

**Kinetics of aqueous photocatalytic oxidation of fulvic acids
in a photocatalysis-ultrafiltration reactor (PUR)**

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Abstract: The photocatalysis of natural organic matter, fulvic acid (FA), by P25 TiO₂ in terms of UV₂₅₄ and TOC concentrations was investigated in this study. The experiments were conducted in a lab-scale photocatalysis-ultrafiltration reactor (PUR) with TiO₂ suspension. Groups of experiments were designed to examine the effects of pH of bulk solution, TiO₂ concentration and additives strength as well as light intensity on the degradation of FA. Results from this study revealed that the degradable behaviour of FA can be reasonably described by first-order kinetics. In addition, it was demonstrated that low pH value, increased additives concentration and relative high light intensity were all beneficial parameters for TOC removal. By inspecting the relationship between rate constant (*k*) and influencing factors, an overall FA oxidation rate kinetic model was established. The utility of the model was demonstrated by the agreement of predictive and experimental results.

Keywords: Fulvic acid; Kinetic modelling; Photocatalysis; Natural organic matter; Ultrafiltration membrane

1. Introduction

It was reported that the natural organic matter (NOM) can be found most commonly in soil, natural water, and sediments which consisted of a mixture of the decomposition products of plant and animal residues [1]. The main components of NOM have been identified as humic acid (HA) and fulvic acid (FA) [2]. Presence of NOW in raw water could affect the water quality during the water purification process. For example, the disinfection by-products (DBPs), like trihalomethanes (THMs), can be formed from chlorination in drinking water containing NOM [3,4]. It has been documented that, in Tianjin, over 70% of NOM in surface waters was fulvic acid [4]. Thus, it is reasonable to believe that FA control can be one of the main targets in surface water treatment. From the literature, it has been accepted that the NOM with the fulvic acids is difficult to remove by the conventional treatment processes. In general, the removal efficiency of TOC in such conventional drinking water treatment processes remains only 10-50% [5].

With regard to the NOM removal, it is noted that the TiO₂-mediated photocatalytic oxidation (PCO) has been the favorable research topic in recent years. In particular, owing to the formation of hydroxyl radicals (·OH), PCO shows an extraordinarily oxidizing power in the reaction mixture and can thus mineralize a myriad of undesirable organic matters to CO₂, H₂O and inorganic

constituents [6]. However, the difficulty of separation of TiO_2 powder after reaction brings about another problem and dims the practical applications of PCO. In spite of the effort of immobilizing the TiO_2 catalysts on certain supporting materials, such as sheets or particles with large surface area (say alumina or silica-gel), to seek the solution of the problem, a drawback of such attempt lies in the mass transfer limitations of pollutants to the surface of the photocatalyst [7,8].

In this study, ultrafiltration (UF) membrane was employed to incorporate with suspension photocatalysis system for the purpose to enhance the TiO_2 separation. Comparing with other PCO, the integrated process described in this paper has two typical advantages. One is the effective separation of TiO_2 particles from its aqueous suspension. The other is the high removal efficiency of NOM which was simulated by fulvic acids in current study. Specific attention was paid on the examination of the effect of some key parameters on the UV_{254} and TOC removal at different reaction conditions. Such parameters include pH, TiO_2 concentration, potassium peroxodisulphate concentration and light intensity. A kinetic model was then developed in this study to describe the effects of these main factors in order to optimize the reactive conditions.

2. Materials and methods

2.1. Materials

Photocatalyst used in this investigation was titanium dioxide Degussa P25, mainly anatase (ca. 70%) under the shape of non-porous polyhedral particles with mean size of ca. 30nm and surface area of $50 \text{ m}^2/\text{g}$. Fulvic acids were provided by Beijing BioChem. Corp with chemical structure to be shown in Fig.1. Polypropylene ultrafiltration (UF) membrane used in the photoreactor was supplied by Seawater Desalination Research Centre, Tianjin. The main characteristics of the membrane are: 1mm internal diameter; nominal pore size of $0.2 \mu\text{m}$; molecular weight cut-off of 50000 Daltons; effective area of 0.197 m^2 and No. of fibers of 50. The pH of the artificial solutions was adjusted by the addition of either H_2SO_4 or NaOH . All reagents utilized were of analytical purity.

2.2. Photoreactor

A continuous flow photocatalytic membrane reactor, as illustrated schematically in Fig.2, was set up in a laboratory scale. It consisted of an annular photocatalytic oxidation unit (270mm in length and 80mm in inner diameter) and an ultrafiltration membrane unit. The photocatalytic unit comprised of an outer cylinder separated by 3.76mm to the inner quartz glass cylinder, between which the solution could be circulated (see Fig. 2). The effective volume was 1400 cm³ including tubes and pump. The 11W low UV lamp emitting a wavelength of predominantly 253.7 nm was suspended vertically inside the quartz glass cylinder. The reaction vessels and a centrifugal pump were connected via a Teflon tube. The ultrafiltration membrane unit was incorporated to separate TiO₂ and, at the same time, to recycle catalyst into the photocatalytic unit. A peristaltic pump was used to pressurize the wastewater containing TiO₂ particle and to circulate it through the ultrafiltration membrane. Compressed air was bubbled upward through the gas diffuser equipped at the bottom of the reactor for providing dissolved oxygen in solution. The reaction temperature was maintained at 30 ± 2 °C with the aid of recirculating cooling water. Additionally, the exterior wall of the reactor was covered with a reflecting aluminum foil to improve the efficiency of UV utilization. At different irradiation time intervals, the samples of FA solution were taken from permeate outlet and analyzed for determination of UV₂₅₄ and TOC. After experiments high circulation velocity with the permeate valve closed to remove the deposited TiO₂ particles from the membrane surface. Gas backflush was applied until the initial permeability had been regained. The ultrafiltration membrane cleaning procedure adopted was a combination of hydraulic and chemical cleaning. The lamp envelop was mechanically cleaned every 24h.

2.3. Experimental procedure for FA degradation

During the experimental period, a total of five sets of tests were designed with different purposes. The experimental conditions for FA degradation are summarized in Table 1. The first set of tests was conducted under different experimental conditions including UV irradiation, photocatalyst and addition of potassium peroxodisulphate (K₂S₂O₈) while the secondary set of tests was carried out under the varied pH values. The third set of tests was performed with various TiO₂ concentrations to identify the optimal catalyst dosage. In order to determine the effect of

additives on FA oxidation, the fourth set of tests was carried out by adding potassium peroxodisulphate with a wide range of concentration. The fifth set of tests was designed to investigate the relationship between FA degradation rate and light intensity.

2.4. Analytical methods

The UV-Vis spectrum of FA was shown in Fig.3. The concentration of fulvic acid was measured by a UV spectrophotometer (Cary 100 spectrophotometer by Varian) at 254nm where the maximum adsorption of FA occurs. The total organic carbon was analyzed with TOC-5000A apparatus (Shimadzu). The pH was measured by a HACA digital pH-meter (model pHs-3C) while the light intensity was monitored by a UV Irradiance Meter (Model UV-A).

3. Results and discussion

3.1 Photodegradation of FA under different experimental conditions

Fig.4 and Fig. 5 illustrate respectively the results of the reduction of UV_{254} and TOC under various experimental conditions, as designed in Table 1. Test A was conducted in UV irradiation condition with a light intensity of $0.75\text{mW}/\text{cm}^2$ only. The experiment showed a slight decrease of UV_{254} and TOC concentration. The test B was carried out under no UV irradiation with only TiO_2 concentration of $0.5\text{g}/\text{L}$. It was found that the slight reduction of UV_{254} and TOC at the early stage of experiment due to adsorption of FA on the surface of TiO_2 . The test C was executed under UV irradiation with the intensity of $0.75\text{mW}/\text{cm}^2$ plus the addition of potassium peroxodisulphate (PP, $\text{K}_2\text{S}_2\text{O}_8$) up to $48\text{mg}/\text{L}$, in which a reduction of UV absorbance and TOC occurred. The test D was performed under UV and TiO_2 conditions, which has the significant reduction of UV_{254} and TOC. The test E was done with the presence of UV irradiation, TiO_2 and PP. It was found from the test that both UV_{254} and TOC were reduced faster than that in Test A to D. Overall, the results of test A to E demonstrated that the UV irradiation, catalyst concentration and PP concentration were three essential parameters to control the FA oxidation efficiency.

3.2 Kinetic modeling for FA degradation

To describe the kinetics of the photocatalytic oxidation of FA, it was assumed that TOC removal rate follows the first-order kinetic model as shown in Eq.(1); the assumption being based on the case of low TOC concentration used in this study.

$$\frac{[TOC]_t}{[TOC]_0} = e^{-kt} \quad (1)$$

Where:

$[TOC]_0$: the initial total organic carbon of FA at time zero (mg/L),

$[TOC]_t$: total organic carbon of FA at time t (mg/L),

k : the first-order degradation rate constant.

Here, the rate constant (k) was considered being affected by several key factors of TiO_2 concentration, $K_2S_2O_8$ concentration (C) and light intensity (I). A pure empirical form of Eq.(2) was then used to present their relations :

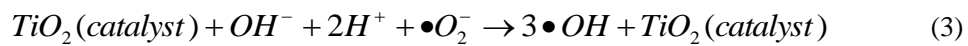
$$k = f(TiO_2, C, I) = m[TiO_2]^a [C]^b [I]^c \quad (2)$$

Where m, a, b, c are constants.

3.3 Effect of pH on FA oxidation rate

The effect of pH on the photodegradation of FA and the relationship between $\ln(TOC_t/TOC_0)$ and time (t) was displayed in Fig.6. It can be seen that the reduction of TOC concentration in FA solution is more efficient in acidic environment than that in the alkaline environment.

The overall photo-reaction can be described as Eq.(3) [9].



Equilibrium constant K_e was written as Eq.(4).

$$K_e = [\bullet OH]^3 / ([OH^-][H^+]^2[\bullet O_2^-]) \quad (4)$$

Since $[OH^-][H^+] = K_w = 1 \times 10^{-14}$, Eq. (4) can be rewritten as Eq.(5).

$$[\bullet OH]^3 = K_e K_w [H^+][\bullet O_2^-] \quad (5)$$

The concentration of $[\bullet OH]$ increases with an increased concentration of $[H^+]$ in the acidic

region. Thus, the photodegradation rate constant of FA was done more rapidly at pH 3.4 than at pH 10.3.

3.4 Effect of TiO_2 concentration on FA oxidation rate

The third set of test was carried out with the different TiO_2 concentration to investigate the effect of catalyst loading on the photocatalytic oxidation of FA solution at pH 6.5. The experiment demonstrated that the TOC concentration of FA decreased with the increase of TiO_2 concentration as shown in Fig. 7. Accordingly, a considerable increase of the rate constant with the increasing concentration of TiO_2 can be observed from Fig.7 till the value of 0.5g/L in TiO_2 to be reached. This can be interpreted as follows. As the amount of catalyst is increased, more catalyst particles and photons become available for adsorption; leading to more molecules of FA to be adsorbed. The density of particles in the area of illumination also increases and so the rate is enhanced. At the same time, due to an increase in the turbidity of the suspension, there is a decrease in UV light penetration as a result of increased scattering effect and hence the photoactivated volume of suspension decreases. Therefore, it is reasonable to infer that, beyond a certain level, additional particles could not be involved in catalyst activity and the rate constant would become slow down. It is proposed in this study that the exponential dependence of the first-order kinetic constant (k) on the TiO_2 concentration can be expressed as Eq. (6)

$$k = k_1[TiO_2]^a \quad (6)$$

Where a is constant and k_1 is the observed oxidation rate affected by the light intensity and $K_2S_2O_8$ concentration. According to experimental results, $k_1=0.0187\text{min}^{-1}$ and $a=0.9297(R^2=0.8832)$. Eq. (6) can be expressed in the form of:

$$k = 0.0187[TiO_2]^{0.9297} \quad (7)$$

3.5 Effect of $K_2S_2O_8$ on FA oxidation rate

Potassium peroxodisulphate ($K_2S_2O_8$) is a kind of oxidative and electron acceptor which has an important effect on photocatalytic oxidation of FA. The fourth set of test was conducted with varied $K_2S_2O_8$ concentration of 0, 12, 24, 48, 80 mg/L respectively at pH 6.5 while the light

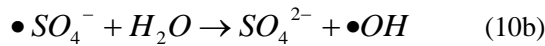
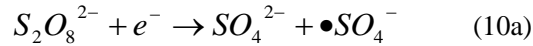
intensity of 0.75mW/cm² and TiO₂ concentration of 0.5g/L remain unchanged. The experimental results are shown in Fig. 8. It is seen from Fig. 8 that the addition of K₂S₂O₈ was an effective way to improve the photocatalytic oxidation of FA. When the concentration of K₂S₂O₈ was low, the increase of K₂S₂O₈ concentration made the rate constant of FA increased rapidly; when the concentration of K₂S₂O₈ reached up to 48mg/L, the rate constant of FA increased slightly. In this study, a relationship between C and k was proposed as the form in Eq. (8).

$$k = k_2[C]^b \quad (8)$$

Where k_2 and b are constants; C is the K₂S₂O₈ concentration. According to current experimental results, $k_2=0.0042\text{min}^{-1}$ and $b=0.2513$ ($R^2 = 0.8795$). So the above equation can be expressed as Eq. (9):

$$k = 0.0042[C]^{0.2513} \quad (9)$$

Addition of K₂S₂O₈ can effectively increase the rate constant of FA since the oxidation proceeds mainly through the formation of the strong oxidisings, i.e. $\text{SO}_4^{\cdot-}$ ($E_0=2.6\text{eV}$) and OH^{\cdot} species as shown in Eqs. (10a) and (10b) [10]. Potassium peroxodisulphate acts mainly as electron trap and hinders the recombination of electron/hole pairs and enhances greatly the photocatalytic oxidation reaction.



3.6 Effect of light intensity on FA oxidation rate

Fig. 9 illustrated the effects of light intensity on FA oxidation rate under the experimental conditions of TiO₂=0.5g/L, K₂S₂O₈=48mg/L, pH=6.5, and light intensity ranged from 0.75 to 2.36 mW/cm². The results from Fig.9 clearly show that the higher the intensity, the greater reaction rates for photocatalysis of FA. In this study, it was proposed that the rate constant affected by the light intensity can be expressed as Eq.(11):

$$k = k_3[I]^c \quad (11)$$

Where k_3 and c are constants. Computed data of current experiment shows that $k_3=0.0131$,

$c=0.4332$ ($R^2=0.9902$). So the above equation might be expressed as Eq.(12):

$$k_3 = 0.0131[I]^{0.4332} \quad (12)$$

Seen from Eq. (12), the degradation rate constant is proportional to the light intensity with the order about 0.4332, indicating that light intensity plays an important role in determining the rate constant.

3.7 Development of rate equation

A series of experiments were carried out in this study to assess the effects of key factors such as TiO_2 concentration, initial pH, $K_2S_2O_8$ concentration, light intensity on the FA degradation. From previous section, the values of a , b , c of 0.9297, 0.2513, 0.4332, respectively, have been determined. By substituting these values to Eq.(2), a comprehensive form of k can be obtained:

$$k = m[TiO_2]^{0.9297}[C]^{0.2513}[I]^{0.4332} \quad (13)$$

When photocatalytic oxidation of FA was under the conditions of $[TiO_2]=0.5g/L$, $K_2S_2O_8$ concentration=48mg/L, light intensity=0.75mW/cm² and $m=0.0112$, Eq.(1) can be arranged as Eq.(14).

$$\frac{[TOC]_t}{[TOC]_0} = e^{-0.0112[TiO_2]^{0.9297}[C]^{0.2513}[I]^{0.4332}t} \quad (14)$$

By using Eq. (14), the calculated results and the experimental results are plotted in Fig. 10. It is seen from Fig.10 that the results obtained from kinetic modeling are in good agreement with experimental data although the estimated value of TOC is slightly higher than the experimental data when the irradiation time is less than 60min and slightly lower than the experimental data when the time is more than 60min.

4. Conclusions

Experimental investigation in this study has demonstrated that the fulvic acid, a major component of NOM, can be degraded by UV radiation in the presence of TiO_2 -P25 as a photocatalyst in a photocatalysis-ultrafiltration reactor. The photocatalysis-ultrafiltration reactor can be considered as a convenient and efficient reactor for organic matters especially NOM

degradation. By examining the key factors including pH values, TiO_2 concentration, potassium peroxodisulphate and light intensity, it is clear that the increase of the $\text{K}_2\text{S}_2\text{O}_8$ concentration, catalyst concentration and light intensity can enhance the TOC removal and beneficially raise the first-order kinetic constant. A kinetic model of FA oxidation process was established to describe the relationship between rate constant (k) and these factors:

$$[TOC]_t = [TOC]_0 e^{-0.0114[\text{TiO}_2]^{0.9297}[\text{C}]^{0.2513}[\text{I}]^{0.4332}t}$$

The results obtained from the kinetic model are in good agreement with experimental data.

Acknowledgements

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Tables

Table 1 Design of the experiments

Test	Description	TiO ₂ concentration (g/L)	Light intensity (mw/cm ²)	PP ^a concentration (mg/L)	pH value
1	A (UV)	0	0.75	0	6.5
	B (TiO ₂)	0.5	0.75	0	6.5
	C (UV+PP)	0.5	0.75	48	6.5
	D (UV+TiO ₂)	0.5	0.75	0	6.5
	E (UV+TiO ₂ +PP)	0.5	0.75	48	6.5
2	pH=3.4	0.5	0.75	0	3.4
	pH=6.5	0.5	0.75	0	6.5
	pH=8.2	0.5	0.75	0	8.2
	pH=10.3	0.5	0.75	0	10.3
3	TiO ₂ =0	0	0.75	0	6.5
	TiO ₂ =0.25	0.25	0.75	48	6.5
	TiO ₂ =0.4	0.4	0.75	48	6.5
	TiO ₂ =0.5	0.5	0.75	48	6.5
	TiO ₂ =0.6	0.6	0.75	48	6.5
4	PP=0	0.5	0.75	0	6.5
	PP=12	0.5	0.75	12	6.5
	PP=24	0.5	0.75	24	6.5
	PP=48	0.5	0.75	48	6.5
	PP=80	0.5	0.75	60	6.5
5	I=0.75	0.5	0.75	48	6.5
	I=1.44	0.5	1.44	48	6.5
	I=2.36	0.5	2.36	48	6.5

PP^a: potassium peroxodisulphate

Figure Captions

Fig.1: The structure of fulvic acids

Fig.2: Schematic diagram of photocatalysis-ultrafiltration reactor

Fig.3: The UV-Vis spectrum profiles of fulvic acids

Fig.4: Changes of UV_{254} with time under different experimental conditions

Fig.5: Changes of TOC with time under different experimental conditions

Fig.6: Kinetic effect of pH value on photocatalytic oxidation of FA

Fig.7: Kinetic effect of PP concentration on photocatalytic oxidation of FA

Fig.8: Kinetic effect of TiO_2 concentration on photocatalytic oxidation of FA

Fig.9: Kinetic effect of light intensity on photocatalytic oxidation of FA

Fig.10: A comparison of the estimated data with the experimental data

Figures

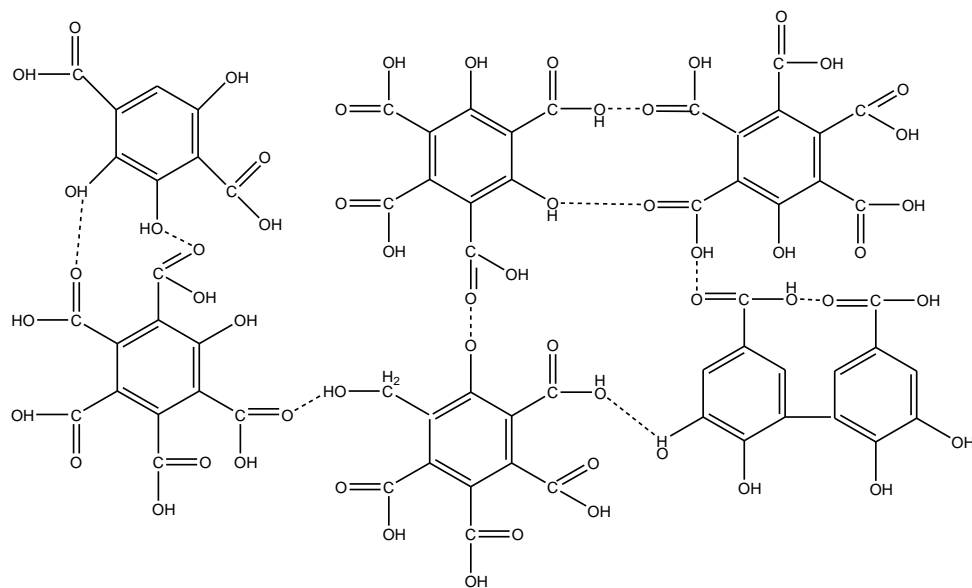


Fig.1. The structure of fulvic acids

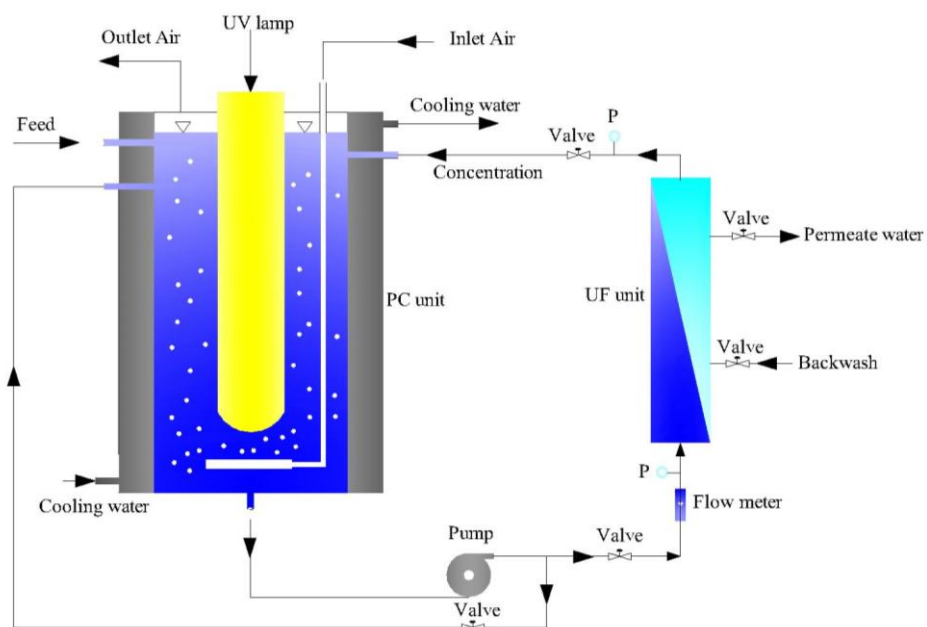


Fig.2. Schematic diagram of photocatalysis-ultrafiltration reactor

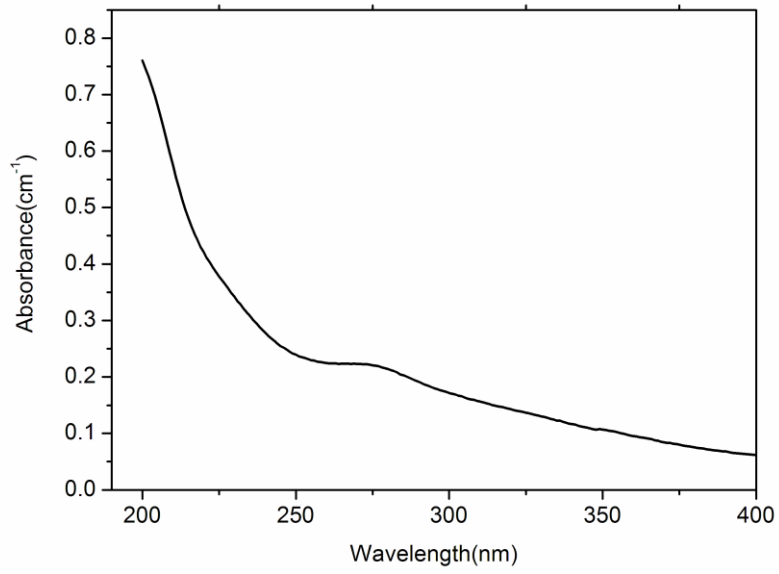


Fig.3. The UV-Vis spectrum profiles of fulvic acids

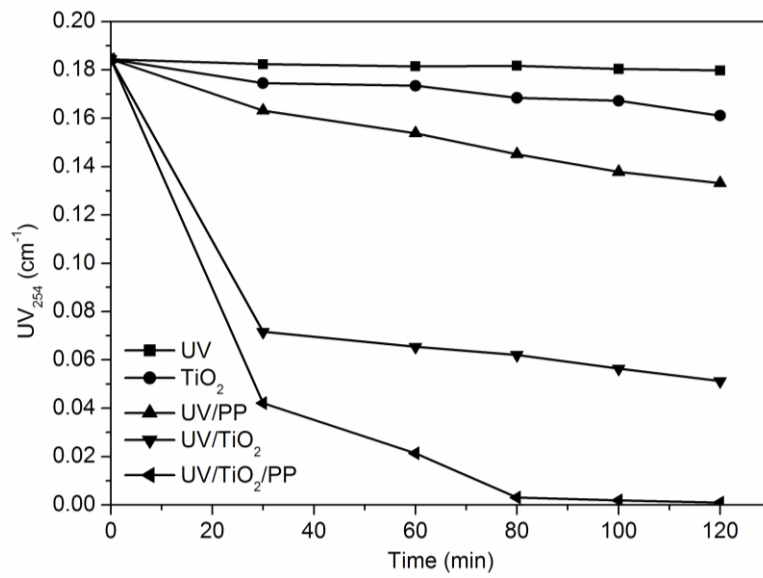


Fig.4. Changes of UV₂₅₄ with time under different experimental conditions

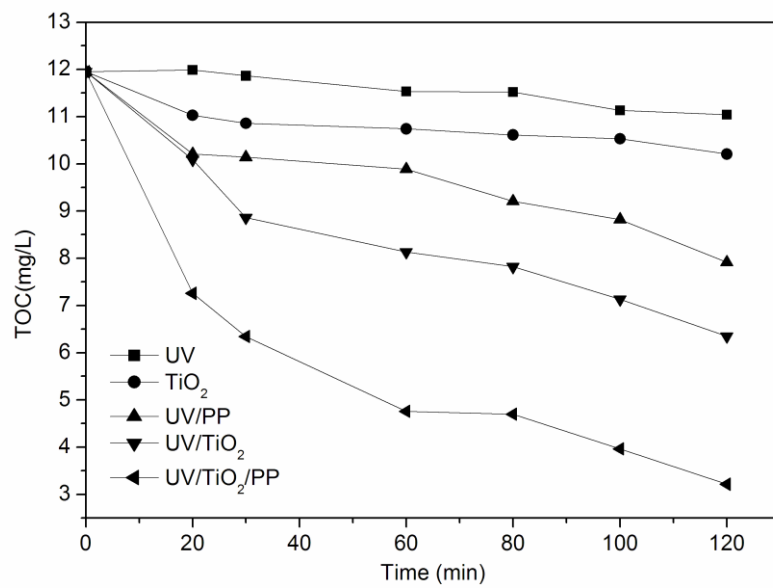


Fig.5. Changes of TOC with time under different experimental conditions

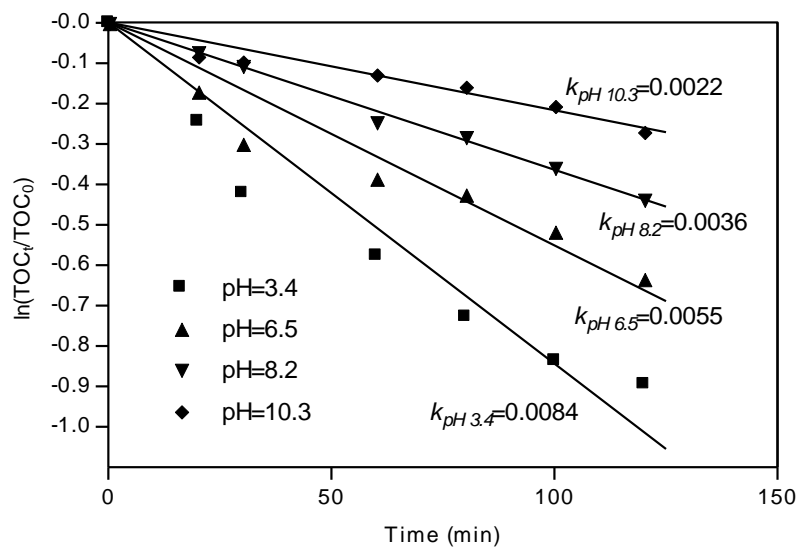


Fig.6. Kinetic effect of pH value on photocatalytic oxidation of FA
(TOC₀=11.95mg/L, TiO₂=0.5g/L, I=0.75mW/cm²)

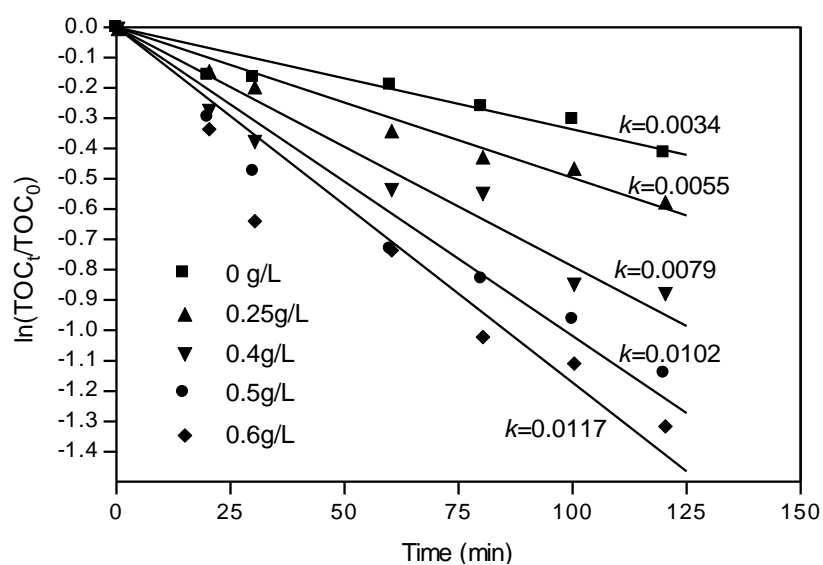


Fig.7. Kinetic effect of TiO_2 concentration on photocatalytic oxidation of FA
($\text{TOC}_0=11.95\text{mg/L}$, $\text{pH}=6.5$, $I=0.75\text{mW/cm}^2$, $\text{PP}=48\text{mg/L}$)

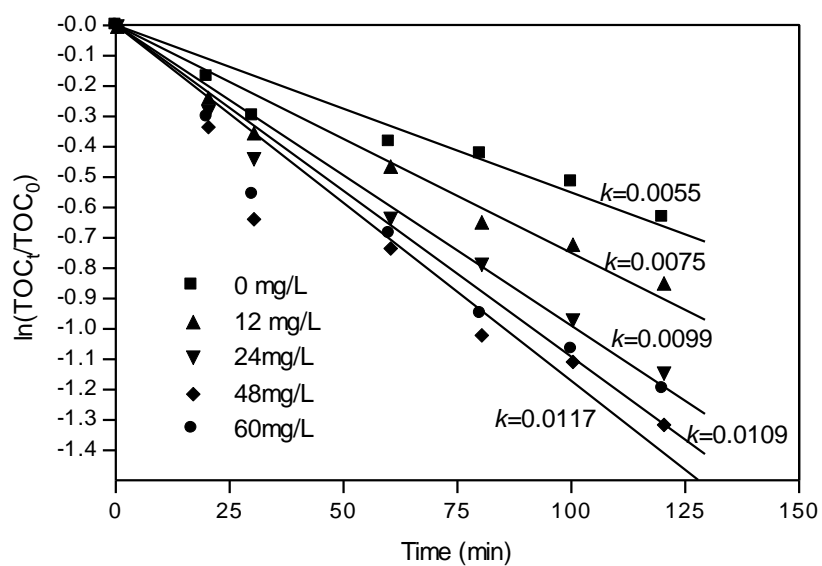


Fig.8. Kinetic effect of PP concentration on photocatalytic oxidation of FA
($\text{TOC}_0=11.95\text{mg/L}$, $\text{pH}=6.5$, $I=0.75\text{mW/cm}^2$, $\text{TiO}_2=0.5\text{g/L}$)

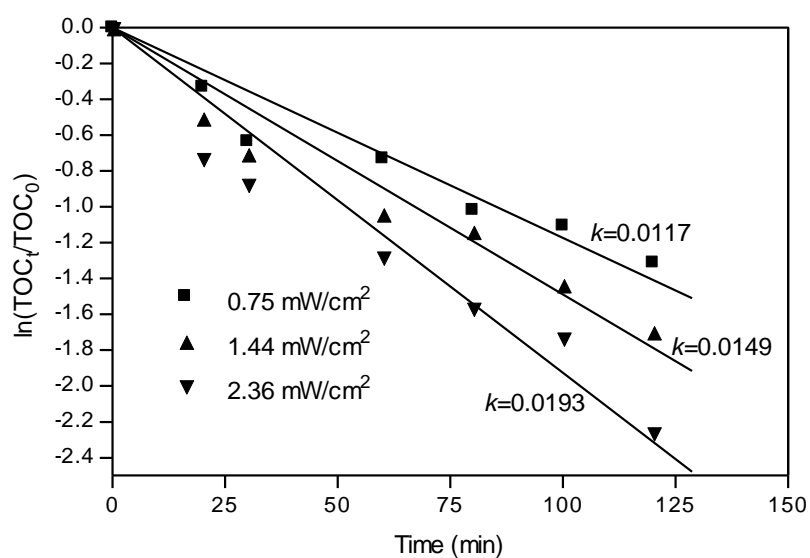


Fig.9. Kinetic effect of light intensity on photocatalytic oxidation of FA
 ($\text{TOC}_0=11.95\text{mg/L}$, $\text{pH}=6.5$, $\text{PP}=48\text{mg/L}$, $\text{TiO}_2=0.5\text{g/L}$)

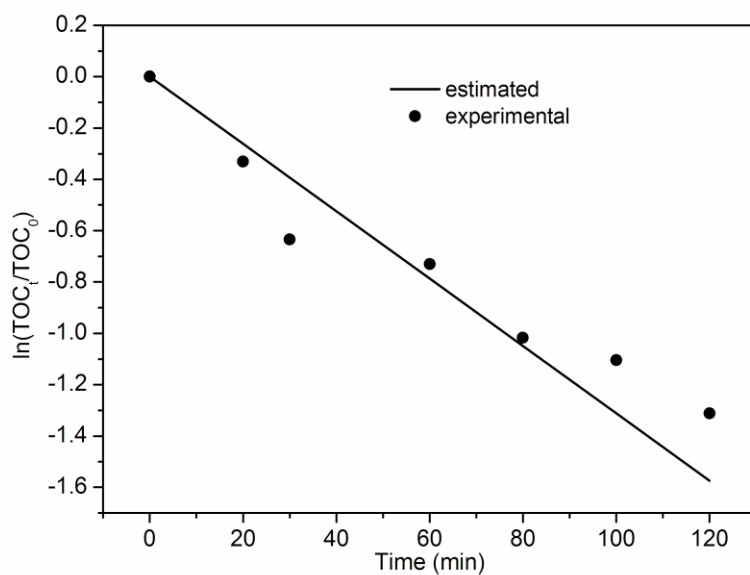


Fig.10. A comparison of the estimated data with the experimental data
 ($\text{TOC}_0=11.95\text{mg/L}$, $\text{pH}=6.5$, $\text{PP}=48\text{mg/L}$, $I=0.75\text{mw/cm}^2$, $\text{TiO}_2=0.5\text{g/L}$)