Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.20214

68 (2017) 107–113
March

Photocatalytic degradation of n-propanol wastewater by TiO_2 combined with Fenton reactions

Huiming Zeng, Liang Lv*, Rui Fan, Yulin Wang, Xiaoli Shen, Jianjun Chen, Jianguang Li

College of Chemical & Materials Engineering, Quzhou University, Zhejiang 324000, China, Tel. +86 570 8026667, Fax +86 570 8026667, email: 419051928@qq.com (H. Zeng), Lianglv_qzxy@126.com (L. Lv), 286289882@qq.com (R. Fan), 57185975@qq.com (Y. Wang), 942884865@qq.com (X. Shen), 408630041@qq.com (J. Chen), 7399385@qq.com (J. Li)

Received 25 January 2016; Accepted 4 September 2016

ABSTRACT

Photocatalytic degradation by ultraviolet (UV)/TiO_2 combined with Fenton reagent was employed in treating high concentration n-propanol solution. The influence of the TiO_2 dosage, the concentration of ferrous ion, the integral H_2O_2 dosage and the optimizing H_2O_2 adding program were investigated by a series of batch experiments. The increasing injection of the hydrogen peroxide during the reaction will make the reaction rate constant (k_1) 6.9% higher than the average injection when the integral H_2O_2 dosage is fixed. The optimized parameters of the combined process can be listed as follow: [Fe^{2+}] was 0.30 g/L, [TiO_2] was 0.08 g/L, and average [H_2O_2]b was 3.85 g/L (which was divided into six different parts, and the increasing gradient was 5%). After 6 h degradation under the ultraviolet (UV) photocatalytic irradiation, more than 88% removal of n-propanol was observed. When the wastewater is treated with the combined process, the degradation of n-propanol can be taken as the pseudo-first order reaction. Based on the experimental data, a semi-empirical model for estimating the reaction rate constant k_1 in cylindrical reactor was built, which will help to investigate the effect of system parameters and support further engineering design.

Keywords: Photocatalytic degradation; Fenton reactions; n-propanol; Kinetics

1. Introduction

N-propanol is a category of ubiquitous organic solvents [1,2] in chemical products, such as ink, coating [3], paint, and spice. Due to its excellent miscibility with water [4], a huge amount of wastewater containing n-propanol was produced from the cleaning procedure of the reacting containers in these chemical industries. Generally, the concentration of n-propanol in wastewater is higher than 1%. Conventionally, the biological treatment is considered as a typical process for the decontamination of natural organic matters. Unfortunately, the wastewater is difficult to be treated by activated sludge process. The difficulty is caused by the five characteristics of the wastewater: toxic impurity, high concentration, little amount, fluctuating flow and far discharge port from the sewage treatment plant. Though the organic matter, such as dye that is difficult to be degraded by biomass, can be treated through absorption by activated carbon (AC) [5,6], the process is still unsuitable for the wastewater with high organic molecule concentration due to the low capacity of AC.

Currently, advanced oxidation processes (AOPs) exhibits itself as a promisingly effective approach for treating organic industrial effluents which are not biodegradable, such as azo-dye in textile industry [7–9], colored coffee effluent [10,11], olive mill effluent [12], wastewater of chemical industries and pharmaceutical wastewater [13,14]. The main feature of AOPs is that the direct oxidants in the reaction system are hydroxyl radicals (·OH), which are mainly responsible for degradation and mineralization of organic pollutants into CO_2 and water. Recently, various AOPs, such as O_3/UV, O_3/H_2O_2, UV/H_2O_2, Fenton reagent, UV/Fenton and UV photo-catalysis [15–18], have been used to treat wastewater with high load of organic matters.

It is economic that the ultraviolet (UV) catalysis process (UV/TiO_2) produces hydroxyl radicals by UV light irradiat-

---

*Corresponding author.

ing the TiO_2 particles. Besides, it operates simply and runs without any toxic matters generation. However, the challenge for this technology is that the efficiency in producing ·OH radicals is still low. Many efforts have been made to intensify its ability to degrade the hardly-decomposed organic matters. Nevertheless, limited papers have been documented to study the effects composed of operating parameters for photo-reactors on degradation of n-propanol with high concentration by the hybrid process. Therefore, a better understanding of the oxidation procedure can lead to rational design and scaling up of photo-reactors.

In this study, a process combining UV/TiO_2 with Fenton reagent [Fe(II)/H_2O_2] had been designed for the fast degradation of n-propanol with small amount of oxidation agent. The synergies and impacts of the hybrid process were studied by a series of experiment, and the operating parameters were optimized by a mathematic model. Additionally, combining a simplified radiation emission model of the light source with a simplified radiation absorption-scattering model in the photo-reactor is very practical and useful for engineering design and scale-up [19]. To the best of our knowledge, no systematic investigation has been reported on the development of model for degradation of n-propanol by combining UV light photo-catalysis with Fenton process. The purpose of this study is to develop a model utilized to design an internal light irradiation slurry photo-reactor for the degradation of highly loaded n-propanol wastewater through the hybrid process. Effects of operating parameters, including the TiO_2 dosage, the concentration of ferrous ion, the integral H_2O_2 dosage and the optimizing H_2O_2 adding program, on the degradation rate of n-propanol have been systematically discussed. On the basis of the experimental data conducted with a range of operation conditions, the mathematic model was proposed to evaluate the performance of hybrid process for the treatment of n-propanol wastewater.

2. Experimental section

2.1. Materials

The hydrogen peroxide (H_2O_2, 30% solution) with analytical grade used as oxidant in the experiment was purchased from Juhua Co. (Zhejiang, China). The $FeSO_4{\cdot}7H_2O$ with analytical grade as the catalyst, n-propanel, potassium permanganate ($KMnO_4$), sulfuric acid, sodium hydroxide and silver sulfate were purchased from Sinopharm Co. (Beijing, China). The titanium dioxide nanometer particle (TiO_2, 99.8%, 10~25 nm anatase) was used as the photo-catalyst, which was purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). These chemicals were used without any further purification.

2.2. Experiments

The experiment was carried out in a stainless steel cylindrical column reactor, the diameter (D_T) and height of which are 0.06 m and 0.50 m, respectively. The working volume is 0.6 L. A 23 w low pressure mercury lamp (ZW23D15Y-Z436 CNLIGHT Co., China) was employed as the UV light source, which offered the radiation peak at 253.7 nm and 185 nm. The light intensity at light source per unit length for UV lamp, S_L, was 6.2 w/m. The mercury lamp was located in the center of the cylindrical column photo-reactor. The distance between the photo-reactor surface and the lamps was 0.0175 m. An air inlet and an outlet were fixed in the reactor and the air was bubbled through the aeration during the reaction. The flow rate of air generated by an aeration pump was 6.7 L/min.

2.3. UV photo-catalysis/Fenton reagent degradation procedure

All the experiments were conducted in the batch mode at room temperature. The 1% (v/v) 1-propanel solution was prepared with the ultrapure water in the experiment as the simulated wastewater. The temperature of the reactor was maintained at 20 ± 1°C. 600 mL of 1% (v/v) 1-propanel solution was placed in the reactor. The order of adding chemical in the experimental was shown as follows: Firstly, H_2O_2 was added to the simulated wastewater and then the pH was adjusted to 3 by adding a few drops of H_2SO_4. Subsequently, $FeSO_4{\cdot}7H_2O$ and TiO_2 were quickly added to the solution. Then the aeration pump and the UV light were turned on. Samples of the solution were taken by a gas-tight syringe hourly.

In this experiment, the main operation conditions are shown as follows: the adding programs of the hydrogen peroxide and the integral dosages of hydrogen dioxide, ferrous and TiO_2. As the degrading duration was long, the hydrogen dioxide was added sequently with an interval of 1 h, while the other reagents were added completely at the beginning. In order to investigate the effect of the hydrogen dioxide concentration on the degradation rate in the experiment, three different kinds of adding procedure had been tested when the integral H_2O_2 dosage and the content of other chemicals remained unchanged. After the optimized adding process of H_2O_2 had been selected, the various degree of H_2O_2 dosage, Fe^{2+} and TiO_2 had been optimized step by step while other conditions were kept constant.

2.4. Analytical method

The concentration of n-propanol was measured in term of COD_{Cr} following the Chinese national standard of GB11914-1989. It is worth noting that prior to the measurement, a series of pretreatment should be done to purify the sample: a few drops of diluted $KMnO_4$ solution was added in the sample to remove the residue of H_2O_2, then pH was adjusted to 7 with diluted NaOH solution to precipitate ferrous and the powder of TiO_2.

3. Theory

3.1. Mechanism

In advance oxidation processes (AOP), hydroxyl radicals (·OH) generated in aqueous solution by Photo-catalysis and Fenton reactions are responsible for the degradation of organic pollutants. The overall mechanism of photo-catalysis and Fenton reaction is shown in Reaction 1 to Reaction 4. At acidic conditions, the following photo-catalysis and Fenton reaction produces hydroxyl radical, which is a powerful oxidizer capable of degrading many organic compounds:

$$H_2O + O_2 + h\nu \xrightarrow{TiO_2} \cdot OH + HO_2 \cdot \tag{1}$$

$$H_2O_2 + Fe^{2+} \rightarrow \cdot OH + Fe^{3+} + OH^- \tag{2}$$

$$Fe(OH)_2^+ + h\nu \rightarrow Fe^{2+} + \cdot OH \tag{3}$$

$$H_2O_2 + h\nu \rightarrow 2 \cdot OH \tag{4}$$

where TiO_2 is UV photo-catalyst in the hybrid process, which produces two powerful oxidant: hydroxyl radial ($\cdot OH$) and peroxide hydroxyl radial ($\cdot HO_2$) in presence of UV irradiation and O_2. Fe^{2+} ion is another chemical catalyst in Fenton reaction, which produces hydroxyl radial ($\cdot OH$) as well via reacting with hydrogen peroxide (H_2O_2). Meanwhile, iron cycle from Fe(II) to Fe(III) was initiated by the UV light irradiation. Furthermore, Fe(III) ion and oxygen could carry off the electron from the surface of the TiO_2 particles, which could prevent the electron hole from reacting with electron so that the efficiency of photo-catalysis reaction can be improved. Hydroxyl radicals and hydroperoxide radials generated in Reactions 1, 2 and 3 can degrade target organic contaminants as well.

The rate and extent of the Fenton and UV photo-catalysis reactions mainly depends on operation parameters, namely light intensity, iron content, TiO_2 dosage, hydrogen peroxide dosage, and pH. According to Pignatello [20], the photo-Fenton reaction can be optimized at pH 2.8 where approximately half of the Fe(III) exists as the form of Fe^{3+} ions and half as Fe $(OH)_2^+$ ions. Iron element is cycled between divalent and trivalent states. In this case, Fe(II) would not be depleted. Therefore, the production of $\cdot OH$ radicals is only limited by the availability of light and H_2O_2. On the other hand, it is reported that in the illuminated TiO_2 system, the surface of catalyst is positively charged at pH values lower than 6.3. Electrostatic attraction between the surface of catalyst and the organic molecule occurs when the cationic organic compound is produced in reaction, it enhances the photo-degradation efficiency [21].

3.2. Kinetics

In this case, a model which is applicable for UV light irradiation and useful for design and scale-up of an internal light irradiation slurry photo-reactor has been developed. The model of photo-catalytic reactors consists of three sub-models: radiation field, mixing and reaction kinetics. For the radiation absorption in this study, the liquid-phase mixing was assumed to be homogeneous and the linear light source model with an absorption-scattering model was used. According to the model [22] provided to estimate the kinetics constant in photo-assisted Fenton degradation azo-dye Orange II, a first order kinetic model was applied, in which a first order kinetics constant, k_1, in Eq. (5) can be expressed in the following simple way:

$$k_1 = K\left[\left(C_{H_2O_2} - i\right)^a - b\left(C_{H_2O_2} - i\right)\right]\left(C_{Fe^{2+}} - c\right)^d \left(C_{TiO_2}\right)^f I_{ave}^g \quad \left(C_{H_2O_2} > i; C_{Fe^{2+}} > c\right) \tag{5}$$

where $C_{H_2O_2}$ total consume of hydrogen peroxide, $g \cdot L^{-1}$; $C_{Fe^{2+}}$ concentration of ferrous ion, $g \cdot L^{-1}$; C_{TiO_2} concentration of nanometer titanium dioxide particles, $g \cdot L^{-1}$: I_{ave} average UV light intensity, $W \cdot m^{-2}$; k_1 first-order reaction rate constant, h^{-1}.

The proportionality constants K, the exponents a, d, f and g were determined by the experimental data obtained in the arrangement of experimental conditions. As the peroxide hydrogen provided hydroxyl radical ($\cdot OH$) in the four ways given by Eq. (1)–(4), whose lives were in the range of 10^{-9} s and 10^{-8} s, there should be a minimum value of peroxide hydrogen concentration to improve the probability of the molecule's receiving irradiation or approaching to ferrous ion, and then to increase the degradation efficiency of the target organism. The minimum value was presented as i. Except for these two main ways, there was another pathway to consume peroxide hydrogen, which was self-decomposition in first-order reaction following Eq. (6). So the total loss in a certain interval time increased linearly with the increase of the $C_{H_2O_2}$, the slope was presented as b.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \uparrow \tag{6}$$

Because all of the ferrous ions were added in the initial stage of the reaction, some of them came into the cycle from Fe^{2+} to Fe^{3+} or $Fe(OH)_2^-$, and the loss of the concentration was denoted as c.

The average light intensity over the cross-sectional area of the internal irradiation cylindrical column photo-reactor, I_{ave}, can be obtained by proper integration of local light intensity, $I(r, \theta)$ as follows:

$$I_{ave} = \frac{1}{A}\int Ids = \frac{1}{A}\iint I(r,\theta) r dr d\theta = \frac{1}{\pi(R^2 - r_0^2)} \int_{r_0}^{R}\int_{0}^{2\pi} I(r,\theta) r dr d\theta \tag{7}$$

where $I(r, \theta)$ is a function of r and θ in the photo-reactor; r and θ as shown in Fig. 1 are the cylindrical radial and angle coordinate, respectively; A is the cross-sectional area of the photo-reactor. Considering the absorption of radiation by slurry solution, Lambert's law was used and he light intensity in the photo-reactor, $I(r, \theta)$ is written as:

$$\frac{I(r,\theta)}{I_0(r_0,\theta)} = \frac{r_0}{r}T \tag{8}$$

where $I_0(r_0, \theta)$ is a light intensity at the quartz tube of UV light. And the relationship of the light permeation ratio T is shown as follows:

$$I_0(r_0,\theta) = \frac{S_L}{2\pi r_0} \tag{9}$$

$$T = \exp\left(-\left(hC_{TiO_2} + jC_{Fe^{2+}}\right)(r - r_0)\right) \tag{10}$$

$$I(r,\theta) = \frac{S_L}{2\pi r}\exp\left(-\left(hC_{TiO_2} + jC_{Fe^{2+}}\right)(r - r_0)\right) \tag{11}$$

From Eq. (7) and Eq. (11), the value of I_{ave} can be calculated:

$$I_{ave}=\frac{S_L\left(1-\exp\left(-\left(hC_{TiO_2}+jC_{Fe^{2+}}\right)\left(R-r_0\right)\right)\right)}{\pi\left(hC_{TiO_2}+jC_{Fe^{2+}}\right)\left(R^2-r_0^{2}\right))} \qquad (12)$$

where S_L is light intensity at light source per unit length, W·m^{-1}.

4. Results and discussion

4.1. Optimizing the H_2O_2 adding program

The Fenton reagent in the combining process will produce more hydroxyl radials (·OH) when the concentration of hydrogen peroxide is increased. In the experiment, other conditions were unchanged: the concentration of n-propanol in the simulated wastewater was 1% (v/v), the total consumption of H_2O_2 during 6 h was 25.9 g/L, the concentration of Fe^{2+} was 0.44 g/L, TiO_2 was 0.4 g/L and the pH was adjusted to 3.

In order to accelerate the degradation, H_2O_2 was divided into 6 parts, and each was added into the reacting system in sequence at the beginning of each hour in the duration. Three programs were designed: Program A, there were two dosages, 4.54 g/(L·time) in the first 3 h and 4.09 g/(L·time) in the next 3 h; Program B, 5.45g/(L·time) was added at the beginning, and the next dosage was cut down by 0.45 g/L orderly; Program C, 3.20 g/(L·time) was added at the beginning, and the next dosage was increased by 0.45 g/L orderly. The effect of combining treatment to degrade the target organic matter was shown in Fig. 1. (the three tests were started at different points-in-time, the interval was 1 h the other series tests operated the same as the present).

It can be seen from Fig. 1 that the integral removal rate of n-propanol was between 80% and 90%, and the COD_{Cr} declined obviously in the different adding programs. Since the value of ln(COD_{Cr}) declined linearly as a function of reaction time, the degrading reaction could be described by pseudo first-order kinetics reaction:

$$r=\frac{d\left(COD_{Cr}\right)}{dt}=k_1COD_{Cr}\ \text{or}\ \ln\left(COD_{Cr}\right)=k_1t+b \qquad (13)$$

where k_1 is the first-order reaction rate constant; b is the initial value of ln(COD_{Cr}).

The COD_{Cr} was used to stand for the concentration of n-propanol in the simulated effluents. In the three tests, the value of k_1 was –0.26, –0.29 and –0.31, respectively. It was revealed that the reaction rate had been increased obviously by adding hydrogen peroxide in program C. The hybrid process for treating the organic wastewater provided hydroxyl radial (·OH) by two ways: one was produced by UV light irradiation and the other was produced by Fenton reagent. While the quantity of hydroxyl radial (·OH) produced by Fenton reagent was determined by the concentration of hydrogen peroxide and the cycle of ferrous ions. As indicated in Fig. 1, the slope of the line was larger when the concentration went up in program C, which means Program C is available for treating highly loaded organic wastewater by the hybrid process. Since the self-decomposition of hydrogen peroxide occurs, it is better to add the hydrogen peroxide by stages, and to keep the dosage of which growing orderly, to improve the degrading rate when the concentration of target organic matters declines.

4.2. The effect of the integral H_2O_2 dosage

In the combining process of UV photo-catalysis and Fenton reagent, the consumption of H_2O_2 determines the cost of treatment. The experimental condition is shown below: the average dosage of the H_2O_2 were 3.39 g/L, 4.30 g/L, 4.48 g/L and 4.73 g/L respectively in the four tests. The H_2O_2 was added six times, and the dosage increased by 5% from the average value, and other operation parameters were kept constant. The decline trends of the ln(COD_{Cr}) in feed water and the effect of H_2O_2 dosage were shown in Fig. 2.

The reaction rate constant(k_1) were –0.290 h^{-1}, –0.297 h^{-1}, –0.286 h^{-1} and –0.268 h^{-1} when the average dosage of H_2O_2 went up from 3.39 g/L to 4.73 g/L (shown in Fig. 2). The model predictive value fitted the experimental data well, of which the curve correlation ratio (R) were 0.9986, 0.9970, 0.9993 and 0.9972, respectively. Then, parameters including *a*, *b* and *i* in Eq. (5), were determined. According to the model, k_1 reached the peak value when the dosage of the H_2O_2 was

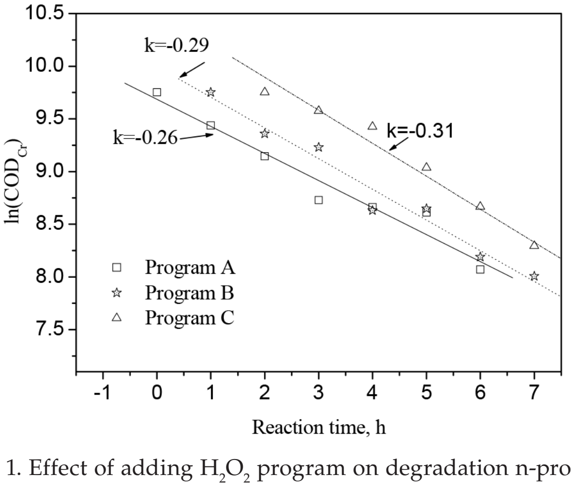

Fig. 1. Effect of adding H_2O_2 program on degradation n-propanol wastewater by TiO_2 combined with Fenton reagent ([n-propanol] = 1%(v/v); total [H_2O_2] = 25.9g/L; [Fe^{2+}] = 0.44g/L; [TiO_2] = 0.4g/L; the pH = 3).

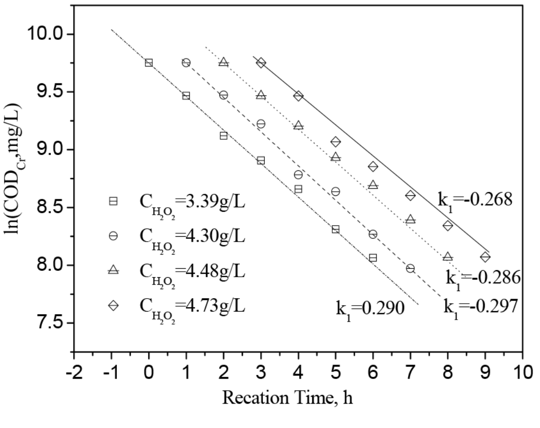

Fig. 2. Effect of H_2O_2 dosage on degradation n-propanol wastewater by TiO_2 combined with Fenton reagent ([n-propanol] = 1%(v/v); [Fe^{2+}] = 0.44g/L; TiO_2] = 0.4g/L; the pH = 3; the dosage of H_2O_2 increased by 5% of the average value).

adjusted to 4.30 g/L. It illustrated that the degradation was accelerated by increasing the concentration of the oxidant (H_2O_2) within a certain range; However, the self-decomposition effect of H_2O_2 would play a more important role when the average dosage of the H_2O_2 was higher than 4.30 g/L.

4.3. The effect of concentration of ferrous ion

In the Fenton reagent, Fe^{2+} is a chemical catalyst to produce ·OH radicals, whose concentration inferences the reaction rate to a certain extent, while excessive Fe^{2+} in the experimental solution may block the ultraviolet light. In the experiment, the effect of three Fe^{2+} dosages, 0.22 g/L, 0.44 g/L and 0.49 g/L, had been investigated, when the rest of the conditions were fixed: TiO_2 dosage was 0.4 g/L, H_2O_2 was added according to Program C with total dosage of 25.9 g/L. Decline of the ln(COD_{Cr}) and the effect of ferrous ions were shown in Fig. 3.

Fig. 3 shows that the degradation reaction rate constant k_1 had been obviously increased by adding 0.44 g/L ferrous ions, which was 7.5% higher than that with the ferrous dosage of 0.22 g/L and 4.3% higher than that with the ferrous dosage of 0.49 g/L. In addition, the parameters *c* and *d* in the model could be determined, then an optimized dosage (0.30 g/L) could be observed after mathematical analysis. This concentration of Fe^{2+} would be qualified to transfer electrons produced by the cycle from Fe^{2+} to Fe^{3+}, and to produce ·OH radicals to degrade target organic matter. The suitable dosage of Fe^{2+} would enhance UV photo-catalysis by limiting the loss of photo-generated positive hole at the surface of TiO_2 particles, which could be prevented from reacting with photo-generated electrons by absorbing the electrons in the cycle [21]. The UV light would also produce ·OH radicals in irradiation of iron carbonyl in wastewater and recover the ferrous as demonstrated in Eq. (3).

4.4. The effect of the TiO_2 dosage

The nanometer TiO_2 with 10–25 nm diameter had been chosen to serve as photo-catalyst in the experiment. Less or excessive catalyst would make reaction rate low, because less catalyst made lower irradiation efficiency while excessive suspending catalyst blocked the transformation of UV light. Thereby, a test had been designed to detect a suitable concentration of TiO_2 for this hybrid process, and the reacting conditions in the experiment were shown as follows: 0.3 g/L, 0.4 g/L and 0.5 g/L for the dosage of TiO_2, 0.44 g/L for Fe^{2+}, H_2O_2 was added according to Program C with the total dosage of 25.9 g/L. Declines of the ln(COD_{Cr}) and the effect of TiO_2 dosage were shown in Fig. 4.

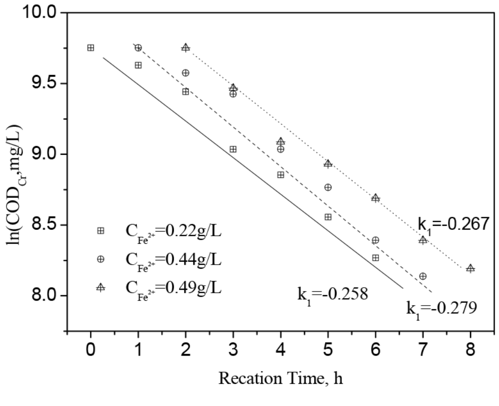

Fig. 3. Effect of Fe^{2+} concentration on degradation n-propanol wastewater by TiO_2 combined with Fenton reagent ([n-propanol] = 1%(v/v); [Fe^{2+}] = 0.44g/L; [TiO_2] = 0.4g/L; the pH = 3; total [H_2O_2] = 25.9 g/L, the dosage from 3.20 to 5.45 g/(L·time), increased by 0.45 g/L per hour).

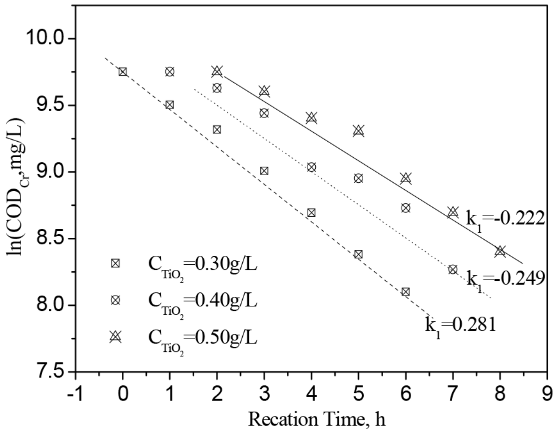

Fig. 4. Effect of TiO_2 dosage on degradation n-propanol wastewater by TiO_2 combined with Fenton reactions ([n-propanol] = 1%(v/v); [Fe^{2+}] = 0.44g/L; the pH = 3; total [H_2O_2] = 25.9 g/L, the dosage from 3.20 to 5.45 g/(L·time), increased by 0.45 g/L per hour).

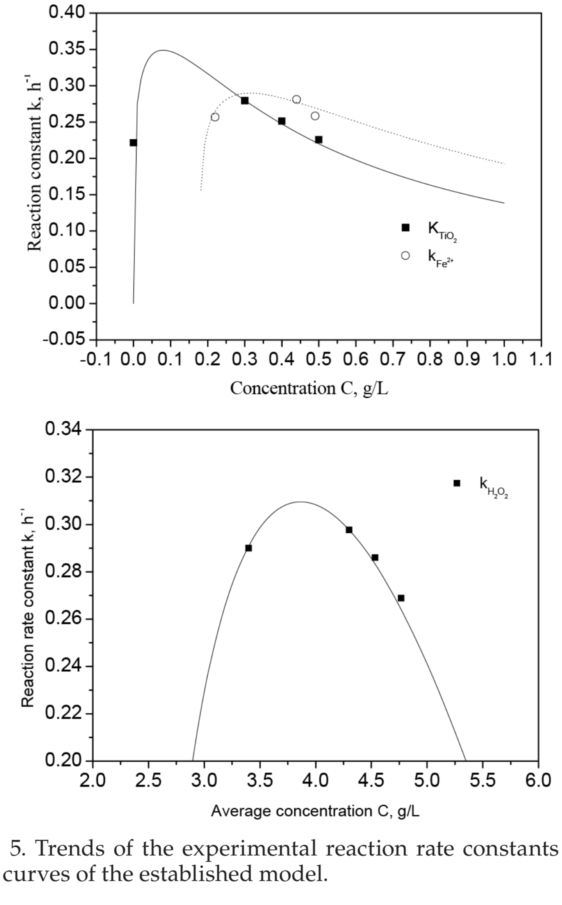

Fig. 5. Trends of the experimental reaction rate constants and the curves of the established model.

Table 1
Fitted values of the constants in Eq. (5) obtained from the present experimental data below

Parameters	Value
K	496.37
a	0.74
b	0.696
c	0.18
d	0.18
f	0.205
g	1.25
h	0.37
i	2.60
j	0.244

It could be found that the value of k_1 would decline because the particles of TiO_2 prevent the light from passing through. The value of k_1 was –0.281 h^{-1}, –0.249 h^{-1} and –0.222 h^{-1} when the concentration of TiO_2 was 0.3 g/L, 0.4 g/L and 0.5 g/L, respectively. The parameters f and g of the model could be ascertained and k_1 reached its peak at –0.35 h^{-1} when the concentration of TiO_2 was 0.08 g/L.

4.5. Fitted values of the constants in the semi-empirical model

The experimental data and the established model curves were shown in Fig. 5. Based on the calculated photo-reactor parameters and the experimental data, the fitted values were listed in Table 1.

The fitted curves concluded that the established model could describe the trends of the reaction rate constant k_1 as the operating parameters were changing. On the other hand, the model can help optimize the operating parameters: $[Fe^{2+}]$ = 0.30 g/L, $[TiO_2]$ = 0.08 g/L, and average $[H_2O_2]$ = 3.85 g/L, the dosage of H_2O_2 was divided into six different parts, and the gradient of increase was approximately 5%.

After the degradation of n-propanol throughout the duration of 6 h under a 23w low-pressure UV mercury lamp irradiation, higher than 88% of the removal efficiency can be observed. The duration was cut down by 96% compared with the biochemical process, whose duration would be about 6.25 d. And the cost can be determined by the consumption of H_2O_2, which was 48.6% lower than Fenton process (the consumption was 45 g/L when the COD_{Cr} removal of organic waste water was 15000 mg/L).

According to the formula $E = hc/\lambda$ and the quantity of the hydroxyl radicals produced by UV irradiation or consumed by the oxidization, the quantum efficiency of lamp is about 59%, where E is the power of a light quantum, λ was the wavelength of the light quantum (the wavelength of the low pressure mercury lamp was 254 nm (95%) and 185 (5%)), c was the speed of light, and h was the Plank constant with the value of 6.626×10^{-34} J·s.

4. Conclusions

After the discussion of the experimental results and the establishment of a semi-empirical model, following conclusion can be reached:

(1) The degradation reaction of the hybrid process complies with pseudo first order kinetics. The step-by-step increased dosage of the hydrogen peroxide can improve reaction rate constant k_1 by 6.9%, compared to the procedure of the balanced adding.

(2) The operation parameters of the hybrid process can be optimized according to the established model: $[Fe^{2+}]$ = 0.30 g/L, $[TiO_2]$ = 0.08 g/L, and average $[H_2O_2]$ = 3.85 g/L, the dosage of H_2O_2 was divided into six different parts, and the gradient of increasing dosage was about 5%. After the degradation throughout the duration of 6 h under a 23 w low-pressure UV mercury lamp irradiation, higher than 88% removal of 1% (v/v) n-propanol can be observed.

(3) The trends of the experimental reaction rate constant k_1 fit well with the curves described by the established model, which illustrate the effect of the concentration of H_2O_2, Fe^{2+} and TiO_2, the structure of reaction vessel, and the UV light irradiation.

Acknowledgements

This work was partially supported by the National Natural Science Foundation (NO.21271116, 21476127, U1607119), the Public Technology Research Program of Zhejiang Province (2013C31108, 2013C33018, 2015C33231), the State Key Laboratory of Chemical Resource Engineering (CRE-2015-C-113), the Science and Technology Department of Quzhou City, and the Young Teachers Scheme of Quzhou University (XNZQN201101, XNZQN201301).

References

[1] D.R. Delgado, F. Martínez, Preferential solvation of some structurally related sulfonamides in 1-propanol+ water co-solvent mixtures, Phys. Chem. Liq., 53 (2015) 293–306.
[2] Z. Cui, Y. Guo, T. Yin, D. Fan, P. Zheng, W. Shen, Liquid–liquid equilibria of 1-octyl-3-methylimidazolium hexafluorophosphate with 1-propanol or tert-butanol in the critical region, Fluid Phase Equilib., 365 (2014) 133–140.
[3] M. Popa, R.A. Mereu, M. Filip, M. Gabor, T. Petrisor, L. Petrisor, Highly c-axis oriented ZnO thin film using 1-propanol as solvent in sol–gel synthesis, Mater. Lett., 92 (2013) 267–270.
[4] Z. Nan, Z.C. Tan, Thermodynamic investigation on the azeotropic mixture composed of water + n-propanol + benzene. Thermochim. Acta, 413 (2004) 267–272.
[5] M. Ghaedi, A.G. Nasab, S. Khodadoust, R. Sahraei, A. Daneshfar, Characterization of zinc oxide nanorods loaded on activated carbon as cheap and efficient adsorbent for removal of methylene blue, J. Ind. and Eng. Chem., 21 (2015) 986–993.
[6] S. Khodadoust, M. Ghaedi, R. Sahraei, A. Daneshfar, Application of experimental design for removal of sunset yellow by copper sulfide nanoparticles loaded on activated carbon, J. Ind. Eng. Chem., 20 (2014) 2663–2670.
[7] D. Li, Y. Guo, C. Hu, C. Jiang, E. Wang, Preparation, characterization and photocatalytic property of the $PW_{11}O_{39}^{7-}$/TiO_2 composite film towards azo-dye degradation, J. Mol. Catal. A-Chem., 207 (2004) 181–191.
[8] I. Poulios, E. Micropoulou, R. Panou, E. Kostopoulou, Photooxidation of eosin Y in the presence of semiconducting oxides, Appl. Catal. B-Environ., 41 (2003) 345–355.
[9] M. Coca, M. Peña, G. González, Chemical oxidation processes for decolorization of brown-colored molasses wastewater. Ozone Sci. Eng., 27 (2005) 365–369.
[10] M. Tokumura, A. Ohta, Z.H. Znad, Y. Kawase, UV light assisted decolorization of dark brown colored coffee effluent by photo-Fenton reaction, Water Res., 40 (2006) 3775–3784.

[11] M. Tokumura, H.T. Znad, Y. Kawase, Decolorization of dark brown colored coffee effluent by solar photo-Fenton reaction: Effect of solar light dose on decolorization kinetics, Water Res., 42 (2008) 4665–4673.

[12] K. Kestioğlu, T. Yonar, N. Azbar, Feasibility of physico-chemical treatment and advanced oxidation processes (AOPs) as a means of pretreatment of olive mill effluent (OME), Process Biochem., 40 (2005) 2409–2416.

[13] L.A. Pérez-Estrada, S. Malato, A. Agüera, A.R. Fernandez-Alba, Degradation of dipyrone and its main intermediates by solar AOPs: identification of intermediate products and toxicity assessment, Catal. Today, 129 (2007) 207–214.

[14] T. An, H. Yang, G. Li, W. Song, W.J. Cooper, X. Nie, Kinetics and mechanism of advanced oxidation processes (AOPs) in degradation of ciprofloxacin in water, Appl. Catal. B-Environ. 94 (2010) 288–294.

[15] J. Feng, X. Hu, P.L. Yue, H.Y.Z. And, G.Q. Lu, Degradation of azo-dye Orange II by photo-assisted Fenton reaction using o novel composite of iron oxide and silicate nanoparticles as a catalyst, Ind. Eng. Chem. Res., 42 (2003) 2058–2066.

[16] H. Kusic, N. Koprivanac, A.L. Bozic, Minimization of organic pollutant content in aqueous solution by means of AOPs: UV- and ozone-based technologies, Chem. Eng., J. 123 (2006) 127–137.

[17] K.V.S. Rao, A. Rachel M. Subrahmanyam, P. Boule, Immobilization of TiO_2 on pumice stone for the photocatalytic degradation of dyes and dye industry pollutants, Appl. Catal. B-Environ., 46 (2003) 77–85.

[18] E. Neyens, J. Baeyns, A review of classic Fenton's peroxidation as an advanced oxidation treatment, J. Hazard. Mater., 98 (2003) 33–50.

[19] G.L. Puma, Dimensionless analysis of photocatalytic reactors using suspended solid photocatalysts, Chem. Eng. Res. Des., 83 (2005) 820–826.

[20] J.J. Pignatello, Dark and photo-assisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environ. Sci. Technol., 26 (1992) 944–951.

[21] S. Khodadoust, A. Sheini, N. Armand, Photocatalytic degradation of monoethanolamine in wastewater using nanosized TiO_2 loaded on clinoptilolite, Spectrochimi Acta Part A, 92 (2012) 91–95.

[22] M. Tokumura, H.T. Znad, Y. Kawase. Modeling of an external light irradiation slurry photoreactor: UV light or sunlight-photoassisted Fenton discoloration of azo-dye Orange II with natural mineral tourmaline powder, Chem. Eng. Sci., 61 (2006) 6361–6371.