

## Research Article

# Effects of KBr and KI on Photocatalytic Degradation of Dye W-7G with Nano-TiO<sub>2</sub> as Catalyst

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Received 14 October 2020; Accepted 26 December 2020; Published 11 January 2021

Academic Editor: Adel A. Ismail

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To investigate the influence of inorganic salt on the photocatalytic degradation, the effects of KBr and KI at various concentrations and pH values on the photocatalytic degradation of dye W-7G using nanoscaled titanium dioxide as photocatalyst in a bubbling fluidized bed photocatalytic reactor (BFBPR) were studied. The results indicated that the degradation apparent rate constant ( $K_{app}$ ) of the system with KI was clearly higher than that with KBr under acidic or alkaline conditions. And the maximum value of  $K_{app}$  (0.01127) appeared at the KI concentration of 0.075 g L<sup>-1</sup> with a pH value of 9.37, meaning the highest degradation efficiency. Furthermore, the possible mechanism of photocatalytic degradation of W-7G in the presence of KBr and KI was proposed, which could provide a theoretical support for the further study of inorganic salt effects on the photocatalytic degradation of dyes.

## 1. Introduction

Because of the complex structure of most reactive dyes, there are many side reactions in the production process, so the rapid degradation of dye wastewater is urgently required. The question has attracted extensive attention of experts and scholars in the field of environment [1]. In recent years, in order to improve the catalytic activity and efficiency of TiO<sub>2</sub> photocatalyst, many research teams developed a variety of new TiO<sub>2</sub>-based photocatalysts and improved the utilization rate of photocatalyst materials to light, mainly studying the influence of catalyst modification on degradation, such as doping modified nano-TiO<sub>2</sub> catalyst and supported nano-TiO<sub>2</sub> catalyst [2, 3].

However, some studies proved that the factors affecting the efficiency of photocatalytic degradation system needed also consider the initial dye concentration, light intensity, initial pH, and salt effect [4]. By changing the amount of

photocatalyst, the pH value, and the initial concentration of the solution, the photocatalytic degradation rules of the two disperse dyes were discussed. The photocatalytic degradation kinetics of the two dyes were studied by the Langmuir-Hinshelwood mechanical formula. The effects of inorganic salts, such as KBrO<sub>3</sub>, KClO<sub>3</sub>, KIO<sub>3</sub>, NaSO<sub>4</sub>, and NaCl, on the degradation kinetics of dyes were further studied [5]. The mechanism of the photocatalysis reaction was put forward, in which the halogen free radicals participated on the basis of studying and analysing the basic mechanism of TiO<sub>2</sub> photocatalysis reaction: when the halogen ions are adsorbed on the catalyst surface, it can capture the photogenerated holes to generate halogen free radicals with high oxidation potential, leading to stimulating the free radical chain reaction of organics to make them degrade rapidly [6]. The conversion of bromine was studied by using the lowest and highest oxidation states Br<sup>-</sup> as the starting compound [7]. It was found that the

pH value affected the conversion of bromine species, because it affected the adsorption of reactants on photocatalysts and controlled the content of  $H^+$  and  $OH^-$  ions in aqueous solutions. Under the condition of strong acidity ( $pH = 1.5$ ), the photocatalytic oxidation of bromine was dominant, while under the condition of strong basicity ( $pH = 13.5$ ), the photocatalytic oxidation and reduction of bromine were inhibited. The degradation process of sulfon-rhodamine B (SRB) in visible light was studied by separating and identifying the intermediate products of diethylation and adding iodine ions as a probe to study the specific mechanism of visible light photocatalysis [8]. The results showed that adding salt solution to the photocatalytic degradation system affected the degradation kinetics and mechanism of the system. However, the study of adding salt to the photocatalytic degradation system lacked systematic analysis, and there was no systematic correlation analysis between the degradation rate constant ( $K_{app}$ ) of photocatalytic degradation and the amount of inorganic salt added [9].

In this case, the effects of inorganic salts KBr and KI on the degradation kinetics of the reactive light-yellow dye of W-7G were studied in an annular coaxial double-cylinder-type reactor (BFBPR) using nano- $TiO_2$  as a photocatalyst. According to the change trends of apparent constant curve of photocatalysis, the main reasons influencing the photocatalytic degradation were deduced, and the possible mechanism of photocatalytic degradation of salt was proposed.

## 2. Experimental Section

**2.1. Materials and Reagents.** Reactive light-yellow dye W-7G with sulfonic group in molecular structure was supplied by Weifang No.2 Printing and Dyeing Plant and used without purification, the maximum absorption wavelength of W-7G solution was 400 nm, and the standard curve under the maximum absorption wavelength was  $A = 21.1441C_t - 0.0634$ . Nano- $TiO_2$  photocatalyst (Degussa P25, with 21 nm primary particle size) was purchased from Degussa Shanghai Branch. Concentrated sulfuric acid ( $H_2SO_4$ , 98.08%), sodium hydroxide (NaOH, AR grade), potassium bromide (KBr, 99%), and potassium iodide (KI, 99%) were supplied by Jiuding Chemical Technology Co., Ltd (Shanghai, China) and used without purification.

**2.2. Photocatalytic Experimental Device.** Photocatalytic experiments were carried out with nano- $TiO_2$  as the photocatalyst in BFBPR, lasting for 2 h in UV light (254 nm maximum emission intensity, 25 W, Shanghai Europe Cheng Industrial Co., Ltd). During the photocatalytic process, samples were taken to determine the absorbance at 20 min interval. The designed reactor consists of an external circulation pump, air pump, circulation tank (working volume includes tube volume, 5 L), tube type, gas distributor, nylon mesh (600 mesh), reaction area in the middle part (1.1 L – maximum working volume  $\times$  500 mm high  $\times$  distance inner wall of the synthetic glass tube and outer wall of quartz

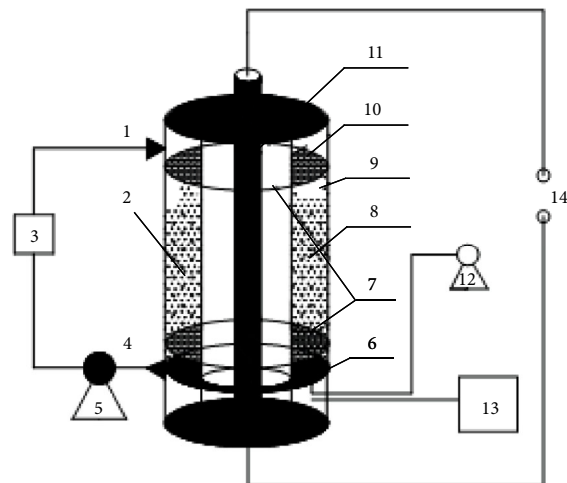


FIGURE 1: Schematic diagram of annular BFBPR. ((1) Sample solution inlet; (2) Catalyst particles; (3) Sample reservoir; (4) Sample solution outlet; (5) Solution circulation pump; (6) Pipe-type gas distributor; (7) Nylon mesh; (8) Reaction pool; (9) Synthetic glass tube; (10) Pyrex glass tube; (11) UV-light; (12) Gas pump; (13) Sampling pore and pH Detector; (14) Electrical source).

glass tube is 10 mm), and internal ultraviolet of the lamp as shown in Figure 1 [10].

**2.3. Experimental Steps and Analysis Methods.** The solution of dye W-7G containing catalyst was circulated for 60 min to achieve adsorption equilibrium [10], and the absorbance of W-7G solution under adsorption equilibrium state was measured with a UV-vis spectrophotometer (T6 ultraviolet-visible spectrophotometer, Beijing spectral analysis instrument Co., Ltd). The obtained data were processed by Origin software, and the maximum absorption wavelength of the solution was determined. The solution of W-7G dye with different gradient concentration was divided equally into five parts, and the catalyst was added to get an appropriate concentration of  $1.5207 g L^{-1}$ . Because there was adsorption on the surface of catalyst particles, the proper content of  $TiO_2$  could produce more active centers, increase the solid-liquid contact surface, and accelerate the photocatalytic degradation reaction rate [11]. In BFBPR device, the irradiation catalysis reaction was carried out, and the absorbance was measured at 20 min interval. According to the obtained data of absorbance, the degradation rate curve was obtained, and the optimal initial concentration of photocatalytic degradation dye was determined. Thus, the optimum dosage and pH value could be determined.

Under the optimum conditions of dye concentration, catalyst dosage, and pH value, KBr and KI salt solution were added and the above operations were repeated. In a certain concentration range, the absorbance had a linear relationship with the solution concentration ( $C$ ). Therefore, the dye concentration could be calculated by measuring the absorbance. According to Lambert's law, the degradation rate of dye was calculated by the relationship

between absorbance and concentration (Formula (1)). To eliminate the experimental error, the experiment was repeated three times with the relative error being less than 2%.

$$\text{Decomposition efficiency, } \eta(\%) = \frac{C_0 - C_t}{C_0} \times 100\% = \frac{A_0 - A_t}{A_0} \times 100\%, \quad (1)$$

where  $C_0$  and  $C_t$  are the initial and  $t$ -minute concentration of the dye;  $A_0$  and  $A_t$  are the initial and  $t$ -minute absorbance of the dye solution, respectively [10].

### 3. Results and Discussion

**3.1. Effect of pH Value.** The influence of pH on the photocatalytic degradation of dye W-7G is complex. Different pH values of medium can produce a great influence on the activity of nano-TiO<sub>2</sub>, including the valence state of the particles, the degree of reunion, and the position of the conduction band and valence band [12]. In this experiment, W-7G was photocatalytic degraded in the range of pH values from 2.42 to 12.05 [13–16].

The dynamic regression curves of photocatalytic degradation with various pH values are shown in Figure 2(a). It could be seen that the curves of  $\ln(C_0/C_t)$  and  $t$  changing with pH value were ideal straight lines with the correlation coefficient higher than 0.9. Figure 2(b) exhibits the curve of apparent reaction rate coefficient data calculated by ORIGIN software, from which the first-order reaction kinetics fitting of  $\ln(C_0/C_t) - t$  relationship of photocatalysis under different pH conditions was carried out. Under acidic conditions, an extreme value of the maximum degradation rate constant was found, which indicated that there existed maximum degradation efficiency. While under alkaline conditions, only a minimum extreme value appeared. From the results, it could be deduced that the pH value had an impact on the photocatalytic degradation of W-7G and the photocatalytic degradation efficiency of TiO<sub>2</sub> in acid medium was higher than that in alkaline medium.

In theory, the pH value can affect the surface charge of the catalyst to affect the adsorption of the dye, for the pH value can determine the surface charge, the degree of ionization and adsorption form of catalyst. The existence of hydrogen ions and hydroxyl ions affects the adsorption of other ions in varying degrees [10]. The point of zero charge (PZC) of TiO<sub>2</sub> is 6.4, and the protonation and deprotonation (Eqns. (2) and (3)) occur in an acidic and alkaline environment, respectively [12]. Under acidic and neutral conditions, hydrogen protons are easily accepted to form positive charge in the catalyst, and under the strong electrostatic attraction, W-7G molecules are easily adsorbed on the surface of TiO<sub>2</sub> through ion groups [11]. At the same time, H<sup>+</sup> linking catalyst adsorption sites and dye functional groups play a “bridge” role, and the W-7G active functional groups enhance its affinity with the photocatalyst surface adsorption sites [5]. However, in the alkaline condition, the functional groups of dye molecules undergo deprotonation reaction with the increase of solution concentration; thus, the electro-

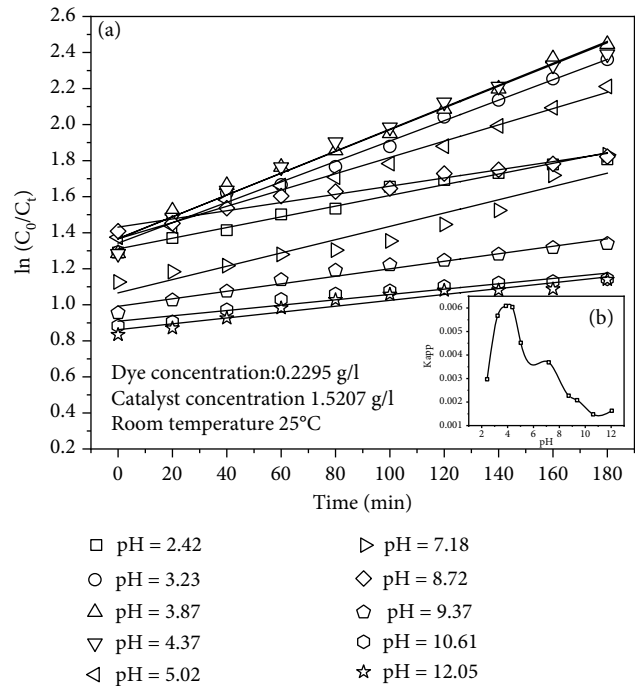
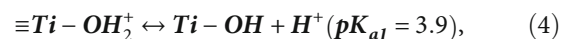
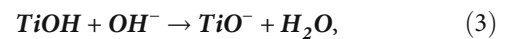
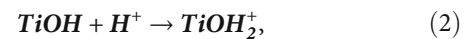
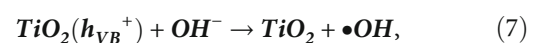
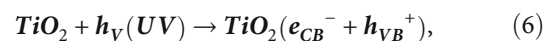


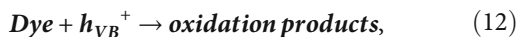
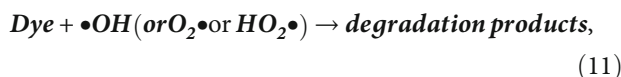
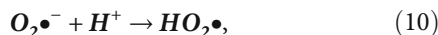
FIGURE 2: Regression curves and the corresponding results for degradation of W-7G at various pH values. (a) Kinetic regression curves. (b) Apparent reaction rate coefficients curve of photocatalytic degradation.

static repulsion between catalyst and dye molecules is not conducive to adsorption, which results in a decline in the adsorption rate and photocatalytic degradation efficiency.



On the other hand, pH value affects the generation of free radicals. During the reaction of photocatalytic degradation of dye W-7G by TiO<sub>2</sub>, there are free radical reaction and hole direct oxidation reaction steps. Under the irradiation of UV lamp, TiO<sub>2</sub> semiconductor can be excited and can produce photogenerated electron-hole pairs. The positive hole reacts with OH<sup>-</sup> or H<sub>2</sub>O to form OH radicals (Eqns. (7) and (8)), and the conduction band electrons react with O<sub>2</sub> when it is adsorbed on the surface of TiO<sub>2</sub> or dissolved in solution to form the superoxide anion radical O<sub>2</sub><sup>-•</sup> (Eqn. (9)), and then O<sub>2</sub><sup>-•</sup> follows to react with H<sup>+</sup> in solution to form radical HO<sub>2</sub><sup>•</sup> (Eqn. (10)). The free radicals (O<sub>2</sub><sup>-•</sup>, HO<sub>2</sub><sup>•</sup>, and •OH) and  $h_{VB}^+$ , e<sup>-</sup> produced by the above reactions can oxidize and degrade organic molecules (Eqns. (6), (11), (12) and (13)) [11, 17].





Therefore, it could be speculated that the main reason for the mechanism change was the positive hole oxidation at acidic pH value and the free radical oxidation at neutral or alkaline pH value.

**3.2. Effect of Salt KBr Addition on Dye Degradation.** The photocatalytic degradation of W-7G dye with the existence of KBr could make the photocatalytic degradation system produce salt effect, which inevitably affected the efficiency of photocatalytic degradation. Because the salt could affect the adsorption and weaken the hole oxidation, the high adsorption efficiency of anionic dyes was found by studying the photocatalytic degradation of anionic dyes K-2BP and X3B on  $\text{TiO}_2$ , and an adsorption model, which was the change of the double electric layer on the solid electrolyte interface, was proposed to explain the effect of salt addition on the adsorption-desorption process [10, 17]. According to the amphoteric characteristics of  $\text{TiO}_2$  (Eqns. (2) and (3)), it was found that the surface of  $\text{TiO}_2$  could form positive or negative charges. Therefore, the adsorption of dye on  $\text{TiO}_2$  surface was favourable under the condition of pH value of 5-6.

The effect of KBr on the apparent rate constant of the photocatalytic reaction is displayed in Figure 3, which is based on the data in Tables 1 and 2. In acidic condition, when the concentration of KBr ranged from 0 to  $0.072 \text{ g L}^{-1}$ , and the rate constant of photocatalytic degradation was lower than the rate constant ( $K_{\text{app}} = 0.00604$ ) without salt, indicating a restraining effect. In the alkaline condition, when the concentration of KBr was respective 0- $0.035 \text{ g L}^{-1}$  and  $0.035$ - $0.072 \text{ g L}^{-1}$ , the rate constant was first higher and then lower than the rate constant ( $K_{\text{app}} = 0.00208$ ) without salt, and the "turning point" in the curve indicated that KBr had a promoting effect at low concentration ( $0$ - $0.035 \text{ g L}^{-1}$ ) and restraining effect at high concentration ( $0.035$ - $0.072 \text{ g L}^{-1}$ ). In addition, the maximum value of  $K_{\text{app}}$  ( $0.0028$ ) was found when the concentration of KBr was about  $0.015 \text{ g L}^{-1}$  at  $\text{pH} = 9.37$ , meaning the better degradation efficiency.

Theoretically,  $\text{Br}^-$  could not only compete for adsorption but also induce free radical reactions. The redox potential of bromine was  $2.0 \text{ V}$  vs. NHE, which had a strong ability of photogenerated hole formation. The different concentration ranges of  $\text{Br}^-$  presented different effects on the photocatalytic degradation of dye W-7G, showing different trends [6]. Due to the competitive adsorption of  $\text{Br}^-$  on the surface, the Ti-Br complex formed on the catalyst surface was gradually significant

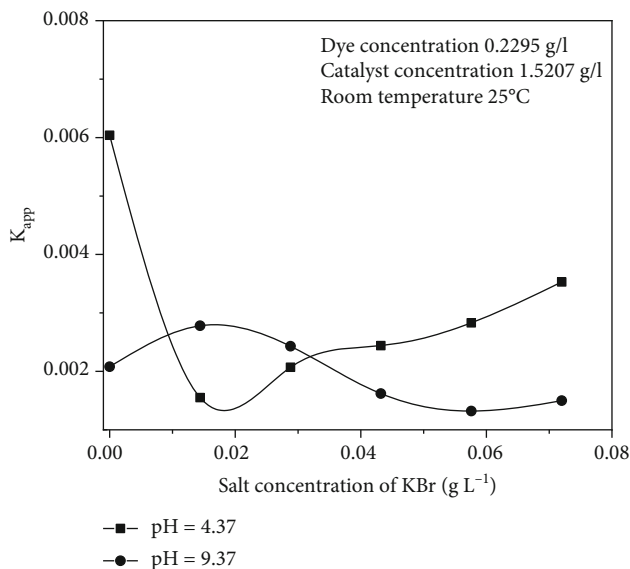
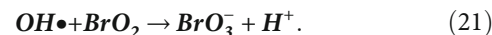
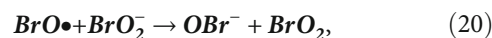
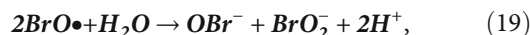
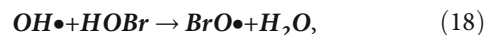
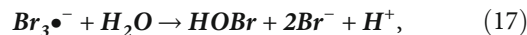
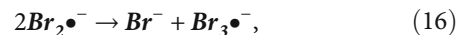
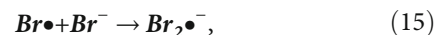


FIGURE 3: Effect of KBr on the apparent rate constant of photocatalytic reaction.

with the increase of concentration and ionic strength, presenting an inhibition effect (Figure 4) [18, 19]. However, in acidic conditions, with the increase of the salt concentration, the curve of the photocatalytic degradation rate constant showed an upward trend of the "inflection point." Because the  $\text{Br}^-$  adsorbed on the inner surface of the catalyst was easy to directly capture photogenerated holes and produced free radicals with high oxidation potential, which led to the chain reaction of free radicals. Therefore, the capture of hydroxyl radicals by  $\text{Br}^-$  (Eqn. (14)) and the promotion of the reaction by  $\text{Br}$  (Eqn. (15)) were a pair of competitive relationships [6, 7]. However, in the alkaline condition, the adsorption of  $\text{Br}^-$  on the surface of the catalyst was not obvious, but the reaction rate of  $\text{Br}^-$  with hydroxyl radical was higher ( $1 \times 10^9 \text{ m}^{-1} \text{ s}^{-1}$ ), so only a small amount of KBr addition could produce a promoting effect.



Therefore, it could be inferred that the addition of KBr in photocatalytic degradation had the double effects of surface adsorption, hole oxidation, degradation, and free radical mechanism degradation. On the one hand, the surface

TABLE 1: Fitting results of first-order reaction kinetics under acidic condition (pH = 4.37).

KBr (g L <sup>-1</sup> )	Fitting formulas	First-order reaction kinetic constant K (min <sup>-1</sup> )	Correlation coefficient (R <sup>2</sup> )
0	$\ln(C_0/C_t) = 0.00604t + 1.36779$	0.00604	0.98436
0.0144	$\ln(C_0/C_t) = 0.00155t + 0.79474$	0.00155	0.99189
0.0288	$\ln(C_0/C_t) = 0.00207t + 0.87837$	0.00207	0.97875
0.0432	$\ln(C_0/C_t) = 0.00244t + 0.89171$	0.00244	0.89722
0.0576	$\ln(C_0/C_t) = 0.00283t + 0.88031$	0.00283	0.94853
0.0720	$\ln(C_0/C_t) = 0.00353t + 1.05364$	0.00353	0.95490

TABLE 2: Fitting results of first-order reaction kinetics under alkaline condition (pH = 9.37).

KBr (g L <sup>-1</sup> )	Fitting formulas	First-order reaction kinetic constant K (min <sup>-1</sup> )	Correlation coefficient (R <sup>2</sup> )
0	$\ln(C_0/C_t) = 0.00208t + 0.99176$	0.00208	0.96747
0.0144	$\ln(C_0/C_t) = 0.00278t + 1.22230$	0.00278	0.97101
0.0288	$\ln(C_0/C_t) = 0.00243t + 1.21928$	0.00243	0.99151
0.0432	$\ln(C_0/C_t) = 0.00161t + 1.24956$	0.00161	0.93309
0.0576	$\ln(C_0/C_t) = 0.00132t + 1.29398$	0.00132	0.97764
0.0720	$\ln(C_0/C_t) = 0.00150t + 1.25826$	0.00150	0.98579

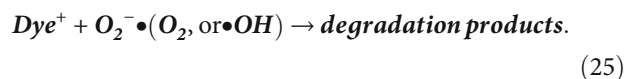
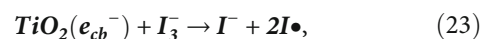
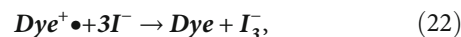
adsorption of catalyst affected the photocatalytic efficiency. Br competitive adsorption on the TiO<sub>2</sub> surface reduced the contact probability between dye and catalyst, which led to the weakening of the reaction mainly on the catalyst surface. On the other hand, with the increase of KBr addition, the solution ion strength increased, and the TiBr complex formed on the catalyst surface was gradually significant. Because the bromine ions (bromic acid and ions) adsorbed on the inner layer of the catalyst surface were easy to capture the photogenerated holes and generate free radicals with high oxidation potential, which could cause free radical chain reaction. In addition, there were transformations of the lowest oxidation state Br<sup>-</sup> and the highest oxidation state BrO<sub>3</sub><sup>-</sup> into bromine in the system. HOBr was formed by OH<sup>•</sup> oxidation of hydrogen bromide, which was finally oxidized to brominated BrO<sub>3</sub><sup>-</sup> (Eqns. (16), (17), (18), (19), (20) and (21)) [7]. Therefore, it showed a downward trend in the alkaline condition. Because the addition of a small amount of KBr was conducive to stimulate the formation of free radicals, participate in the free radical reaction in the solution [20, 21]. However, with the increase of KBr concentration, the deg-

radation rate constant changed from higher to lower than that without salt [20, 21].

In sum, the degradation rate was not affected by its actual position in the photocatalytic degradation process, whether it was in solution or on the photocatalyst or on another “inert” carrier. Because there was a relaxation transformation from hole oxidation to free radical oxidation in the reaction system, the exchange of these compounds between the two carriers could contact the catalyst quickly. The surface of the reaction site was easy to degrade, which had been confirmed by the theory proposed by Minero [10, 22].

**3.3. Effect of Salt KI Addition on Dye Degradation.** Similarly, there was competitive adsorption of I<sup>-</sup> on the surface of TiO<sub>2</sub> catalyst. In the TiO<sub>2</sub> photocatalytic dye degradation system, I<sup>-</sup> was adsorbed on the catalyst surface and oxidized to I<sub>3</sub><sup>-</sup> by dye cation free radical, the dye with positive ion radicals returning to the ground state (Eqn. (22)), so the overall inhibition appeared. The existence of I<sup>-</sup> slowed down the charge recombination between the dye-positive ion radicals and the conduction band electrons and promoted the formation of O<sub>2</sub><sup>-•</sup> [8]. Furthermore, I<sup>-</sup> could recover the positive ion radicals of dye, which made the concentration of dye radicals on the catalyst surface very low. Meanwhile, the increased O<sub>2</sub><sup>-•</sup> was a very strong nucleophilic reagent, which caused superoxide radical attack (Eqns. (23), (24) and (25)).

The fitting results of first-order reaction kinetics at pH = 4.37 and pH = 9.37 are displayed in Tables 3 and 4, respectively. Based on the data, the effect of KI on the apparent rate constant of the photocatalytic reaction was obtained, as shown in Figure 5. Under acidic conditions, when the concentration of KI was 0-0.051 g L<sup>-1</sup>, the rate constant of photocatalytic degradation was lower than the rate constant (K<sub>app</sub> = 0.00604) without salt; however, when the concentration of KI was 0.051-0.075 g L<sup>-1</sup>, the higher rate constant was found. A “turning point” also appeared in the curve with first decreasing and then increasing trend. And the maximum value of K<sub>app</sub> (0.0028) was found at the KBr concentration of about 0.075 g L<sup>-1</sup>, meaning the maximum degradation efficiency. While in the alkaline condition, the rate constant of KI salt was always higher than that without salt in the concentration of KI being 0-0.075 g L<sup>-1</sup>, indicating a promoting trend, and the maximum value of K<sub>app</sub> was 0.00904 at the KI concentration of 0.075 g L<sup>-1</sup>.



In theory, when a small amount of KI is added in acidic condition, I<sup>-</sup> can be adsorbed on the surface of the catalyst owing to adsorption, which weakens the photocatalytic degradation and inhibits the reaction. When KI concentration

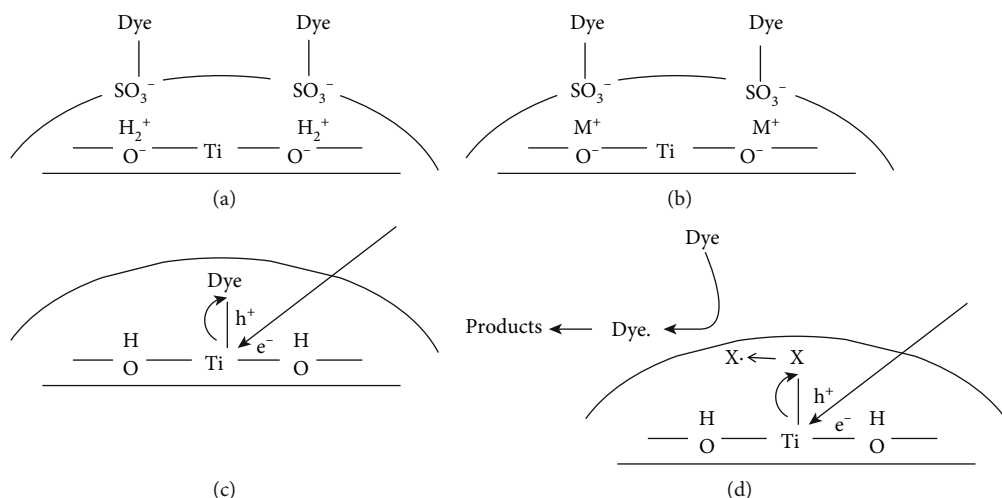


FIGURE 4: Adsorption models of W-7G in  $\text{TiO}_2$  solution and schematic diagram of the photocatalysis mechanism involving anion radicals: (a) at acidic conditions ( $\text{pH} < \text{p}i$ ); (b) at alkaline conditions ( $\text{pH} > \text{p}i$ ); (c) radical reaction with dye molecules adsorbed on the surface; (d) radical reaction with halogen ions adsorbed on the surface.

TABLE 3: Fitting results of first-order reaction kinetics under acidic condition ( $\text{pH} = 4.37$ ).

KI ( $\text{g L}^{-1}$ )	Fitting formulas	First-order reaction kinetic constant $K$ ( $\text{min}^{-1}$ )	Correlation coefficient ( $R^2$ )
0	$\ln(C_0/C_t) = 0.00604t + 1.36779$	0.00604	0.98436
0.015	$\ln(C_0/C_t) = 0.00229t + 1.16133$	0.00229	0.95046
0.030	$\ln(C_0/C_t) = 0.00387t + 1.15179$	0.00387	0.95654
0.045	$\ln(C_0/C_t) = 0.00511t + 1.08786$	0.00511	0.99453
0.060	$\ln(C_0/C_t) = 0.00767t + 1.02007$	0.00767	0.98888
0.075	$\ln(C_0/C_t) = 0.00904t + 0.94221$	0.00904	0.99318

TABLE 4: Fitting results of first-order reaction kinetics under alkaline condition ( $\text{pH} = 9.37$ ).

KI ( $\text{g L}^{-1}$ )	Fitting formulas	First-order reaction kinetic constant $K$ ( $\text{min}^{-1}$ )	Correlation coefficient ( $R^2$ )
0	$\ln(C_0/C_t) = 0.00208t + 0.99176$	0.00208	0.96747
0.015	$\ln(C_0/C_t) = 0.00390t + 1.29248$	0.00390	0.97642
0.030	$\ln(C_0/C_t) = 0.00436t + 1.28807$	0.00436	0.98953
0.045	$\ln(C_0/C_t) = 0.00592t + 1.32775$	0.00592	0.97836
0.060	$\ln(C_0/C_t) = 0.00880t + 1.64147$	0.00880	0.92191
0.075	$\ln(C_0/C_t) = 0.01127t + 1.61774$	0.01127	0.98540

is higher than  $0.051 \text{ g L}^{-1}$  at the pH, the photocatalytic rate constant of KI salt is higher than that without salt. It may be due to the conversion of the major factor from  $\text{I}^-$  adsorption on the catalyst surface to  $\text{I}^-$  participation in free radical

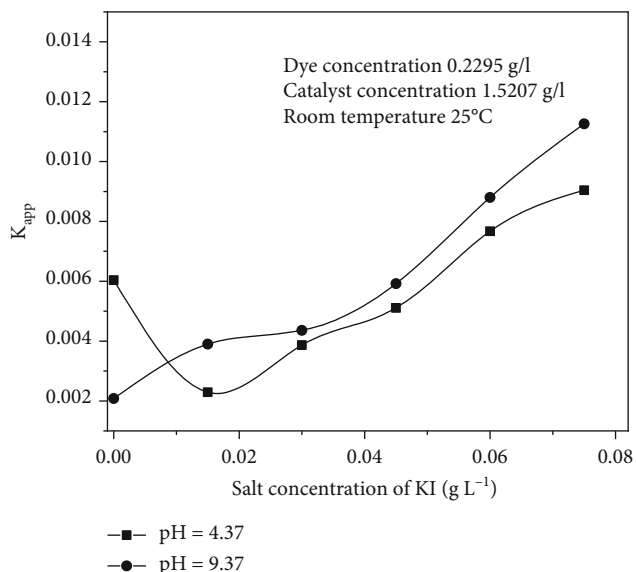


FIGURE 5: Effect of KI on the apparent rate constant of photocatalytic reaction.

reaction and the increase of iodine ion, which leads to the increase of  $\text{O}_2^{\cdot-}$  free radical. In a word, the synergistic effect of multiple factors promotes the influence. Besides, the addition of  $\text{I}^-$  can restore the dye positive ion free radical and make the dye accumulate on the surface of catalyst. The  $\text{O}_2^{\cdot-}$  radicals on the surface of catalyst exhibit a mechanism of superoxide attack, which leads to the free radical chain reaction and improves the photocatalytic degradation rate [23, 24].

Therefore, when KI salt was added, the competitive adsorption of  $\text{I}^-$  on the catalyst surface occurred. With the increase of KI concentration, the free radical effect increased gradually. And the degradation rate constant of acid-base condition showed an upward trend. That the existence of  $\text{I}^-$  affected the free radical reaction theory proposed above was verified.

## 4. Conclusions

The effect of inorganic salt KBr and KI on the photocatalytic degradation of W-7G was investigated at different pH values using nano-TiO<sub>2</sub> as photocatalyst. The results indicated that KBr salt possessed an inhibitory effect at pH = 4.37 with the concentration of KBr ranging from 0 to 0.072 g L<sup>-1</sup>, while KI salt showed an inhibitory effect with the concentration of 0-0.051 g L<sup>-1</sup> and promoting effect with the concentration of 0.051-0.075 g L<sup>-1</sup> at the same pH value. When the pH value was adjusted to 9.37, a promoting effect was found at the presence of KBr at the concentration of 0-0.035 g L<sup>-1</sup> and KI at the concentration of 0-0.075 g L<sup>-1</sup>, but the opposite effect occurred at the concentration of KBr ranging 0.035 to 0.072 g L<sup>-1</sup>. In addition, the degradation apparent rate constant ( $K_{app}$ ) of the system with KI was clearly higher than that with KBr under acidic or alkaline conditions. And the maximum value of  $K_{app}$  (0.01127) appeared at the KI concentration of 0.075 g L<sup>-1</sup> with a pH value of 9.37, meaning the highest degradation efficiency. In addition, a possible mechanism of photocatalytic degradation of W-7G in the presence of KBr and KI was provided, which could offer a theoretical support for the further study of inorganic salt effects on the photocatalytic degradation of reactive dyes or other organic substances [25].

## Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

## Acknowledgments

The research was supported by the Nature Science Foundation of Shandong Province (No. ZR2017MB057), Weifang Scientific Development Plan 2019 (No. 2019GX010), Weifang Hi-Tech Zone Science and Technology Benefit Plan 2019 (No. 2019KJHM14), and Doctorate Program Foundation of Weifang University (No. 2017BS09).

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