 3.1.3. Quantum yield calculation of PAA in UV / PAA system

From the above data, the quantum yields of PAA<sup>0</sup> and PAA<sup>-</sup> can be calculated:

$$\Phi_{254\text{nm},PAA^0} = 1.08 \text{ mol} \cdot \text{Einstein}^{-1}$$

$$\Phi_{254\text{nm},PAA^-} = 1.93 \text{ mol} \cdot \text{Einstein}^{-1}$$

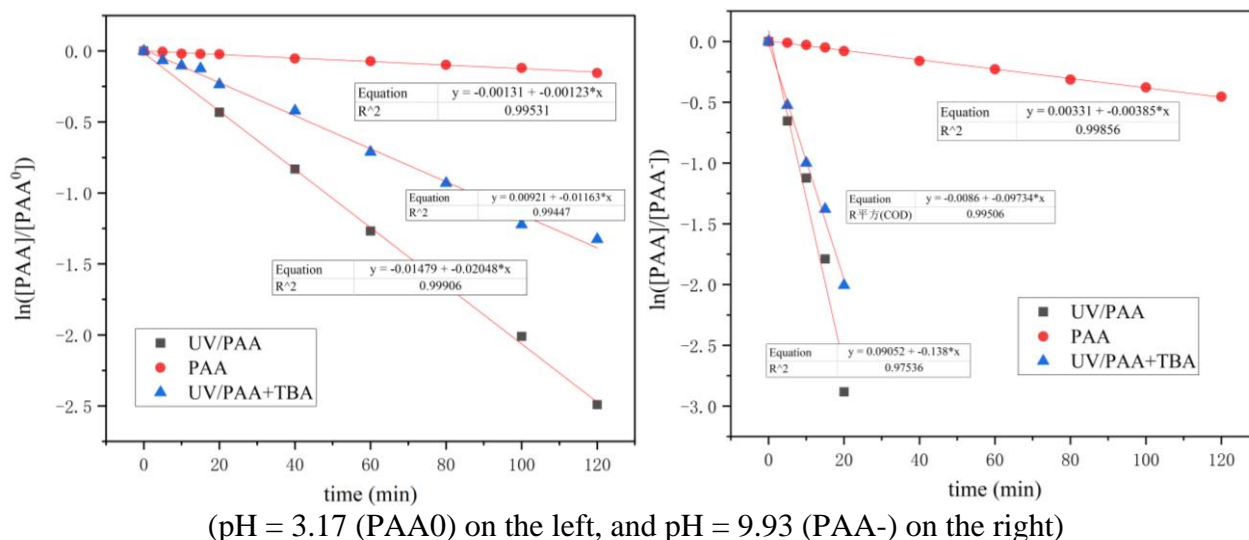
The quantum yield of photolysis of H<sub>2</sub>O<sub>2</sub> at 254 nm was found to be:

$$\Phi_{254\text{nm},H_2O_2} = 0.50 \text{ mol} \cdot \text{Einstein}^{-1}$$

This indicates that the photolysis of PAA may produce more •OH or other active free radicals than photolysis of H<sub>2</sub>O<sub>2</sub>, which can trigger chain reaction of molecules in the system, which proves the reaction potential of UV / PAA system.

### 3.1.4. Photolysis mechanism of PAA

-centration of PAA in the UV / PAA system, the system without ultraviolet radiation (PAA system) and the system with free radical quenching agent TBA (UV / PAA + TBA system) were measured with time, and the photodegradation kinetic curves (PAA<sup>0</sup>, PAA<sup>-</sup>) were drawn. The system without UV irradiation was used as blank system to eliminate the influence of PAA self-decomposition and evaluate the effect of UV correctly; The purpose of this study is to study the effect of free radicals produced in the process of continuous photolysis of PAA on the photolysis of PAA.



**Figure 7.** photodegradation kinetic curves of PAA system and UV / PAA + TBA system

From the photodegradation kinetic curve of PAA system, it can be seen that PAA has a certain degree of self-decomposition, but the amount of self-decomposition is small, and it can keep its active components well in a short reaction time. Combined with the reaction of wastewater of water treatment plant in this paper, the general reaction time is not more than two hours, combined with the actual application of water supply and drainage, the reaction speed needs to be improved. Therefore, it can be concluded that PAA self-decomposition can produce active factors for UV / PAA system, and the effect of organic pollutants treatment can be approximately ignored.

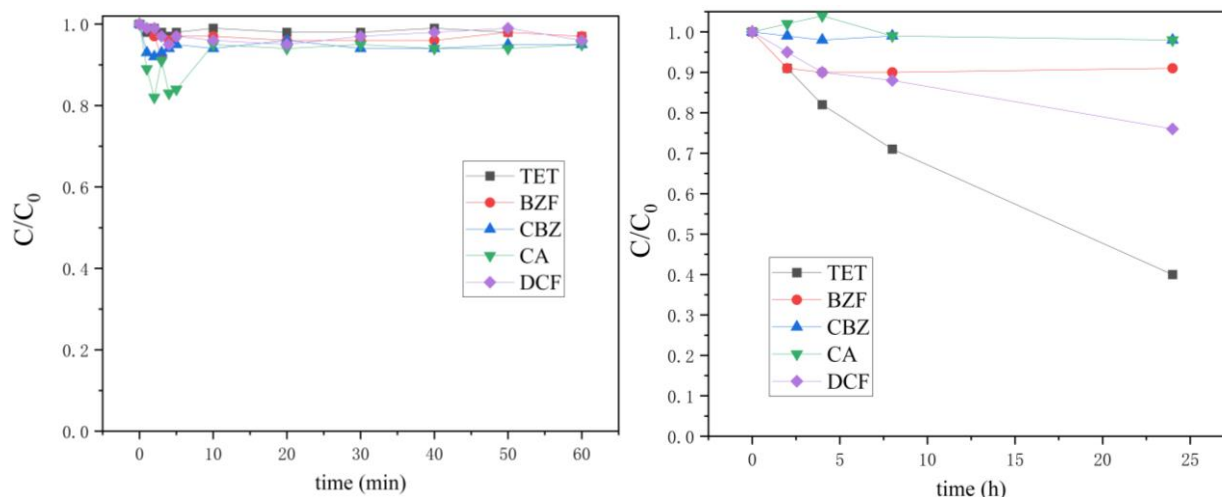
-UV / PAA + TBA system, the addition of TBA inhibited the photolysis of the two kinds of PAA to a certain extent, which indicated that  $\cdot\text{oh}$  was produced-photolysis of PAA, and  $\cdot\text{OH}$  could further react with PAA to accelerate its photolysis. However, under UV radiation, PAA was directly photolysis mainly due to UV action, especially for PAA<sup>-</sup>, even if all the  $\cdot\text{OH}$  generated-system was quenched in advance, The photolysis reaction of PAA<sup>-</sup> was not affected. Therefore, the direct photolysis of UV / PAA system is mainly due to the direct action of UV light, and the indirect photolysis is partly due to the interaction between  $\cdot\text{OH}$  and PAA or intermediate products.

It can be concluded that the main reaction of peracetic acid in UV / PAA system is still the initial reaction of free radical chain reaction, (O-O bonds are all cleaved, and acetoxy radical ( $\text{CH}_3\text{C}(=\text{O})\text{O}\cdot$ ) is produced; The higher quantum yield of PAA<sup>-</sup> is due to the combination of the dominant role of direct photolysis of ultraviolet light and the strong ultraviolet absorption capacity of PAA<sup>-</sup>.

### 3.2. UV / PAA degradation of pollutants in Waterworks wastewater

#### 3.2.1. Degradation efficiency of single PAA system on Pollutants

Before studying the degradation efficiency of UV / PAA, it is necessary to study the degradation efficiency of PAA alone. First of all, we do not irradiate the UV light to the initial concentration of  $1\mu\text{M}$ . The concentration of pollutants in the solution was measured in 60min; At the same time, the efficiency of the reaction system for increasing PAA dose and reaction time was determined, To the initial concentration of  $1\mu\text{M}$ ,  $1\text{g} / \text{L}$  PAA solution was added into the contaminant solution of M for 24 h



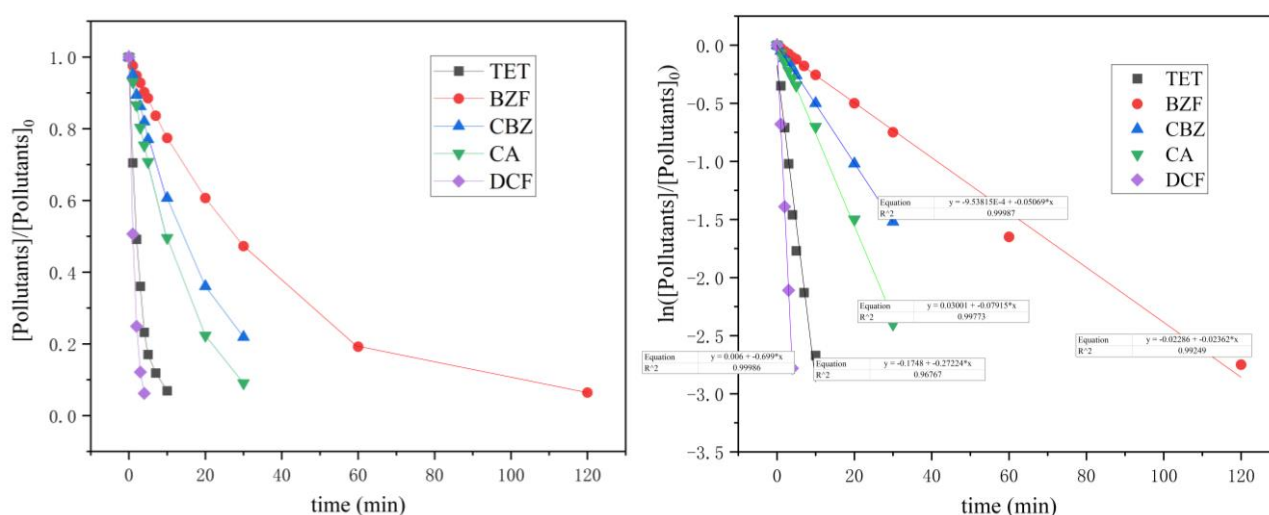
(The initial pollutant concentration is  $1\mu\text{M}$ . Left  $[\text{PAA}] = 1\text{ mg / L}$ , right  $[\text{PAA}] = 1\text{ g / L}$ )

**Figure 8.** degradation of pollutants by PAA alone system

Under the action of  $1\text{ mg / L}$  PAA within one hour, the degradation of several pollutants is very little, and almost no degradation reaction occurs; When PAA dosage was increased to  $1\text{ g / L}$  and the reaction time was extended to 24 hours, only TET and DCF showed obvious elimination (62.50% and 29.70% respectively), but the removal rate of most drugs was still less than 11%, and the removal effect was not ideal. So, the reactivity of PAA to the typical pollutants studied is low, and PAA alone is not an effective oxidant to eliminate organic pollutants in the wastewater of waterworks. In the process of experiment, the influence of free radicals produced by PAA before UV irradiation on the experiment can be ignored. If the PAA solution is kept for a long time, the quenching test can be carried out before UV irradiation 10 mm TBA was added into the reaction solution before UV irradiation to remove the influence of free radical oxidant decomposed by PAA when not irradiated, and correctly evaluate the role of UV in the system.

### 3.2.2. Degradation efficiency of UV / PAA system for pollutants

The initial degradation concentration was  $1.0\mu\text{M}$  in  $1\text{ mg / L}$  PAA solution with  $\text{pH} = 7.10$ . The reaction kinetics curve of pollutant degradation was drawn as follow.



**Figure 9.** kinetic curve of pollutant degradation in UV / PAA system

Obviously, under the action of UV / PAA system, several pollutants have been completely degraded, the degradation rate of pollutants is more than 93.5%, most of the pollutants can be degraded in 20-30 minutes.

Similarly, the chemical kinetics of pollutants degradation in UV / PAA system also follows pseudo first order kinetics (as shown in the right figure of Fig. 8, the natural logarithm of degradation rate is

linear with time, which conforms to the rate equation of basic integral form of first-order reaction kinetics:  $\ln(a/c) = kt$

### 3.2.3. Comparison of degradation efficiency of UV / PAA system

According to the literature review, several pollutants in UV / PAA system can act with UV alone. In the UV / H<sub>2</sub>O<sub>2</sub> system, the degradation reaction rate constants of the same pollutants can be compared under the same reaction conditions [19]

**Table 2.** Comparison of degradation rate constants of different photochemical reaction systems

Contaminants	$k_{UV/PAA}$	$k_{UV/H_2O_2}$	$k_{UV}$
TET	$2.72 \times 10^{-1}$	$8.07 \times 10^{-2}$	$5.10 \times 10^{-2}$
BZF	$2.36 \times 10^{-2}$	$2.14 \times 10^{-2}$	$2.01 \times 10^{-2}$
CBZ	$5.07 \times 10^{-2}$	$2.11 \times 10^{-2}$	$4.90 \times 10^{-3}$
CA	$7.92 \times 10^{-2}$	$1.77 \times 10^{-1}$	$1.95 \times 10^{-1}$
DCF	1.38	1.31	0.79

The results show that UV / PAA system is more effective in the degradation of some pollutants compared with the traditional system; On the other hand, ultraviolet radiation alone can also cause direct photolysis of some pollutants, It also shows that the UV / PAA system can maximize the treatment efficiency by coupling the direct photolysis of UV and the oxidation of organic pollutants by PAA producing active factor, which has a good development prospect in the future practical application of water treatment.

### 3.3. UV / PAA degradation of free radicals in wastewater of waterworks

#### 3.3.1. Contribution of pollutant degradation

UV / PAA process can degrade the refractory pollutants in the wastewater of waterworks through the combination of photodegradation of pollutants by ultraviolet direct photodegradation of PAA to produce  $\cdot OH$  and other free radicals to oxidize organic pollutants. Therefore, we will study the mechanism of free radical reaction in UV / PAA system, mainly focusing on the contribution of free radicals in the reaction process.

From the photolysis experiment of PAA, we can know that PAA can photolysis under UV irradiation, mainly producing hydroxyl radical  $\cdot OH$ . The effects of other radicals such as superoxide radical  $\cdot O_2^-$ , peroxy hydroxyl radical  $\cdot HO_2$ , alkyl radical  $R\cdot$ , alkoxy radical  $RO\cdot$ , can be classified into three processes Ultraviolet direct photolysis,  $\cdot OH$  oxidation, another free radical oxidation.

The contribution of the three processes to the degradation of pollutants is quantitatively described by the rate constant

$$k_{UV/PAA} (\text{min}^{-1}) = k_{UV} + k_{\cdot OH} + k_{\text{other radicals}}$$

We can combine the hydroxyl radical quencher tert butyl alcohol (TBA) to study the contribution of each process. By measuring the kinetic curves of the reaction after adding TBA into the system, the corresponding reaction rate constants were calculated

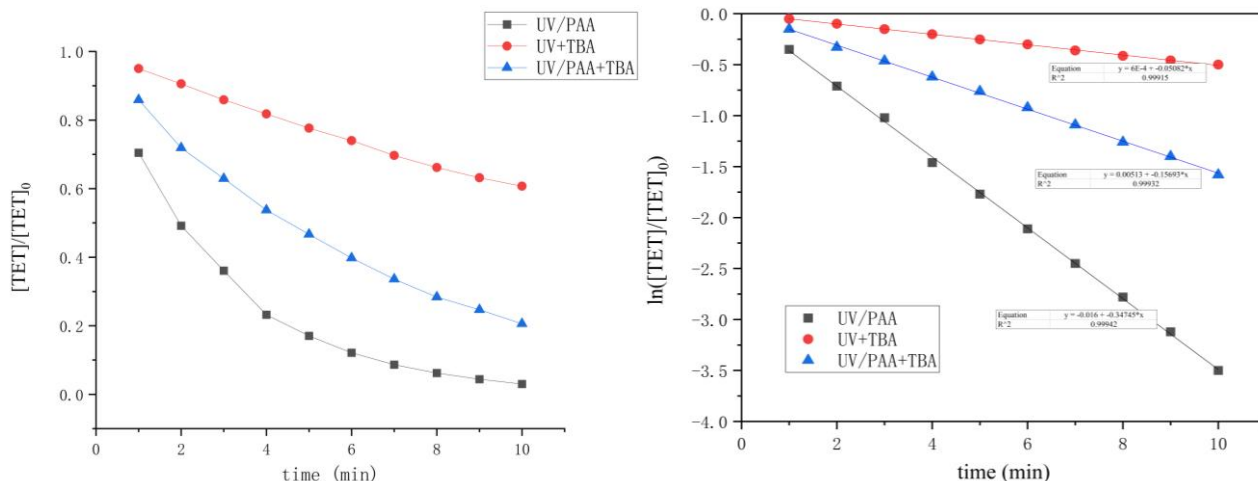
$$\begin{aligned} k_{UV} &= k_{UV+TBA} \\ k_{\cdot OH} &= k_{UV/PAA} - k_{UV/PAA+TBA} \\ k_{\text{other radicals}} &= k_{UV/PAA+TBA} - k_{UV+TBA} \end{aligned}$$

The direct photodegradation of UV can be investigated by adding TBA (UV + TBA system) to the UV system without PAA. At this time, there is only direct photolysis of UV in the system, and the rate constant is  $k_{UV}$ ; The oxidation of  $\cdot OH$  can be used to investigate the difference of pollutant degradation concentration and its rate constant after adding TBA into UV / PAA system is  $k_{\cdot OH}$ . It can also be expressed as the difference value of the rate constants of UV / PAA system and UV / PAA + TBA system  $k_{UV/PAA}$ ,  $k_{UV/PAA+TBA}$ ; The oxidation of other free radicals can be characterized by the difference of pollutant degradation rate between two UV chemical reaction systems without PAA, whose rate constants called  $k_{\text{other radicals}}$ .

### 3.3.2. degree contribution of UV / PAA system

We chose tetracycline hydrochloride (TET) as the pollutant object of the system digestion, because the degradation effect of Tet was good in the experiment of UV / PAA degradation of water plant wastewater pollutants, and the reaction rate was moderate, which was convenient for us to sample and observe.

The initial concentration was 1 $\mu$ M. The kinetic curves of Tet of m in three systems (UV + TBA, UV / PAA and UV / PAA + TBA) (pH = 7.10) were obtained:



**Figure 10.** reaction kinetics curves of Tet in UV + TBA, UV / PAA and UV / PAA + TBA systems

It can be seen from the figure that the reaction kinetic models of the three systems follow the first-order reaction law, so the rate constants of the three systems can be obtained

$$k_{UV+TBA} = 0.05082 \text{ min}^{-1}$$

$$k_{UV/PAA+TBA} = 0.15693 \text{ min}^{-1}$$

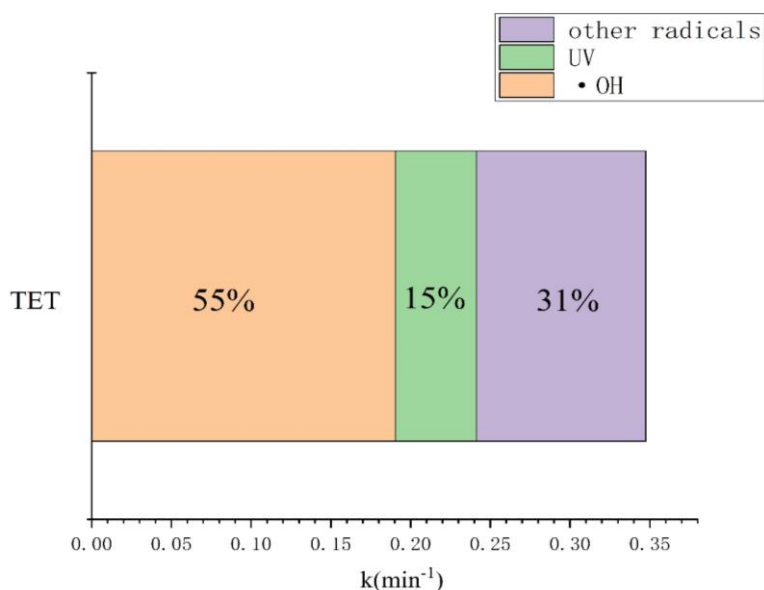
$$k_{UV/PAA} = 0.34745 \text{ min}^{-1}$$

According to the calculation, it can be concluded that:

$$k_{UV} = 0.05082 \text{ min}^{-1}$$

$$k_{OH} = 0.19052 \text{ min}^{-1}$$

$$k_{\text{other radicals}} = 0.10611 \text{ min}^{-1}$$

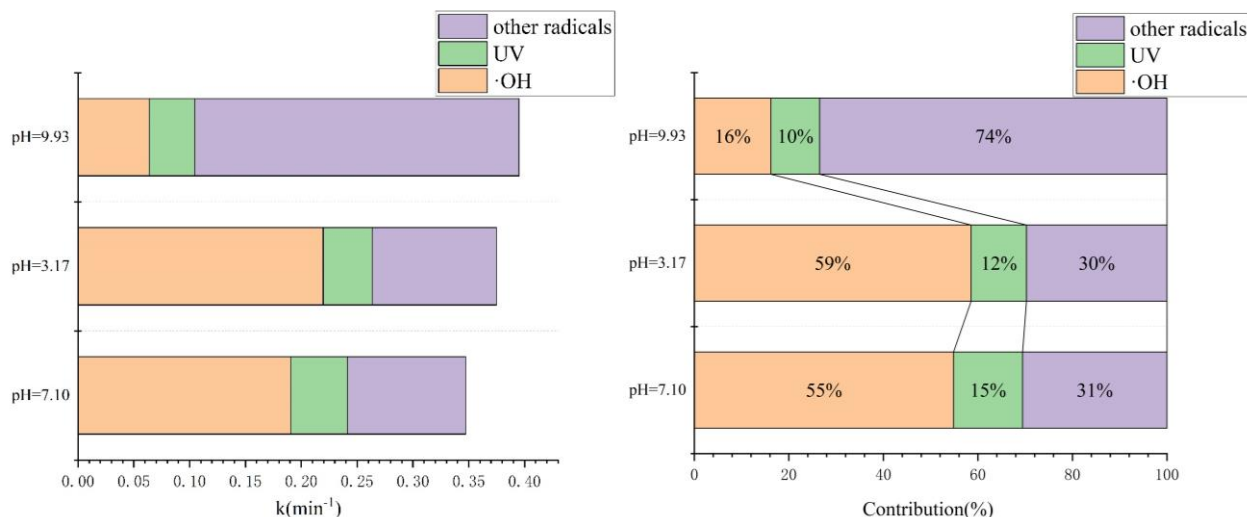


**Figure 11.** contribution distribution of UV / PAA system

It can be seen that under this condition, hydroxyl radicals play a major role in the reactive substances, and the contribution of other radicals is secondary.

### 3.3.3. The effect of different PAA forms (PAA0, PAA-) on the reaction contribution in UV / PAA system

Finally, we will study the effects of different forms of PAA (PAA0, PAA-) on the contribution of UV / PAA system to degradation of pollutants. Other experimental conditions kept unchanged,  $1\mu\text{M}$  of TET was used as the degradation object, and the reaction rate constants of each process were calculated by adjusting  $\text{pH} = 3.17$  (PAA0) and  $\text{pH} = 9.93$  (PAA-), The distribution of contribution degree is shown in the figure below:



**Figure 12.** contribution of UV / PAA0 and UV / PAA- systems to degradation reaction

From the study of the contribution degree of the two systems with  $\text{pH} = 3.17$  and  $\text{pH} = 9.93$ , it can be seen that the acidic PAA0 can complete the degradation of pollutants by activating hydroxyl radicals. However, when the reaction conditions become alkaline and the main form of PAA is PAA-, the contribution of hydroxyl radicals is very small, Other free radicals ( $\cdot\text{OH}$ ,  $\cdot\text{O}_2^-$ ,  $\cdot\text{HO}_2$ ,  $\text{R}\cdot$ ,  $\text{RO}\cdot$ , etc.) are the main pollutants to be degraded.

Combined with the chemical properties of PAA0 (formula (1-7)), it can be seen that the main reaction of PAA0 is to produce hydroxyl radicals. Under acidic conditions, the proportion of other radicals produced by the reaction of PAA0 with hydroxyl radicals in the system is small; However, for PAA under alkaline conditions, most of the hydroxyl radicals produced by chain reaction react with PAA- and intermediate products in the system, and new free radicals are produced to participate in the reaction.

## 4. Summary and prospect

In this paper, advanced oxidation technology based on free radical catalysis was used to study the efficiency and mechanism of advanced treatment of refractory pollutants in the wastewater of waterworks by coupling UV chemical reaction system with peroxyacetic acid. The main achievements of this paper are summarized as follows.

1. From the point of view of ultraviolet photolysis of peracetic acid, the molar absorptivity of PAA0 and PAA- was determined by taking the existing forms of PAA0 and PAA- as breakthrough; The photodegradation process of PAA0 and PAA- was measured. The first order kinetics of photolysis of PAA was proved and the rate constant of photolysis was calculated; The quantum yield of PAA in UV / PAA system was calculated by molar absorption coefficient and photolysis rate constant, which proved the reaction potential of UV / PAA system; The photodegradation mechanism of PAA was given by adding TBA, that is, the direct photodegradation of ultraviolet was the main factor, and the indirect photolysis was assisted by the interaction of  $\cdot\text{OH}$  and PAA or intermediate products.

2. The degradation efficiency of TET, BZF, CBZ, CA and DCF in the UV / PAA system was studied. The corresponding photochemical reaction process was measured, and the first-order reaction

kinetics of pollutants degradation was proved; The degradation rate constants of different photochemical reaction systems were compared, thus the efficiency advantage of UV / PAA system was explained.

3. The radical reaction mechanism of UV / PAA system for the degradation of pollutants in the wastewater of waterworks was studied. According to the direct photolysis of UV, the oxidation of  $\bullet\text{OH}$  and the oxidation of other free radicals, the reaction contribution of UV / PAA system was quantitatively described according to its rate constant; Taking TET as the research object, it was confirmed that the main contribution degree of UV / PAA system was hydroxyl radical  $\bullet\text{OH}$ ; The effects of PAA0 and PAA- on the contribution degree of the reaction were studied. It was concluded that PAA0 mainly completed the degradation of pollutants by activating hydroxyl radicals, while the hydroxyl radicals produced by PAA0 reacted with PAA- and intermediate products in the system to form new free radicals and participate in the degradation of pollutants.

Peracetic acid is an environment-friendly alternative disinfectant, and its usage is increasing. This study comprehensively analyzes the feasibility and superiority of ultraviolet / peracetic acid in advanced wastewater treatment from two aspects of treatment efficiency and mechanism, which can provide important theoretical basis for further research on practical process design of UV / PAA and other means to activate PAA.

The research results of this paper will promote the development of UV / PAA as a new degradation strategy of micro pollutants in water, and promote its continuous optimization. As a new oxidant, there are still many deficiencies in the research of PAA. In the follow-up research, more research should be carried out on PAA and UV / PAA system. For example, the degradation efficiency of UV / PAA in actual water matrix should be evaluated; Furthermore, the reactivity and structural selectivity of free radicals and active groups other than hydroxyl radicals were further evaluated, and the degradation pathway of UV / PAA system in a specific pollutant was further studied, and the toxicity of the transformed products was evaluated; In order to improve the reaction rate and reduce the production of by-products, we can activate free radicals or adjust reaction conditions.

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